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Control and Manipulation of Ferroelectric Polarization Order to Elicit Novel Phenomena

By

Pravin Kavle

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Engineering – Materials Science and Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Lane W. Martin, Chair

Professor Ramamoorthy Ramesh

Professor Ali Javey

Summer 2024

Control and Manipulation of Ferroelectric Polarization Order to Elicit Novel Phenomena

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by

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Abstract

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Doctor of Philosophy in Engineering – Materials Science and Engineering

University of California, Berkeley

Professor Lane W. Martin, Chair

Understanding materials systems at the nanoscale and how they give rise to their macroscale properties dictates the central mission of materials science and engineering. My Dissertation is focused on understanding the control and manipulation of ferroelectric polarization to produce new phenomena and to expand the utility of ferroelectric materials. While much work has been done on individual thin films of canonical ferroelectrics such as PbTiO_3 and prototypical dielectric material SrTiO_3 , the demand for novel phenomena calls for a thorough understanding of their structure-property control in thin film form wherein structures, properties, and function well beyond those found in parent single composition films can be elicited by standard routes such as substrate-induced, strain-controlled pathways. The work herein is primarily based on the development of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ epitaxial thin-film system as a new platform for investigating the behavior of ferroelectric polarization under different chemistries and heterostructure formats such as single-layer, multilayer, and superlattice geometries to elicit novel phenomena. First, using a combination of the Ginzburg-Landau-Devonshire thermodynamic models, phase-field simulations, epitaxial thin-film growth, and characterization, I probed the mixed-phase domain structure evolution in $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films, and its connection with Euler characteristics, thermal-annealing effects, and dielectric susceptibility. Therein, I observed that varying strontium content provides deterministic strain-driven control of hierarchical domain structures in $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ solid-solution thin films wherein two types, c/a and a_1/a_2 , of nanodomains can coexist. A relationship between the different mixed-phase domain patterns and their topological nature is established using the Euler characteristic. In turn, the dielectric properties were also measured, and it was found that the connected-labyrinth domain patterns exhibit the highest dielectric permittivity due to the highest shared interdomain perimeter. After exploring the mixed-phase domain architectures in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films, I studied the understudied area of in-plane polarized ferroelectrics. Interlayer coupling, such as exchange interactions at the interface between an antiferromagnet and a ferromagnet, can produce exotic phenomena that are not present in the parent materials in magnetic systems. There is considerably less work on analogous ferroelectric counterparts. Here, $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films showing purely in-plane polarized domains with different chemistries have been used to create exchange-interaction-like behavior in ferroelectrics and to generate multistate memory. In this work, electric or polarization analogs of such exchange interactions are reported, and their physical origins are explained for bilayers of in-plane polarized

$\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ferroelectrics. Further control over the strontium content and thickness of the layers provides for deterministic switching properties of the bilayer systems resulting in phenomena analogous to an exchange-spring interaction. Eventually, with the control of these interactions, multistate-memory function and lowering coercivity of high coercivity in-plane ferroelectrics was reported in in-plane bilayer geometries. Next, I explored the fully-ferroelectric $(\text{PbTiO}_3)_n/(\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3)_n$ superlattice system wherein in-plane ferroelectric polarization in the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ provides the appropriate boundary conditions for the formation of the ferroelectric polar vortices. These superlattices exhibit substantially enhanced piezoelectric and ferroelectric responses in the out-of-plane direction, which arises from the ability of the polarization in both layers to rotate in the out-of-plane direction under the field. In the in-plane direction, the layers are found to be strongly coupled during switching, and in heterostructures with $(\text{PbTiO}_3)_n/(\text{SrTiO}_3)_n$ ferroelectric-dielectric building blocks, it is possible to produce multistate switching and polarization stability. This research further expands the realm of systems able to support emergent dipolar texture formation, and it does so with entirely ferroelectric materials, thus greatly improving their response to applied fields. Lastly, I investigated the potential of BaTiO_3 ferroelectric thin films for low-voltage operation for ferroelectric field effect transistors (FEFET) applications. In this work, ultrathin SrRuO_3 is used as channel material. Herein, I showed significant channel resistance modulation as a function of applied gate voltage in the low-voltage regime. This work demonstrates a potential route towards the inclusion of low coercive field ferroelectric materials in FEFET applications for future generation fully oxide devices. Overall, my work presented in this Dissertation provides new insights into understanding the fundamental mechanisms of emergent ferroelectric properties and demonstrates new routes to engineering domain structures for the enhanced dielectric response, exotic in-plane polarization switching in ferroelectric bilayer thin films, polar textures generation in superlattices, and usage of low coercivity material for FEFET applications.

To my family and friends

Acknowledgments

I am deeply grateful to Prof. Lane W. Martin for the invaluable opportunity to work in his laboratory and for his unwavering support throughout my graduate studies. Prof. Lane exemplifies a visionary scientist and academic mentor, possessing a wealth of knowledge and a meticulous attention to detail. His commitment to mastering the experimental facilities, conducting rigorous research, and fostering a culture of proactive learning has truly made our research group an unparalleled environment for cutting-edge exploration. I also thank Prof. R. Ramesh for his kind encouragement and being a constant source of inspiration throughout my Ph.D. program.

Arvind Dasgupta served as my first mentor in the Prometheus group, and his distinction remains unparalleled in my memory. His contagious enthusiasm, profound expertise, and meticulous approach played a pivotal role in integrating me as a researcher. I extend my heartfelt gratitude for the countless hours he dedicated to training me in tools and explaining complex concepts, an investment I have diligently strived to pay forward to the next generation of the lab.

I want to thank phase-field collaborators, Aiden M. Ross, Dr. Jacob A. Zorn, Dr. Bo Wang, and Prof. L.-Q. Chen for their significant contribution to my Ph.D. program. Your support allowed me to work on the most challenging ideas. I sincerely thank Harikrishnan K. P., Prof. Yu-Tsun Shao, and Prof. David A. Muller for providing the TEM facility for some of the most demanding samples. I am also grateful to Jiyuan Yang and Prof. Shi Liu for providing valuable support from the molecular dynamics aspects. I extend my sincere appreciation to Dr. Kyle Kelley, Dr. Rama Vasudevan, Prof. Sergei Kalinin, Dr. Marti Checa, Dr. Liam Collins, and Dr. Neus Domingo from Oak Ridge National Lab for their invaluable contributions in bringing my research on in-plane ferroelectrics to the forefront of the field. Also, thanks to Dr. Shriram Shivaraman and Dr. Ian A. Young (Intel Corporation), Prof. Yachin Ivry (Technion, Israel), Prof. Seungbum Hong (KAIST), Prof. Elizabeth Nowadnick (UC Merced), and Prof. Seung Sae Hong (UC Davis) for expanding my research purview by having extensive collaboration on projects related to the barium titanate.

Prof. Lucas Caretta, Dr. Eric Parsonnet, Dr. Peter Meisenheimer, Dr. Sajid Husain, Dr. Hongrui Zhang, and Dr. Piush Behera from Ramesh lab have consistently demonstrated unparalleled efficiency, always staying one step ahead in every endeavor. Being in the presence of such critical and intelligent minds has been a tremendous learning experience for me. Our impromptu coffee and lunch meetings have been catalysts for generating new ideas, and I hope I've contributed, even if just a bit, to your research pursuits. Piush, you will always hold a special place as one of my dearest friends. Thank you, Prof. Suraj S. Cheema, Prof. Jieun Kim, and Dr. Piush Behera, for your willingness to listen to my grievances and for offering valuable suggestions.

Ching-Che (Leo) Lin is among the most multi-talented graduate students, and he has shown unwavering passion, a rigorous approach, and consistent dedication to Nano-lab work. His expertise in handling complicated electronics has significantly contributed to the success of my Ph.D. journey. I thank Dr. Tae Yeon Kim and Ching-Che (Leo) Lin, with whom I shared a special bond of friendship. I deeply appreciate your unwavering love and support throughout the concluding stages of my Ph.D. journey. Our long discussions at the foothill dining hall, coffee walks, and outings have been a tremendous source of joy and enriched our friendship in ways that I will treasure for years. I wish I could have carved out a bit more time to spend with you both.

I want to thank all the current and past Prometheus and Ramesh lab group members. I want to extend my appreciation to Dr. Hossein Taghinejad, Dr. Kaushalya Jhuria, Dr. Hanuman Singh, Dr. Cheng-Hsiang (Jason) Hsu, Prof. Jeffrey Bokor, and Ashwath Bhat for providing me with the necessary measurement tools for an extended period. Thank you, Maya Ramesh, for being a great undergraduate student and establishing the baseline for my Ph.D. work during the pandemic.

In addition, I want to thank my Dissertation committee members, Prof. Ali Javey and Prof. R. Ramesh, for their kind comments and guidance in keeping me on track with my Ph.D. program. Thank you, Prof. Zakaria Al-Balushi and Prof. Jie Yao, for serving on my qualifying exam. I am grateful to Prof. Zakaria Al-Balushi, Prof. Oscar Dubon, and Dr. Matthew P. Sherburne for their unwavering support, uplifting words, and genuine concern for my well-being. I cannot forget the office staff, Ariana, Madina, and Jennifer, for their help with academic and non-academic issues.

I would like to gratefully acknowledge various funding sources that supported the research presented in this Dissertation, including the Army Research Office via Grant W911NF-21-1-0118 and the ETHOS MURI via cooperative agreement W911NF-21-2-0162. I want to acknowledge the support from the Intel Corp. under the COFEEE program. Additional support from the National Science Foundation under Grant DMR-2102895 and Grant DMR-2329111 and the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract Nos. DE-SC-0012375 and DE-AC02-05-CH11231 (Codesign of Ultra-Low-Voltage Beyond CMOS Microelectronics (MicroelecLBLRamesh)) for the development of materials for low-power microelectronics is acknowledged.

I am deeply grateful for the guidance provided by my mentors at my undergraduate alma mater, the Indian Institute of Technology-Bombay. Prof. Rajiv O. Dusane, Prof. Prita Pant, Prof. Parag Bhargava, Prof. Ankur Soam, and Dr. Lekha Peedikakkandy have been instrumental in shaping my undergraduate journey. I want to acknowledge Prof. Satish Ogale, Prof. J. M. D. Coey, Dr. M. Venkatesan, and Dr. Karsten Rode for introducing me to the world of complex-oxides and pulsed-laser deposition technique, which ultimately motivated me to start my Ph.D. in this area.

Thanks to Rustem, Piush, Sanghoon, Daewoon, Yunyeong, Nathan, Kevin, Enze, Zishen, Muhamod, Evan, and Caitlin for sharing the MSE batch camaraderie since day one. I want to thank my IIT-Bombay friends, Ashay, Saurabh, Sumedh, Amit, Nitish, Uday, Yash, Kunal, and Dhruv, for their constant motivation and support. Thanks to all my TSMC teammates and mentors, Dr. S. P. Jeng, Dr. S. M. (Eric) Chen, Dr. P. Y. Lin, Dr. P.Y. (Peter) Lai, C. H. (Jackson) Lin, S. T. Hung, T. M. (Charles) Lai, T. J. (Jerry) Fang, Y. J. (Rosa) Lin and Jay Hou, for keeping in touch even after so many years and motivating me to join the IC packaging world again. Additionally, I would like to express my sincere gratitude to Gyan Prakash, Aditya Jadhav, and Antariksh Bothale for their invaluable assistance in guiding me and preparing me to re-enter the semiconductor industry.

I express my deepest gratitude to my sister, Chhaya Patil, and my brother, Amey Kawale for supporting me as a local guardian. I sincerely appreciate Yvonne Burgess and Chris for the incredible three years I spent under your roof. Your unwavering hospitality has been a blessing, providing me with a supportive environment throughout my Ph.D. journey. Finally, I sincerely thank my mother for her love and unconditional support for my graduate studies and decisions in life. I am glad that I have accomplished more than I would ever have imagined five years ago.

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Fig. 3.7 2D reciprocal space mapping (RSM) studies about the 220_o -diffraction peak of the DyScO_3 (110) substrates showing the 002- and 200-diffraction peaks of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films corresponding to the tilted c and tilted/ x kyrmion a domain variant for a) $x = 0$, b) $x = 0.06$, c) $x = 0.17$, d) $x = 0.20$, e) $x = 0.23$, f) $x = 0.25$, g) $x = 0.27$, and h) $x = 0.30$.

Fig. 3.8 a) RSM about the 220 -diffraction peak of the DyScO_3 (110) substrate revealing 002- and 200-diffraction peaks for the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films corresponding to the tilted c and tilted/untitled a domain variants, respectively, for an $x = 0.20$ heterostructure. b) Schematic of the domain tilting phenomenon observed in the c/a domain stripes with characteristic angles defined. c) Measured tilt angles for the c and a domains and the net tilt angle between them as a function of film composition.

Fig. 3.9 From left to right, a binarized image used for analysis based on the experimental AFM data, the AFM topography image, the corresponding phase-field simulation, and a binarized image used for analysis based on the phase-field simulation for $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films with a) $x = 0.06$, b) $x = 0.17$, c) $x = 0.23$, and d) $x = 0.27$ (experimental x values noted here, but corresponding phase-field x values are noted on the figure).

Fig. 3.10 a) Calculated normalized Euler characteristic (χ_N) vs. strontium content (x) for the experimental part (red circles) and phase-field generated (blue squares). b) Derivative of the part-wise fitted curve of the normalized Euler characteristic (χ_N) for the experimental and simulated data. Extrema of the derivative of the experimental curve (red line) are used to demarcate various topological regions observed in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films.

Fig. 3.11 AFM topography images of 100-nm-thick $\text{Pb}_{0.83}\text{Sr}_{0.17}\text{TiO}_3$ thin films grown on DyScO_3 (110) substrates in the a) as-grown state and the same area after annealing at 270°C for b) 24 hours and c) 190 hours.

Fig. 3.12 Reciprocal Space Mapping (RSM) about the 220_o-diffraction peak of the DyScO_3 (110) substrate showing the 002- and 200-diffraction peak of $\text{Pb}_{0.83}\text{Sr}_{0.17}\text{TiO}_3$ thin films a) before annealing and b) after 190 Hrs. Of annealing at 270 °C. Box shows the location of a domain which is selected for zoom in scan to detect changes in satellite peaks intensity due to periodicity enhancement. c) Zoom in RSM scan around a domain location showing satellite periodicity peak arising from alternating stripes of c/a and a_1/a_2 domains in the as-grown sample. d) Zoom in RSM scan around the a domain location showing considerable enhancement in the satellite peaks due to the large-scale domain realignment occurring during the extended annealing process. Normalized intensity at the position at $Q_z = 0.3926$ for e) before annealing and f) after annealing process exhibiting apparent enhancement in stripe ordering during the annealing process.

Fig. 3.13 a) Domain fraction of c/a domains as a function of annealing duration. b) Room-temperature wide-angle θ -2 θ X-ray diffraction scans for as-grown and after 190 Hrs. of annealing. c) Normalized Euler Number as a function of annealing time.

Fig. 3.14 Phase-field simulations showing similar domain alignment phenomenon in the connected-labyrinth structure for the a) as-grown state and after annealing for b) 300k and c) 600k timesteps.

Fig. 3.15 Temperature-dependent evolution of hierarchical domain architectures during different annealing cycle stages. Corresponding domain architecture of a) initial domains at $T = 298$ K, b) at the end of 150k annealing timesteps with $T = 550$ K, c) at the end of the 600k annealing timesteps with $T = 550$ K, and d) after the 600k annealing timesteps at $T = 298$ K. e) Corresponding phase fraction of c/a domains is tracked throughout the annealing process.

Fig. 3.16 Time-dependent evolution of hierarchical domain architectures during annealing wherein a domain coarsening and straightening increases with annealing time. The corresponding domain architecture at 300 K of a) as-grown film and after b) 150k, (c) 300k, (d) 450k, and e) 600k steps displaying increasing realignment of c/a and a_1/a_2 domain stripes in a hierarchical domain structure. f) Energy of domain structure as a function of simulation steps (equivalent to annealing time). Points at 150k, 300k, 450k, and 600k timesteps showing an increasing annealing period and corresponding energy lowering. g) elastic, h) Landau, i) electric, and j) gradient energy contributions to the total energy computed from phase-field studies during different annealing cycles after 150k, 300k, 450k, and 600k timesteps (equivalent to annealing time).

Fig. 3.17 Various types of defects are observed in the $\text{Pb}_{0.83}\text{Sr}_{0.17}\text{TiO}_3$ thin films such as a) threefold junctions, b) stripe end-points, c) fourfold junctions (saddle points), d) handle defects, e) disconnected stripes, f) droplets, g) target skyrmions, and h) dislocations.

Fig. 3.18 The defect densities of three- and four-fold junctions (d_{type1}) and the stripe end-points (d_{type2}) as a function of annealing time. The insets show the dislocation and four-fold defect types.

Fig. 3.19 Room temperature ferroelectric hysteresis response the various $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films measured at 10 kHz.

Fig. 3.20 Dielectric permittivity (ϵ_r) as a function of strontium content (x).

Fig. 3.21 AFM topography images of 100-nm-thick $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin film grown on DyScO_3 (110) substrate with a) $x = 0.06$, b) $x = 0.17$, c) $x = 0.20$, d) $x = 0.23$, e) $x = 0.25$, and f) $x = 0.27$. The images are $5 \times 5 \mu\text{m}^2$. The bright region shows c/a domain region and dark region describes a_1/a_2 domain area. These images are converted into black and white contrast for MATLAB based image processing methods. Corresponding compositions are g) $x = 0.06$, h) $x = 0.17$, i) $x = 0.20$, j) $x = 0.23$, k) $x = 0.25$, and l) $x = 0.27$. The shared perimeter between c/a and a_1/a_2 domain area identified for m) $x = 0.06$, n) $x = 0.17$, o) $x = 0.20$, p) $x = 0.23$, q) $x = 0.25$, and r) $x = 0.27$.

Fig. 3.22 a) Domain fraction of a_1/a_2 and c/a domains as a fraction of strontium content (x) in 100-nm-thick $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films grown on DyScO_3 (110) substrates. A shared perimeter between a_1/a_2 and c/a domain is derived from AFM images for each strontium content for an image size of $5 \times 5 \mu\text{m}^2$. B) Shared perimeter between c/a and a_1/a_2 domains normalized by majority phase as a function of strontium content (x).

Fig. 3.23 a) Dielectric permittivity as a function frequency measured at different applied background dc electric fields for $x = 0.00$ heterostructure. b) Intercepts obtained from a linear logarithmic fit of the dielectric permittivity–frequency plot at various applied background dc electric fields are plotted as a function of the applied dc electric fields for $x = 0.00$ heterostructure.

Fig. 3.24 a) Zero-field permittivity intercept of Intrinsic-only, combined intrinsic-extrinsic contribution, and the difference between them (extrinsic-only contribution) is plotted as a function of strontium content (x). b) Phase-field simulations for permittivity coefficient (k_{33}) for mixed-phase $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin film with $x = 0.1875$.

Fig. 4.1 a) Wide-angle θ - 2θ X-ray diffraction scans for 100-nm-thick $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films grown on DyScO_3 (110) substrate. From top to bottom, $\text{Pb}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ (green), $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ (red), and $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (blue). b) Zoom-in scan around 220 diffraction condition of DyScO_3 (110) substrate.

Fig. 4.2 2D reciprocal space mapping (RSM) about the 332_o -diffraction peak of DyScO_3 (110) with a pair of vertical dashed red lines representing domain periodicity satellite peaks for the 100-nm-thick a) $\text{Pb}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$, b) $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ and, c) $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$.

Fig. 4.3 a) 2D reciprocal space mapping (RSM) about the 240_o -diffraction peak of the DyScO_3 (110) with a pair of vertical dashed red lines indicating the positions of the domain periodicity reflections originating from in-plane $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ domains and b) Similar RSM about the 220_o -diffraction peak of the DyScO_3 (110) where such domain periodicity satellite peaks are missing due to the absence of any regular arrangement of out-of-plane polarization in the pure in-plane domain.

Fig. 4.4 Domain structures representation of domains separated by a domain wall predicted in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films. a) aa_1/aa_2 structure with polarization along $[\bar{1}10]$ and $[\bar{1}\bar{1}0]$ directions. b) a_1/a_2 domain structure with tetragonal symmetry and the polarization alternating along $[100]$ and $[010]$.

Fig. 4.5 Lateral PFM (L-PFM) images of 100 nm-thick a) $\text{Pb}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$, b) $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$, and c) $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$.

Fig. 4.6 a) AFM topography showing substrate terraces and b) Vertical PFM (V-PFM) probing the out-of-plane polarization of 100-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ thin films grown on DyScO_3 (110).

Fig. 4.7 Domain periodicity extracted from 2D-RSM and L-PFM for each composition shows a good match.

Fig. 4.8 a) Different local domains based on the in-plane directions. Different superdomain types based on the global polarization direction. B) type I+, c) type I-, d) type II- and e) type II+. F) Representation of different global dipole direction based on superdomain types.

Fig. 4.9 a) L-PFM scan for a 0° device after applying $\mathbf{E}$ along the $[100]$ showing type-I- and -II+ superdomains. Inset showing the corresponding phase of the superdomains. b) Same area is then analyzed after applying $\mathbf{E}$ along the $[\bar{1}00]$ showing type-I+ and -II- superdomains. c) Switching pathway analyzed for a 0° device after application of $\mathbf{E}$ along the $[\bar{1}00]$ on a type-I- superdomain variant subsection (shown in red color box) showing stepwise 90° switching and 180° switching pathway.

Fig. 4.10 a) L-PFM scan for a 45° device after applying $\mathbf{E}$ along the $[\bar{1}\bar{1}0]$ showing the resulting type-I- superdomain. Inset showing the corresponding phase of the superdomains. b) The same area is then analyzed after applying $\mathbf{E}$ along the $[\bar{1}10]$ showing the resulting type-I+ superdomain. c) Switching pathway analyzed for a 45° device after applying $\mathbf{E}$ along the $[\bar{1}\bar{1}0]$ on a type-II+ superdomain showing a 90° switching pathway to convert it into type-II- superdomain.

Fig. 4.11 a) Polarization-electric field hysteresis loops measured at 1 kHz frequency for a) 50-nm-thick $\text{Pb}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ (green), $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ (red), and $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (blue) heterostructures. B) Bilayer of 50-nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 50-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ exhibiting ferroelectric bias and coercivity hardening behavior with minor (red) and major (black) loops, respectively. Switching steps are further analyzed using phase-field simulations starting with c) the initial state, d) after the first switching event of the top $x = 0.6$ layer (The magenta regions at the domain wall between the a_{1+} and a_{2+} domains have polarization pointing along the $[110]$), e) after domain

reshuffling in the bottom $x = 0.4$ layer, and f) after complete bilayer switching. For c)-f), i) shows the equilibrium domain structure of the bilayer system, ii) shows the corresponding elastic-energy distribution, and iii) shows a simplified version of the domain arrangement at the interface at each switching step.

Fig. 4.12 Polarization-electric field hysteresis loops measured at 1 kHz frequency for a bilayer of 50 nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 50-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ exhibiting four states.

Fig. 4.13 a) The PUND studies reveal the pathway to the different polarization states at a constant pulse width of 1 ms and 4 ms as a function of different pulse voltages. b) The long-term retention and stability of the multiple polarization states. c) Stability of the multiple polarization states after long fatigue cycles.

Fig. 4.14 Bilayer of 50-nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 50-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ separated by a 20-nm-thick SrTiO_3 spacer layer exhibiting lattice decoupling phenomenon.

Fig. 4.15 2D reciprocal space mapping (RSM) about the 332_{O} -diffraction peak of the DyScO_3 (110) with pair of vertical dashed red lines indicates the positions of the in-plane domain periodicity reflections of a) 50 nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ with the periodicity $\lambda_{\text{RSM}} = 69.7$ nm. b) 50-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ with a periodicity of $\lambda_{\text{RSM}} = 52$ nm and, c) 50-nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 50-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ with 20-nm-thick SrTiO_3 layer as a buffer layer. The periodicity of the $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ layer becomes 72 nm, and the periodicity of the $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ layer becomes 50 nm, close to the original periodicity of each layer with the implementation of the buffer layer.

Fig. 4.16 Polarization-electric field hysteresis loops for a bilayer of 75-nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 50-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ exhibiting three distinct states.

Fig. 4.17 Bilayer of 50-nm-thick $\text{Pb}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ on top of 50-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ exhibiting exchange-spring-like behavior.

Fig. 4.18 Bilayer of 40-nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 40-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ exhibiting two states with coercivity softening of the hard layer.

Fig. 4.19 2D reciprocal space mapping (RSM) showing the common periodicity of $\lambda_{\text{RSM}} = 50$ nm for the whole structure.

Fig. 4.20 Switching steps for bilayer with 40-nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 40-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ are analyzed starting with a) the initial state, b) after the first switching event of the top $x = 0.6$ layer, and after c) complete switching of the bilayer. For each a-c), the i) equilibrium domain structures of the bilayer system, ii) corresponding elastic-energy distribution, and iii) simplified version of domain arrangement at the interface at each switching step.

Fig. 5.1 a) Schematic illustration of the trilayers. 2D reciprocal space mapping (RSM) about the 220_{O} -diffraction condition of DyScO_3 (110) and along 332_{O} -direction with a pair of red arrows representing vortex periodicity for trilayers b) $x = 0$, c) $x = 0.3$, d) $x = 0.5$ and e) and tilted domains for $x = 0.6$. f) Vortex periodicity measured as a function of the lead content (x) for the trilayer system.

Fig. 5.2 a) Ptychographic reconstruction of the $x = 0.3$ trilayers with the white rotating arrow showing the lattice distortion corresponding to the vortex core. b) Ptychographic reconstructed image shows the displacement of the centroid of the A -site cations with respect to the centroid of the oxygen atoms mapped out for each pseudo-cubic unit cell. Zoom-in regions showing pseudo-cubic unit cells with different atoms having specific colour codes for the c) $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ region, d) vortex top side, e) vortex left side, f) vortex bottom side, and g) vortex right side.

Fig. 5.3 a) Ptychographic image showing the displacement of the centroid of the B-site cations with respect to the centroid of the oxygen atoms mapped out for each pseudo-cubic unit cell. b) Ptychographic image showing the displacement of the centroid of the A-site cations with respect to the centroid of the B-site cations for each pseudo-cubic unit cell. c) HAADF reconstructed image showing the displacement of the centroid of the A-site cations with respect to the centroid of the B-site cations mapped out for each pseudo-cubic unit cell.

Fig. 5.4 Molecular dynamics (MD) simulations displaying structural evolution as a function of lead content (x) with a) $x = 0.0$, b) $x = 0.1$, c) $x = 0.2$, d) $x = 0.3$, e) $x = 0.4$, f) $x = 0.5$, g) $x = 0.6$, and h) $x = 0.7$.

Fig. 5.5 Molecular-dynamics (MD) simulations revealing a) vortex formation in the PbTiO_3 layer and in-plane domains in the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layer for $x = 0.3$ trilayers along with b) a zoom-in of the region at the interface region showing alignment of in-plane components in the same direction.

Fig. 5.6 a) Out-of-plane polarization-electric field hysteresis loops measured at 10 kHz for $x = 0, 0.3, 0.5$, and 0.6 , $p = 5$ superlattices. b) Out-of-plane switching current-electric field hysteresis loops measured at 10 kHz for the superlattices with $x = 0.0, 0.3, 0.5$, and 0.6 , $p = 5$ superlattices.

Fig. 5.7 Various switching steps are as extracted from phase-field simulations at different electric field starting with the a) initial state at E_0 , b) intermediate stage at $E_1 > E_0$, c) next intermediate stage at $E_2 > E_1$, and d) final state at E_3 .

Fig. 5.8 Electromechanical strain (in percent) -electric field loops measured at 10 kHz for $x = 0, 0.3, 0.5$, and 0.6 , $p = 5$ superlattices.

Fig. 5.9 Corresponding MD simulations displaying out-of-plane switching of the $x = 0.3$ superlattices starting with the a) initial state at E_0 with a b) zoom-in area around the interface and the c) final state at E_1 with a d) zoom-in area around the interface at fully switched state

Fig. 5.10 Molecular dynamic (MD) simulations displaying domain structure evolution on application of out-of-plane E on $x = 0.0$ superlattices at values of a) 0 kV cm^{-1} , b) 100 kV cm^{-1} , c) 200 kV cm^{-1} , d) 400 kV cm^{-1} , e) 600 kV cm^{-1} , f) 800 kV cm^{-1} , and g) 1000 kV cm^{-1} .

Fig. 5.11 Molecular dynamic (MD) simulations displaying domain structure evolution on application of out-of-plane E on $x = 0.6$ superlattices at values of a) 0 kV cm^{-1} , b) 100 kV cm^{-1} , c) 200 kV cm^{-1} , d) 400 kV cm^{-1} , e) 600 kV cm^{-1} , f) 800 kV cm^{-1} , and g) 1000 kV cm^{-1} .

Fig. 5.12 Schematic of interdigitated electrodes (IDE) on the trilayer structures.

Fig. 5.13 In-plane polarization-electric field hysteresis loops measured at 1 kHz for the a) $x = 0$ and b) $x = 0.3$ trilayers. c) Remanent polarization and coercivity field of the trilayers as a function of lead content (x) in the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ layer.

Fig. 5.14 Cross-section views of various switching steps for the $x = 0.3$ trilayers extracted from phase-field simulations including the a) initial state, b) intermediate state, and c) final state after completing switching process. Corresponding 3D views of the mesoscale equilibrium domain structures of the trilayer system showing the a-c, i, P_x component of the top $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layer and the a-c, ii, P_z component of the PbTiO_3 layer at each switching step.

Fig. 5.15 a) Schematic of the $x = 0.3/0$ multilayer with a SrTiO_3 spacer layer of 50-unit cells. b) 2D reciprocal space mapping (RSM) about the 220_{O} -diffraction condition of DyScO_3 (110) and along 332_{O} -direction with a pair of red and orange arrows representing vortex periodicity for the of $x = 0.3/0$ multilayer with SrTiO_3 spacing layer of 50 unit cells. c) Cross-sectional view of the phase-field simulations for the same multilayer structure at its ground state.

Fig. 5.16 a) In-plane polarization-electric field hysteresis loops measured at 1 kHz for the same multilayer structure wherein the inset shows the positive side of a PUND analysis revealing the multistate character. Cross-sectional phase-field simulations for b) an intermediate switching step and c) the fully switched state.

Fig. 5.17 a) The long-term retention of the multiple polarization states and the b) stability of the multiple polarization states after repeated switching cycles.

Fig. 5.18 a) Schematic of $x = 0.3/0$ multilayer with SrTiO_3 spacing layer of 16 unit cells. b) Phase-field simulations generated multilayer structure for the ground state. c) In-plane polarization-electric field hysteresis (P. vs. E.) loops measured at 1 kHz frequency for multilayer structure and inset showing positive side of the PUND analysis showing multistate characteristics. d) Phase-field simulations generated intermediate switching step and e) fully switched state. f) The long-term retention and stability of the multiple polarization states. g) Stability of the multiple polarization states after long fatigue cycles.

Fig. 5.19 a) Schematic of $x = 0.3/0$ multilayer without SrTiO_3 spacing layer. b) Phase-field simulations generated multilayer structure for the ground state. c) In-plane polarization-electric field hysteresis (P. vs. E.) loops measured at 1 kHz frequency for multilayers. d) Phase-field simulations generated fully switched state of the multilayers.

Fig. 6.1 Fig. 6. Schematic of trilayer heterostructure with a) 10 nm SrRuO_3 /100 nm BaTiO_3 /10 nm SrRuO_3 and b) 5-unit cells SrRuO_3 /100 nm BaTiO_3 /10 nm SrRuO_3 . Corresponding x-ray diffraction line scan for c) 10 nm top SrRuO_3 case and d) 5-unit cells top SrRuO_3 case. Asymmetric reciprocal space mapping for e) 10 nm top SrRuO_3 case and f) 5-unit cells top SrRuO_3 case. Polarization vs. electric field hysteresis loop for g) 10 nm top SrRuO_3 case and h) 5-unit cells top SrRuO_3 case.

Fig. 6.2 Polarization vs. electric field hysteresis loop for a) 5-unit cells top SrRuO₃ case, b) 6-unit cells top SrRuO₃ case, c) 7-unit cells top SrRuO₃ case and d) 10 nm top SrRuO₃ case.

Fig. 6.3 Resistivity vs. temperature data of a) 5-unit-cell SrRuO₃ and b) 6-unit-cell SrRuO₃.

Fig. 6.4 Schematic of trilayer heterostructure with fabricated FEFET structure showing source, drain and gate configuration.

Fig. 6.5 Microfabrication process for Hall-bar devices. a) Mask layer 1 consisting of alignment marks. b) Spin coating of photoresist and photolithography exposure. c) Photoresist development. d) Pt metal sputtering. e) Remaining photoresist stripped using acetone. f) Final image of Pt alignment marks. g) Cross section of the sample after step 1 completion. h) Mask layer 1 consisting of alignment marks. i) Spin coating of photoresist and photolithography exposure of hall bars. j) Photoresist development step. k) Ion milling of external SrRuO₃ beyond defined hall bars. l) Insulating Al₂O₃ layer sputtering. m) Final image after Pt alignment marks and hall bar lithographic step. n) Cross section of the sample after step 2 completion. o) Mask layer 3 consisting of alignment Pt contact pad. p) Removal of photoresist in acetone. q) Spin coating of photoresist and photolithographic exposure. r) Pt contact pads area after development step. s) Final device. Photoresist was removed in acetone after deposition of Pt. t) Optical microscope image of an actual sample after completion of all steps. u) Cross section of the sample after all steps completion.

Fig. 6.6 a) Schematic cross section illustrations of the FeFET device under test. b) Schematic of the FeFET device in the hall bar geometry. c) V_{DS} and V_{GS} profile schematic used for testing procedure.

Fig. 6.7 a) Schematic cross section illustrations of the FeFET device under test. b) Schematic of the FeFET device in the hall bar geometry. c) V_{DS} and V_{GS} profile schematic used for non-volatile testing procedure.

Fig. 6.8 a) Channel resistance hysteresis loop for an all-oxide FEFET. Channel resistance is measured with the gate voltage on. Note that the counterclockwise direction of the loop indicating the ferroelectric switching process. Schematic diagram of a simplified model for the field effect in a n-type FEFET at b) channel depletion and, at c) channel accumulation state.

Fig. 6.9 Various current measured during FEFET measurements in the volatile testing case. a) Simultaneous measurement of I_{DS} and I_{GS} as a function of V_{DS}. Zoom in view of I_{GS} as a function of V_{DS} for better visualization.

Fig. 6.10 Channel resistance hysteresis loop for an all-oxide FEFET of 7-unit cell SrRuO₃ channel.

Fig. 6.11 a) Channel resistance is measured with non-volatile testing. b) Pulsed switching measurement showing total switched polarization magnitude and remanence after back-switching.

Fig. 6.12 a) Schematic of trilayer heterostructure with fabricated FEFET structure for 6-unit-cell thick SrRuO₃ channel showing source, drain and gate configuration. Channel resistance is measured at various temperatures with volatile testing at b) 300K, c) 180K, d) 78K and, non-

volatile testing at e) 300K, f) 180K and, g) 78K. h) Graph indicating channel modulation (%) as a function of system temperature for volatile and non-volatile testing.

Fig. 6.13 Polarization vs. electric field hysteresis loops for 300K, 240K, 180K, 120K and, 78K for SrRuO₃ (10nm)/BaTiO₃ (100nm)/SrRuO₃ (10nm) heterostructure measured at 1KHz.

Fig. 6.14 Channel modulation hysteresis loops for FEFET structure made up of 6-unit-cell thick SrRuO₃ channel thickness. Channel resistance is measured at various temperatures with volatile testing at a) 300K, b) 240K, c) 180K, d) 120K, e) 78K and, non-volatile testing at f) 300K, g) 240K, h) 180K, i) 120K, j) 78K.

Fig. 6.15 a) Schematic of trilayer heterostructure with fabricated FEFET structure for 5-unit-cell thick SrRuO₃ channel showing source, drain and gate configuration. Channel resistance is measured at various temperatures with volatile testing at b) 300K, c) 180K, d) 78K and, non-volatile testing at e) 300K, f) 180K and, g) 78K. h) Graph indicating channel modulation (%) as a function of system temperature for volatile and non-volatile testing.

Fig. 6.16 Channel modulation hysteresis loops for FEFET structure made up of 5-unit-cell thick SrRuO₃ channel thickness. Channel resistance is measured at various temperatures with volatile testing at a) 300K, b) 240K, c) 180K, d) 120K, e) 78K and, non-volatile testing at f) 300K, g) 240K, h) 180K, i) 120K, j) 78K.

Fig. 7.1 a) upgraded version of PbTiO₃ to Pb_{1-x}Sr_xTiO₃ (x = 0.6), b) downgraded version of Pb_{1-x}Sr_xTiO₃ to PbTiO₃ (x = 0.6), c) upgraded-downgraded version of PbTiO₃ to Pb_{1-x}Sr_xTiO₃ to PbTiO₃ (x = 0.6), d) downgraded-upgraded- downgraded version of Pb_{1-x}Sr_xTiO₃ to PbTiO₃ to Pb_{1-x}Sr_xTiO₃ (x = 0.6).

Fig. 7.2 a) HAADF image of the compositionally graded 50 nm upgraded version of PbTiO₃ to Pb_{0.4}Sr_{0.6}TiO₃ 50 nm thin film which shows diffraction contrast corresponding to *c* and *a* domains. b) DPC image showing polarization corresponding to *c* and *a* domains.

Fig. 7.3 MD simulation generated stacked trilayer of (Pb_{0.5}Sr_{0.5}TiO₃)₁₆/(PbTiO₃)₁₆ heterostructure. Schematic showing mapped ordered vortices in the two PbTiO₃ layer and spiral staircase-like polar topology in the connecting Pb_{0.5}Sr_{0.5}TiO₃ layer. Top view of Pb_{0.5}Sr_{0.5}TiO₃ layers with layer number c) 15, d) 23, e) 27, and f) 31.

LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
DSO	DyScO ₃
GLD	Ginzburg-Landau-Devonshire
GSO	GdScO ₃
HAADF	High-angle annular dark field
IP	In-plane
MBE	Molecular beam epitaxy
MD	Molecular dynamics
MIT	Metal-insulator-transition
MPB	Morphotropic phase boundary
NSO	NdScO ₃
OOP	Out-of-plane
P-E	Polarization-electric-field hysteresis
PFM	Piezoresponse force microscopy
PLD	Pulsed-laser deposition
PMN	PbMg _{1/3} Nb _{2/3} O ₃
PMN-PT	0.68PbMg _{1/3} Nb _{2/3} O ₃ -0.32PbTiO ₃
PSTO	Pb _{1-x} Sr _x TiO ₃
PUND	Positive-up-negative-down
PZT	PbZr _{1-x} Ti _x O ₃
r.l.u.	Reciprocal lattice unit
RHEED	Reflection high energy electron diffraction
RSM	Reciprocal space mapping
SRO	SrRuO ₃
STEM	Scanning transmission electron microscopy
TEM	Transmission electron microscopy
XRD	X-ray diffraction

LIST OF SYMBOLS

$E_{c_{avg}}$	Average coercive field
E_{c-}	Negative coercive field
E_{c+}	Positive coercive field
$E_{imprint}$	Electrical imprint
$P_{r_{avg}}$	Average remanent Polarization
$P_{s_{avg}}$	Average saturation Polarization
P_{r-}	Negative remanent polarization
P_{r+}	Positive remanent polarization
P_{s-}	Negative saturation polarization
P_{s+}	Positive saturation polarization
2D	Two-dimension(al)
3D	Three-dimension(al)
a	In-plane pseudocubic lattice parameter
c	Out-of-plane pseudocubic lattice parameter
d	Planar atomic spacing
d_{33}	Longitudinal piezoelectric coefficient
E	Electric-field
E_C	Coercive field
f	Frequency
H, K, L	Reciprocal lattice vectors [100], [010], [001]
k	Dielectric constant
O	Orthorhombic
P	Polarization
P_{rem}	Remanent polarization
P_{sat}	Saturation polarization
R	Rhombohedral

r_A	Radius of A -site cations in an ABO_3 perovskite oxide
r_B	Radius of B -site cations in an ABO_3 perovskite oxide
r_O	Radius of oxygen in an ABO_3 perovskite oxide
T	Temperature
T	Tetragonal
u.c.	Unit-cell
x, y, z	Pseudocubic [100], [010], [001]
ϵ_0	Permittivity of free space
ϵ_r	Dielectric permittivity
χ	Dielectric permittivity
ω	Frequency
A	Capacitor area
C	Capacitance
D	Electric displacement
G	Gibbs free energy
I	Electric current
R	Resistance
T_c	Curie temperature
V	Voltage
Z	Atomic number
Z	Impedance – Impedance spectroscopy
c	Curie constant – Curie-Weiss law
d	Film thickness
q	Electronic charge
t	Time
t_G	Goldschmidt's tolerance factor
t_R	Retention time
x	Mechanical strain

δ	Dielectric loss
δ	Dielectric loss
ε	Dielectric permittivity
ε_0	Dielectric permittivity of free space
ε_r	Dielectric constant or relative dielectric permittivity
θ	Angle between incident beam and normal to the lattice planes – X-ray diffraction
θ_B	Bragg angle – X-ray diffraction
π	Pyroelectric coefficient

CHAPTER 1

Fundamentals of Ferroelectrics

In this Chapter, I provide an overview of the basic concepts of ferroelectrics and related materials. First, I review the crystallographic origin of ferroelectricity in perovskite oxide systems and discuss the onset of ferroelectricity further in the view of coordination chemistry and phonon theory. Second, several classical perovskite ferroelectric material systems and thin films (which will later be used in this Dissertation) are then introduced. Third, I provide a brief background on ferroelectric thin films, specifically the nature of domain-structure formation and potential pathways for controlling the same therein. This is followed by a brief discussion of the general properties of ferroelectric materials. Finally, I present the organization of the Dissertation and the central questions it aims to answer.

1.1 Introduction to Ferroelectrics

Ferroelectricity is the material property wherein spontaneous polarization can be reversed by applying an electric field. Such an effect was first detected in 1920 by Valasek in Rochelle salt [1], and is named with the prefix "ferro" in analogy to ferromagnetism. The switchable polarization states in ferroelectrics lead to (at least) bi-stability of the primary order parameter polarization; a feature which is promising for non-volatile memories [2] and low-power logic applications [3]. Also it makes such materials useful in a wide range of electronics such as sensors, actuators [4], capacitors, piezoelectric, and pyroelectric devices for energy harvesting [5], etc. due to the coupled dielectric, piezoelectric, and pyroelectric properties. To utilize ferroelectric materials for engineering applications, it is key to study and recognize the origin of spontaneous polarization. Thus, in this Section, I discuss the crystallographic and physical origins of ferroelectricity from the perspective of crystal symmetry, coordination chemistry, and soft-phonon theory.

1.1.1 Crystallographic Signatures

Ferroelectrics perovskites are a subtype of a broader range of compounds possessing the perovskite structure with the generic chemical formula ABO_3 and the unit-cell is schematically shown here (Fig. 1.1). In such representations, the A -site cations are located at the corners and are generally occupied by cations with slightly larger radii while the B -site cations are located at body centers and are generally occupied by cations with smaller radii. For oxides, unsurprisingly, oxygen anions occupy the face centers of the unit cell. Ferroelectricity is, however, only present in a small subgroup of perovskite oxides. For example, no spontaneous polarization is observed in paraelectric $SrTiO_3$ at room temperature. The simplest criterion is to examine the material symmetry (Fig. 1.2). Among the 32 possible crystallographic point groups, 20 do not possess an inversion center and thus exhibit piezoelectricity such that when external stresses are applied a polarization is induced. Among these piezoelectric systems, 10 point groups can sustain a unique polar axis (are said to have a spontaneous polarization) and also exhibit pyroelectric response wherein a temperature change leads to polarization change. Ferroelectricity, in turn, is found only in a small subgroup of the polar, pyroelectric material classes wherein the polarization is switchable with an applied electric field.

Another empirical criterion to determine the stability of ferroelectricity in perovskite structure is with the *Goldschmidt tolerance factor* [6], defined as $t = \frac{r_A + r_B}{\sqrt{2}(r_A + r_B)}$, where r_A , r_B , and r_O represent the ionic radii of the A , B , and oxygen ions, respectively (Fig. 1.3). For example, $SrTiO_3$ has a tolerance factor of ~ 1 , and is known to be a cubic insulator. When this factor is not 1, structural distortions break the cubic symmetry. For example, $BaTiO_3$ has a $t > 1$, and

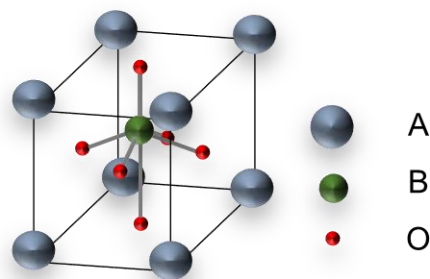


Fig. 1.1 The schematic representation of atomic structure in an ABO_3 perovskite oxide.

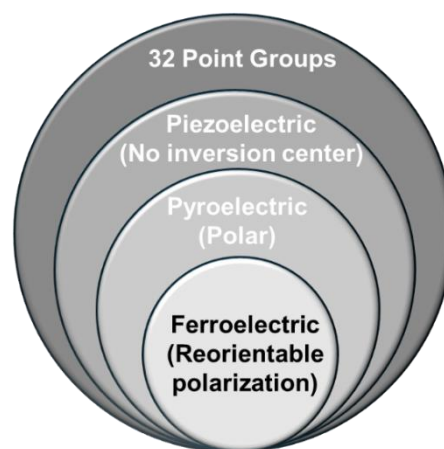


Fig. 1.2 Classification of the crystallographic groups by their electrical properties.

distortions of the Ti^{4+} cations lead to ferroelectric ordering. On the other hand, CaTiO_3 has a $t < 1$, which leads to rotations of the oxygen octahedra around the B-site, causing antiferrodistortive ordering. Finally, for large deviations of tolerance factor from unity the perovskite structure becomes unstable.

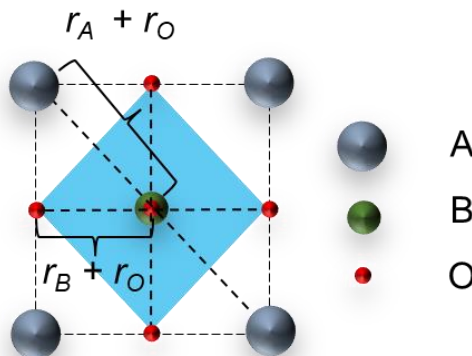


Fig. 1.3 Illustration of the parameters used in tolerance factor calculation. Note that atomic size is shown instead of realistic ionic size.

1.1.2 Origins of Ferroelectricity – Coordination Chemistry

In this Section, I discuss the origin of ferroelectricity with hybridization concept in the perovskite oxides. From the atomic level, ferroelectricity results from the competition between short-range repulsive forces favoring a centrosymmetric, non-ferroelectric structure and long-range attractive Coulomb forces favoring an ionically off-centered ferroelectric structure [7,8]. The situation wherein this balances tips towards the latter has been referred to as the *second-order Jahn-Teller* effect [9,10], and describes how the distorted ferroelectric structure can be stabilized via changes in the chemical bonding through two different mechanisms. In ABO_3 perovskites which have a transition-metal cation with a nonmagnetic d^0 electronic structure at the B site, weakening of the short-range repulsive forces and formation of covalent bonds between empty transition metal d orbitals and filled oxygen $2p$ orbitals [7,8] are known to be responsible for the onset of ferroelectricity. BaTiO_3 is a classic example of such a B-site-driven ferroelectric, where the hybridization of titanium $3d$ states with the oxygen $2p$ states results in the displacement of the titanium ions towards an oxygen ion (so as to slightly increase the electronic occupation of the titanium orbitals) and formation of a spontaneous polarization, while the barium $5p$ states remain inactive [7]. On the other hand, in PbTiO_3 , lead $6s$ and O $2p$ are strongly hybridized. The Pb-O bonding interaction, and the smaller ionic radius of Pb^{2+} compared with Ba^{2+} , lead to the larger strain in PbTiO_3 that reduces some Pb-O distances; the Ti-O repulsion prevents the volume shrinking enough to stabilize the cubic phase. This gives rise to loss of the center of symmetry and A-site-driven ferroelectric distortions in PbTiO_3 [7,8]. In other systems, such as BiFeO_3 with non- d^0 B-site cations, ferroelectric distortions are (nearly) completely driven by the stereochemical activity of lone pair electrons on A-site cations [11].

1.1.3 Soft-Phonon Mode Theory of Ferroelectricity

Soft-mode theory can also be used to explain the origin of ferroelectricity [12]. For non-primitive lattices such as perovskite oxides, there are two types of phonon modes: acoustic and optical phonons. Acoustic phonons relate to the coherent movement of atoms while the optic phonons refer to the out-of-phase movement of atoms. At the transition temperature (T_c), the temperature at

which paraelectric to ferroelectric phase transition takes place, phonon "softening" occurs such that the frequency of the transverse optical phonon becomes zero at the center of first Brillouin zone. Translating this into real space, indicates the onset of spontaneous polarization at the phase transition, due to the softening of optical phonon mode at the zone center ($k = 0$) corresponding to an off-centering displacement in an infinite region ($\lambda \rightarrow \infty$) of the real-space lattice. Soft-mode theory, once again, provides an explanation for the origin of ferroelectricity.

1.2 Complex-Oxide Materials

The following sections briefly introduce the core complex-oxide perovskite materials studied and utilized in this Dissertation.

1.2.1 PbTiO₃

PbTiO₃ is considered one of the most important members of the perovskite ferroelectrics. PbTiO₃ has several desirable properties, including high pyroelectric coefficient, high spontaneous polarization, and high Curie temperature [13]. PbTiO₃ is a technologically important component in PbZr_xTi_{1-x}O₃ (PZT), (1-x)PbZn_{1/3}Nb_{2/3}O₃-xPbTiO₃ (PZN-PT), and (1-x)PbMg_{1/3}Nb_{2/3}O₃-(x)PbTiO₃ (PMN-PT), which are integral part of various electronic devices, such as capacitors, ultrasonic transducers, optoelectronics, and thermistors [14–16]. Additionally, PbTiO₃ is a promising material for pyroelectric infrared detector applications due to its large pyroelectric coefficient and relatively low permittivity [15]. PbTiO₃ has also been extensively used in a range of piezoelectric applications, and it is the end member of several technologically significant ferroelectric perovskite series, such as PZT, PZN-P, and PMN-PT. At ambient temperature, PbTiO₃ has a strong anisotropy that develops during cooling through the cubic-to-tetragonal phase transition at $\sim 490^\circ\text{C}$ [17]. This anisotropy, as measured by the tetragonality of the unit cell (c/a), and can be as high as ~ 1.06 [18].

1.2.2 SrTiO₃

SrTiO₃ is one of the most studied perovskite systems and has been considered important for electronic, dielectric, and thermoelectric applications. The dielectric permittivity (ϵ_r) of SrTiO₃ is ~ 300 at room temperature and rapidly increases upon cooling to values of 20,000 in the quantum paraelectric state below 10 K [19]. Similarly, SrTiO₃ has drawn interest as a candidate material for thermoelectric applications based on its large carrier effective mass and resulting large thermopower [20,21]. More generally, SrTiO₃ is one of the most widely studied perovskite oxides and is highly susceptible to donor-doping by cationic substitution, oxygen vacancies, and field effects that result in a dramatic range of transport properties ranging from insulating to metallic to superconducting states [22,23]. Despite its intrinsic paraelectric nature, it is possible to stabilize ferroelectric order via a variety of methods such as substrate-induced strain [24,25], cation doping [26], ¹⁸O isotope substitution [27], defect engineering [28], etc. Advances in thin-film epitaxy have emphasized the role of substrate-induced strain in stabilizing ferroelectricity and enhancing the ferroelectric transition temperature (T_c) in SrTiO₃ thin-film heterostructures.

1.2.3 Pb_{1-x}Sr_xTiO₃

PbTiO₃ and SrTiO₃ have been shown to form a complete solid solution [29–31] of the form Pb_{1-x}Sr_xTiO₃ (PSTO). In turn, tuning the chemistry allows for precise compositional control over the phase-transition temperature and ferroelectric properties, allows for a tunable dielectric constant

[29–31], tunable polarization [32], and variable pyroelectric responses [33,34]; making $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ attractive for applications from microwave devices and pyroelectric-energy harvesters. Experimental studies indicate that the cubic-to-tetragonal ferroelectric phase transition temperature of the solid solution system decreases linearly with increasing SrTiO_3 composition [29–31]. High quality $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films with different strontium contents have been grown on DyScO_3 substrates to change the magnitude of the strain in a continuous manner [35]. Higher strontium contents has shown the formation of interesting completely in-plane domain formation in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system [36].

1.2.4 BaTiO_3

BaTiO_3 is among the most widely used and studied ferroelectric materials, and even eighty years after its discovery, it remains critical for applications such as multilayer ceramic dielectrics. BaTiO_3 was the first perovskite ferroelectric to be discovered during World War II in between 1941 and 1944 independently in the United States, Russia, and Japan [37]. It undergoes sequential phase transitions from cubic to tetragonal to orthorhombic and to rhombohedral structures upon cooling from high temperature. The cubic phase is non-polar and paraelectric. In bulk, BaTiO_3 undergoes a first-order phase transition from a paraelectric-cubic phase to a ferroelectric-tetragonal phase at a T_c of $\approx 120^\circ\text{C}$ [38]. This transition gives rise to a phase with a spontaneous polarization of $\approx 30 \mu\text{C cm}^{-2}$ along the [001] of the unit cell. The additional ferroelectric-to-ferroelectric transitions from tetragonal to orthorhombic to rhombohedral phases occur at $\approx 0^\circ\text{C}$ and $\approx -70^\circ\text{C}$, respectively [38]. Over the years, BaTiO_3 has been used in a wide variety of applications in various forms of crystals, bulk ceramics, multilayers, and thin films. The ability to be used in so many different applications is a consequence of the complex coupling and the various interactions associated with ferroelectric phenomena.

1.2.5 SrRuO_3

SrRuO_3 is a member of the larger class of ruthenates and is another extensively studied perovskite systems over the past few decades. In the bulk, SrRuO_3 is a strong itinerant ferromagnetic material below $\sim 160 \text{ K}$ due to the more localized $4d$ electrons in ruthenium. The electrical transport of bulk SrRuO_3 shows Fermi-liquid behavior at low temperatures, while it exhibits bad-metal behavior at higher temperature [39–41]. In recent years, epitaxial thin-film versions of SrRuO_3 have become the more widely adapted approach in the study of strong electron correlation phenomena. Beyond the interests in strain engineering, orientation-dependent studies, or thickness-dependent properties in epitaxial SrRuO_3 thin films have garnered considerable attention [41]. Epitaxial SrRuO_3 is simultaneously the most widespread epitaxial electrode for studies on complex oxide ferroelectric in heterostructures geometry.

1.3 Domains in Ferroelectrics

The regions of the crystal with uniformly oriented spontaneous polarization are called domains, and adjoining ferroelectric domains are separated from one another by domain walls which are on the order of a few units cells across [42,43].

1.3.1 Domain Formation in Thin Films

Domains in ferroelectrics are formed to minimize the electrostatic and elastic energies due to formation of spontaneous polarization and strain [42,43]. In this Dissertation, focus has been placed on the tetragonal system only with ferroelectric materials such as PbTiO_3 , SrTiO_3 and

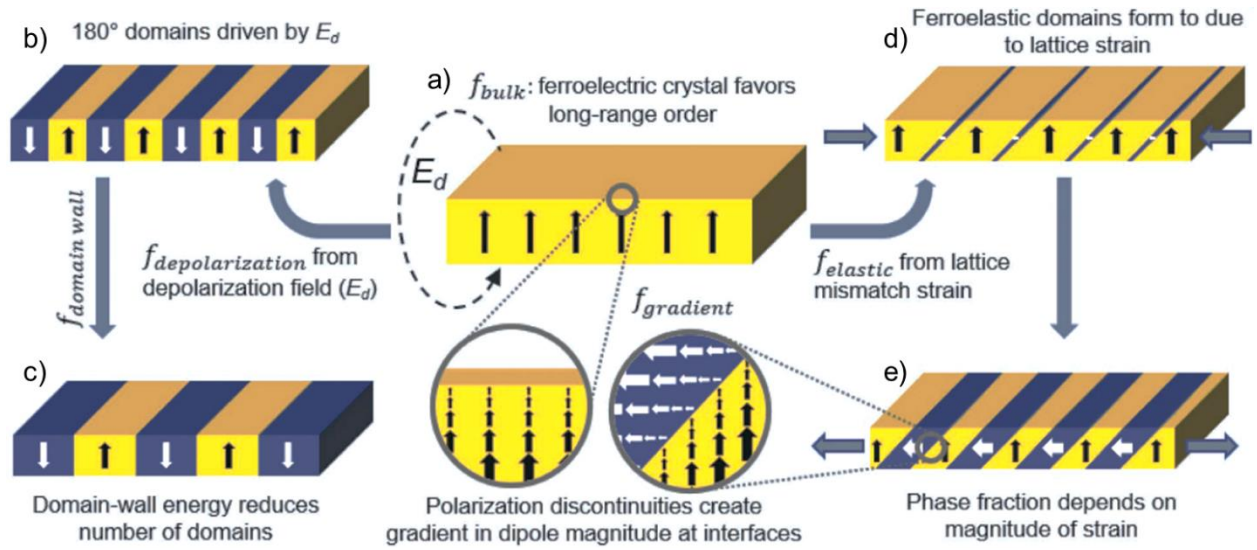


Fig. 1.4 Schematics of a) single domain structures, b) ferroelectric domain structures with 180° domain walls, c) domain structures with reduced 180° domain wall numbers, d) ferroelastic domain structures with ferroelastic 90° domain walls and e) domain structures with reduced 90° domain wall numbers [44].

BaTiO₃. Therefore, the discussion is limited to tetragonal systems only. An abrupt fall-off of polarization at the surface of a ferroelectric increases the electrostatic energy by giving rise to a surface charge density σ ($\sigma = P \cdot \hat{n}$, where $\hat{n}$ is the vector perpendicular to the film surface). This results in an electric field (*i.e.*, the depolarization field) being generated in the opposite direction (Fig. 1.4a) to the spontaneous polarization [42–44]. To minimize this electrostatic energy, the system can compensate for the depolarization field by covering the surface with neighbouring charged material particles, or by electrical conduction through the crystal, or reorganizing the polarization into domains with oppositely oriented polarization. The walls separating the regions of anti-parallel polarization are called 180° domain walls (Fig. 1.4b and c). Because the origin of these domains is purely electrostatic in nature, these are called ferroelectric domain walls. In addition to reducing the electrostatic energy, domains can also form to reduce the elastic energy of the ferroelectric phase [42]. Non-180° walls separating domains with different strain states are called ferroelastic domains (Fig. 1.4d and e). Such non-180° walls with head-to-tail polarization vectors can also lower the electrostatic energy of the system. Non-180° domain walls are, therefore, both ferroelectric and ferroelastic in nature. Such a combination of electric and elastic boundary conditions can lead to complex domain structures with many 180° and non-180° domain walls. The presence of domain walls, however, leads to additional domain-wall energy. Ultimately, the domains form to minimize the total of Landau, elastic, electric, and gradient energy terms [45].

1.3.2 Strain Engineering Domain Structures

There are several ways to control and engineer domain and domain-wall structures in ferroelectric thin films. In this Section, I focus on introducing a widely used strain-engineering method. Thin-film epitaxy allows one to manipulate the strain state of the thin-film by using a range of available single-crystal substrates. Like the effect of pressure on phase evolution in bulk system, biaxial strain applied to thin films also influences the phase and domain structure of ferroelectric thin films. For instance, PbTiO₃ exhibits a rich temperature vs. strain phase diagram (Fig. 1.5) encompassing a variety of structural phases as a function of strain [46]. The ferroelectric phase

adopts a tetragonal structure for all imposed strain conditions. Out-of-plane polarized c domains (Fig. 1.6a) are favored in the compressive strain regime, c/a domain structures (Fig. 1.6b) with a combination of out-of-plane and in-plane polarized domains are favored in the intermediate strain regime, and a_1/a_2 domain structures with orthogonally in-plane polarized a_1 and a_2 domains are favored in tensile strain regimes (Fig. 1.6c). Additionally, recent work suggests that a mixed-domain region occurs near the c/a and a_1/a_2 domain boundary exhibiting intriguing hierarchical superdomain structures [45]. This mixed-phase domain region can be explained using analogy to "spinodal decomposition", where the variable for such decomposition is strain [47]. Such strain-spinodal concepts are used to control coexisting domain structures in a variety of ferroelectric thin films such as BiFeO_3 [48], $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ [49], etc.

The epitaxial growth of thin films grown via (pulsed laser deposition) PLD and (molecular-beam epitaxy) MBE has been developed immensely in the last decade and these techniques are now regularly capable of producing high-quality stoichiometric ferroelectric thin films with unit-cell level control of thickness on single crystalline substrates [50]. Metal-organic chemical vapor deposition (MOCVD) is mainly suitable for large area deposition, but the growth systems are complex and need careful tuning of the precursor chemistries, flow rates, partial pressures, and growth temperature to obtain stoichiometric thin films. In PLD, a pulsed laser is used to create a plasma plume from a target of the desired film composition and the plume is directed towards a hot substrate on which the material is deposited. This makes PLD relatively easy to operate and provides for a high throughput. MBE enables very high-quality thin films and exceptional control of stoichiometry and thickness but suffers from low throughput and high operational costs. Consequently, a number of materials can typically be grown in a single PLD chamber allowing for seamless integration of ferroelectric thin films with dielectrics, metals, superconductors, and more. At the same time, complex oxide metals such as SrRuO_3 and wide range of substrates with different orientations and miscuts have also been manufactured to provide for fully epitaxial ferroelectric capacitor geometry with oxide metal top and bottom electrodes and epitaxial strain in

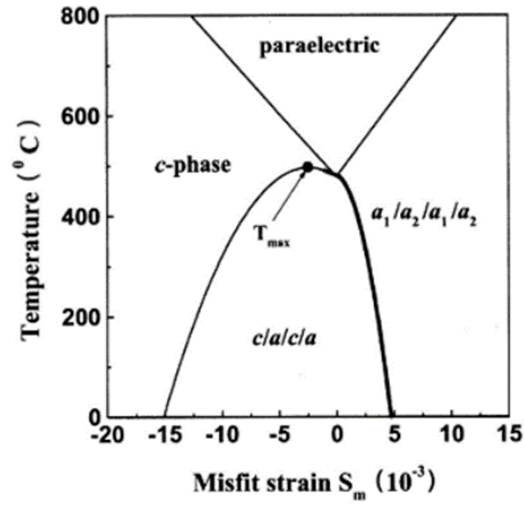


Fig. 1.5 The schematic of a ferroelectric polarization-electric field (P vs. E.) hysteresis loop.

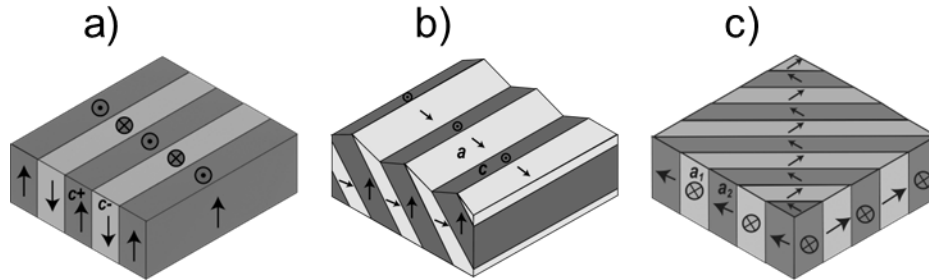


Fig. 1.6 Schematics of a) c domains, b) c/a domains, and (c) purely in-plane a_1/a_2 domains.

the range of $\sim 2\%$ for a variety of ferroelectric materials [50]. This has produced an array of

spectacular results in the past decade, such as strain-induced enhancement of T_c in BaTiO_3 [51], strain-induced ferroelectricity in SrTiO_3 [25], and electrode control of domain morphologies [52]. The growth of epitaxial thin films has also enabled the integration of ferroelectrics into multifunctional architectures such as highly tunable ferroelectric-dielectric superlattices [53], and ferroelectric field effect devices [54].

1.3.3 Compositional Control of Structural Phases

Besides strain engineering, chemical composition can also drive the formation of various structural phases. For example, in $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT), one of the most broadly investigated piezoelectric and ferroelectric materials, a rich phase diagram (Fig. 1.7) containing a variety of structural phases as a function of titanium content has been found [55]. The titanium-rich ferroelectric phases adopt a tetragonal structure, and a rhombohedral structure for the zirconium-rich side. For the endpoint compound PbZrO_3 , the structure adopts an antiferroelectric orthorhombic phase. Depending on the ratios of lead zirconate and lead titanate it contains, and the temperature, a PZT composition has a particular crystal structure, as indicated in the phase diagram [55]. The morphotropic phase boundary (MPB), located where the zirconate-to-titanate ratio is 52:48, indicates the transition from rhombohedral to tetragonal ferroelectric structure.

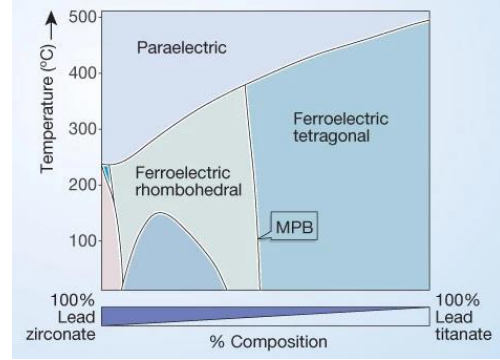


Fig. 1.7 Temperature-composition phase diagram of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) material [55].

1.4 Properties of Ferroelectric Materials

As mentioned at this Chapter's opening, ferroelectric materials are used in a wide range of electronic applications due to their switchable spontaneous polarization and the coupled dielectric, piezoelectric, and pyroelectric properties. In this Section, I review these properties in detail.

1.4.1 Dielectric Susceptibility

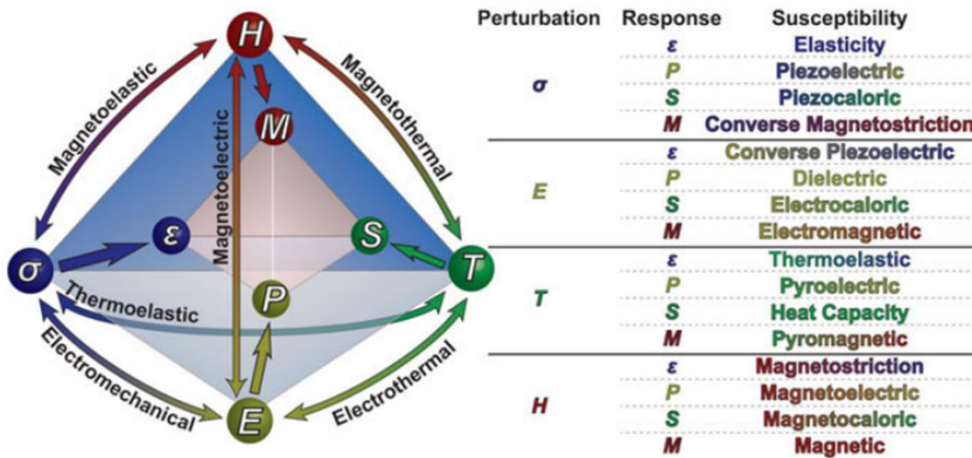


Fig. 1.8 Heckman diagram describing the relationships between electrical, mechanical, and thermal variables [56].

Ferroelectric materials demonstrate strong thermo-electro-mechanical coupling as described by a Heckmann diagram (Fig. 1.8) [56]. The most exciting and technologically significant properties of ferroelectrics result from their linear, small-signal susceptibilities to electric fields, mechanical stresses, and temperature which give rise to strong dielectric, piezoelectric, and pyroelectric effects, respectively [56,57]. These materials are often used near structural or polar instabilities (near T_c) where their susceptibilities are usually maximized. Dielectric permittivity (ϵ) describes how the polarization (P) is perturbed by an applied electric field as [58]:

$$P_{ii} = \epsilon_{ij}E_j \quad (3)$$

This linear relation is only valid in the low field regimes for nonlinear dielectrics such as ferroelectrics. Outside such linear regime, polarization value depends on higher-order terms of the field. Dielectric permittivity value changes as a function of temperature and reaches a maximum near T_c , accompanied by a peak in the dielectric loss. For thin films with an applied electric field in the out-of-plane direction (i.e. along the c axis), the component ϵ_{33} is usually measured. This can be obtained by determining the capacitance (C) of a ferroelectric capacitor structure with an area A and thickness t where $A = \epsilon_0\epsilon_{33}A/t$ with an applied AC electric field and utilizing it to derive the dielectric susceptibility. For the case of ferroelectric thin films, special attention has to be given to the electrode material, applied electric field magnitude, and the parasitic capacitances during measurement. It has been shown in previous studies that the nature of the electrode plays a critical role in the measurement of ferroelectric susceptibilities. Metal electrodes result in the formation of a dead-layer and space charge accumulation at the interface with the ferroelectric material due to the poor chemical and structural compatibility [59,60]. This results in an inactive interface layer and thus incorrect measurements of dielectric properties using the formula above. This problem can be largely resolved by using epitaxial oxide electrodes such as SrRuO_3 , and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. In this work, epitaxial electrodes of SrRuO_3 have been used for all the ferroelectric capacitor-based measurements. Similarly, applied electric field magnitude is also an important measurement consideration. Normally, the dielectric susceptibility of a ferroelectric refers to the reversible or the small-signal response of the ferroelectric material and is independent of the applied electric field magnitude. At large electric fields, the response of the ferroelectric is no longer linear due to switching and resulting domain wall motion. To measure the true linear response of the material, electric field amplitude dependent studies called Rayleigh analysis is usually performed to confirm that the linear behavior is indeed valid at the applied electric fields [61]. Apart from that, careful calibration of the parasitic capacitances in the measurement circuit is also required due to cabling, fixtures, etc. since the measured capacitances can often be small (< 1 nF) and comparable to the parasitic contributions. Above T_c , the temperature dependence of dielectric permittivity is known to follow the Curie-Weiss law [58]:

$$\epsilon = \frac{c}{T - T_0} \quad (4)$$

where c is the Curie constant, T is the temperature, and T_0 is the Curie-Weiss temperature. Dielectric permittivity in ferroelectrics is also a strong function of applied frequency. This frequency dependence originates from the presence of several mechanisms contributing to the dielectric response together with intrinsic electronic and ionic contributions, as well as extrinsic space charge and dipolar contributions [43,62]. Strong dielectric-loss peaks also appear near the relaxation frequency of each dielectric contribution.

1.4.2 Piezoelectric susceptibility

In addition to a strong dielectric susceptibility, ferroelectrics also exhibit strong piezoelectric responses. Piezoelectric susceptibility of ferroelectrics leads to the formation of polarization charges because of the application of a mechanical stress (X), which can be described by direct piezoelectric effect [58]:

$$P_{ii} = d_{ijk} X_{jk} \quad (5)$$

where d_{ijk} is the piezoelectric coefficient.

Moreover, application of an electric field to piezoelectric materials gives rise to a strain (x) through converse piezoelectric effect (with a converse piezoelectric coefficient that is thermodynamically identical to the direct piezoelectric coefficient) [58]:

$$x_i = d_{ijk} E_k \quad (6)$$

If the resulting strain varies as the square of the field function, it is acknowledged as the electrostrictive effect. The factor of piezoelectric coupling, k may be described as the square root of the ratio of the energy obtained in electrical form to net energy provided in mechanical form (direct effect) or the square root of the ratio of the energy obtained in mechanical form to net energy supplied in electric form (converse effect), i.e. on applying an electric field, it determines the percentage of the energy transformed from electrical to mechanical form (or alternatively on applying stress to a ceramic or crystal). The conventional values of k are 0.1, 0.4, and 0.5–0.7 for quartz, BaTiO₃, and PZT, respectively [63].

1.4.3 Pyroelectric susceptibility

Lastly, pyroelectric susceptibility leads to a change in the spontaneous polarization with temperature. The pyroelectric coefficient (π) is defined as [58]:

$$\pi_i = \frac{\partial P_i}{\partial T} \quad (7)$$

For a ferroelectric material, this is commonly measured by applying a known temperature change and evaluating the change in polarization that results. The polarization change is measured by monitoring the current that flows between the short-circuited electrodes (i.e., the pyroelectric current) to compensate for the polarization value change. As the current in the external circuit is related to the out-of-plane polarization change, the component π_3 is usually measured and is the most practically relevant component considering device geometry. Multiple techniques have been developed to apply this measurement principle such as, pulsed-laser based heat sources, constant rate temperature ramp in ovens, and phase-sensitive techniques using sinusoidal temperature oscillations [64–67]. Among these, the phase-sensitive measurements are the most preferred for accurate quantitative measurements in thin films case [65,66]. This is due to the difficulty in measuring the temperature rise of the sample and the contribution of thermally stimulated non-pyroelectric currents in the other two techniques.

1.4.4 Spontaneous Polarization Switching

Switching of spontaneous polarization between by application of an external electric field is a requirement for ferroelectricity. This kind of polarization switching gives rise to a polarization-electric field hysteresis loop (Fig. 1.9). This ferroelectric hysteresis loop is a plot of the integrated switching current (which arises from the polarization) as a function of the applied electric field and is one of the direct experimental proofs of ferroelectricity [62]. As discussed previously, ferroelectrics may split into different kinds of domains depending on imposed mechanical and

electrostatic boundary conditions. If equal fractions of oppositely polarized domains exist in the system, it gives rise to a zero net macroscopic polarization (point A, Fig. 1.9). In this case application of a small positive electric field, linearly increases the polarization value according to the relation [58]:

$$D = \epsilon E \quad (1)$$

where D is the electric displacement, ϵ is the dielectric permittivity, and E is the externally applied electric field on ferroelectric under test. However, higher values of applied electric fields can favor the domains with a spontaneous polarization parallel to the direction of the applied electric field. In response to larger electric fields, the system tries to maximize the domain fraction with energetically favorable polarization directions via movement and redistribution of the domain walls, rapidly increasing the measured charge density (segment BC, Fig. 1.9). The total polarization response in this regime contains the macroscopic spontaneous polarization (P_s) and the polarization due to application of the external electric field and is strongly nonlinear:

$$D = \epsilon E + P_s. \quad (2)$$

Once the movement and redistribution of the domain walls is complete the macroscopic spontaneous polarization reaches a saturation value, P_{s+} (point C, Fig. 1.9), and the ferroelectricity again behaves linearly with the electric field (segment CD, Fig. 1.9). If the field starts to decrease most of the domains do not have a driving force for switching back to their original polarization direction, and resulting non-zero macroscopic polarization is achieved at zero applied electric field (point E, Fig. 1.9). The polarization at zero electric field is known as the remanent polarization, P_{r+} . Remanent polarization is often smaller than saturation polarization due to the back-switching of some domains to their original polarization direction after removing the electric field. A negative electric field is then needed to bring the polarization to zero (point F, Fig. 1.9), and is called the negative coercive field, E_{c-} . Further increase of the field in the negative direction gives rise to a new alignment of domains and saturation in the negative direction, P_{s-} (point G, Fig. 1.8). Upon increasing the external field to zero from the negative side, a negative remanent polarization, P_{r-} , is achieved (point H, Fig. 1.9). Reversal of the field to and above the positive coercive field, E_{c+} , brings the polarization to zero (point I, Fig. 1.9) and its positive saturation value, P_{s+} , respectively, and completes the cycle. In this case, the polarization reversal occurs by domain-wall motion, and by nucleation and growth of new reversed domains. The growth of existing and nucleated domains involves the domains' forward growth and sideways propagation [56,57]. An ideal hysteresis loop is symmetrical such that the positive and negative values of P_s , P_r , and E_c are identical. The shape of the loop, however, may be influenced by a variety of reasons, including the charged defects, strain gradients, chemical gradients, and asymmetric electrodes.

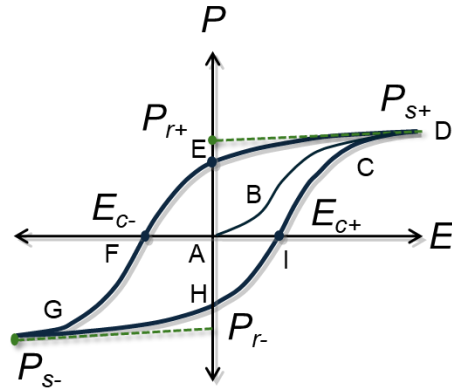


Fig. 1.9 The schematic of a polarization vs. electric field (P vs. E) hysteresis loop.

1.5 Statement of Thesis and Central Questions

In this Dissertation, I focus on developing new directions to engineer domain structures in ferroelectric thin films and integrate them in various heterostructures to reveal novel phenomena and access a broader range of properties. Here, moving beyond simple lattice-mismatch strain with different substrates, I demonstrate that chemistry, such as strontium content in $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ (PSTO) solid solutions, is a powerful approach to attain deterministic control of on-demand domain structures. These engineered ferroelectric heterostructures are then explored for innovative interfaces-driven interactions in multilayer and superlattice geometry for polarization switching in both in- and out-of-plane direction, allowing for new functionalities in ferroelectric device applications, including multistate memories. To integrate the ferroelectric switching capabilities with its interface-driven interactions to extend its utility beyond mere memory applications, BaTiO_3 ferroelectric thin films have been investigated for low-voltage operation ferroelectric field effect transistors (FEFET) for potential logic applications using the ferroelectric-ruthenates interfaces. In the scope of this overarching theme, I focus on the following questions in this Dissertation, summarized as follows:

1. Can geometric, topologically distinct phases be readily tuned in the hierarchical, mixed-phase domains thin films structures made up of PSTO and what are the implications of such control structure means for property evolution?
2. Is it feasible to achieve interface-related phenomena akin to exchange-interaction behavior observed in magnetism in ferroelectric-ferroelectric thin film multilayers and utilize them for potential memory applications?
3. Can emergent polar structures be produced in these all-ferroelectric superlattices, and if they can, how does this impact their overall response to applied stimuli?
4. Can metal-ferroelectric interfaces combine logic and memory functionalities at the single-device level to produce highly energy-efficient computing with viable ferroelectric field-effect transistors (FEFETs) operating at <200 mV while maintaining a viable memory window?

1.6 Organization of the Dissertation

The remainder of this thesis is organized as follows:

Chapter 2 describes the synthesis and general characterization techniques of perovskite oxide thin films, and the methods and background on electrical testing of various device structures fabricated with thin-film heterostructures.

Chapter 3 demonstrates chemistry as a major tuning parameter while maintaining a consistent substrate for deterministic strain-driven control of hierarchical domain structures in $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ solid-solution thin films wherein two types, c/a and a_1/a_2 , of nanodomains can coexist. Further, the relationship between the different mixed-phase modulation patterns, their topological nature and resultant properties is established.

Chapter 4 details developing a chemistry tunable purely in-plane ferroelectric domain system of PSTO and their switching characteristics in the bilayer configuration where interfacial coupling-induced electric analogs of exchange-interaction-like behavior have been observed. The physical origins of these interactions have been explained using phase-field simulations, and their utilization has been shown towards multistate memory applications.

Chapter 5 demonstrates the possibility of polar vortices formation in all-ferroelectric trilayers, multilayers, and superlattices built from the fundamental building block of $(\text{PbTiO}_3)_n/(\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3)_n$, and resultant enhanced piezoelectric and ferroelectric responses in the out-of-plane direction along design principles for getting in-plane multistate functionality.

Chapter 6 describes the synthesis, characterization, and fabrication of devices based on BaTiO_3 as a ferroelectric component and ultrathin SrRuO_3 as channel material for a promising FEFET model system demonstration. The modulation of channel resistance is then investigated in relation to applied gate voltage and system temperature for various ultrathin SrRuO_3 channel thicknesses.

Chapter 7 provides a summary of the findings in this thesis, as well as a discussion of future work.

CHAPTER 2

Synthesis and Characterization of Ferroelectric Thin Films

This Chapter gives an overview of the basic methodology used in this work to study ferroelectric thin films. First, I briefly introduce the synthesis of epitaxial ferroelectric thin films using pulsed-laser deposition. Second, I introduce the processing methods used to fabricate samples for both out-of-plane parallel plate and in-plane interdigitated electrode-based studies and Hall bar devices. Finally, I discuss the characterization methods used in this work, including X-ray diffraction, atomic force microscopy, piezoresponse force microscopy, and electrical/dielectric/ferroelectric/transport characterization measurements.

2.1 Synthesis of Ferroelectric Thin-Film Heterostructures

2.1.1 Pulsed-Laser Deposition

In this work, pulsed-laser deposition method was used for the growth of epitaxial complex-oxide ferroelectric thin-film heterostructures. The prevalent use of this deposition for the growth of complex oxides is due to numerous advantages it has over other thin-film growth techniques. Pulsed-laser deposition has attracted considerable interest due to its fairly simple and inexpensive setup, its high output, the potential to create high quality of thin films, and the flexibility it offers to synthesize a wide range of oxide material systems [68]. Sintered hot-pressed ceramic disks or single crystals are used as targets in this method. Multiple targets can be placed in a growth chamber at a one-time allowing for *in situ* growth of ferroelectrics, dielectrics, metals, etc. The addition of double-differentially pumped reflection high-energy electron diffraction (RHEED) to the growth chamber further enables *in situ* growth monitoring, expanding ones capability to control thicknesses at the unit-cell level. Such abilities, combined with the advancement of a variety of single-crystal substrates and surface cuts (orientations) and treatments has enabled the growth of high-quality epitaxial thin films with unit-cell-level precision of artificial nanostructures and superlattices with atomically sharp interfaces. It is possible to achieve (with care) correct, stoichiometric target material transfer through optimization of the growth conditions such as in varying some combination of deposition pressure, heater temperature, laser repetition rate, laser fluence, and post-growth cool-down pressure, etc.

Pulsed-laser deposition is a physical vapor deposition technique which deposits a laser ablated material onto a substrate. The growth process comprises short (tens of nanoseconds) and precisely energy monitored laser pulses, followed by annealing in the time intervals between the laser pulses. A high-power, excimer pulsed laser is focused using optics on a material target of the

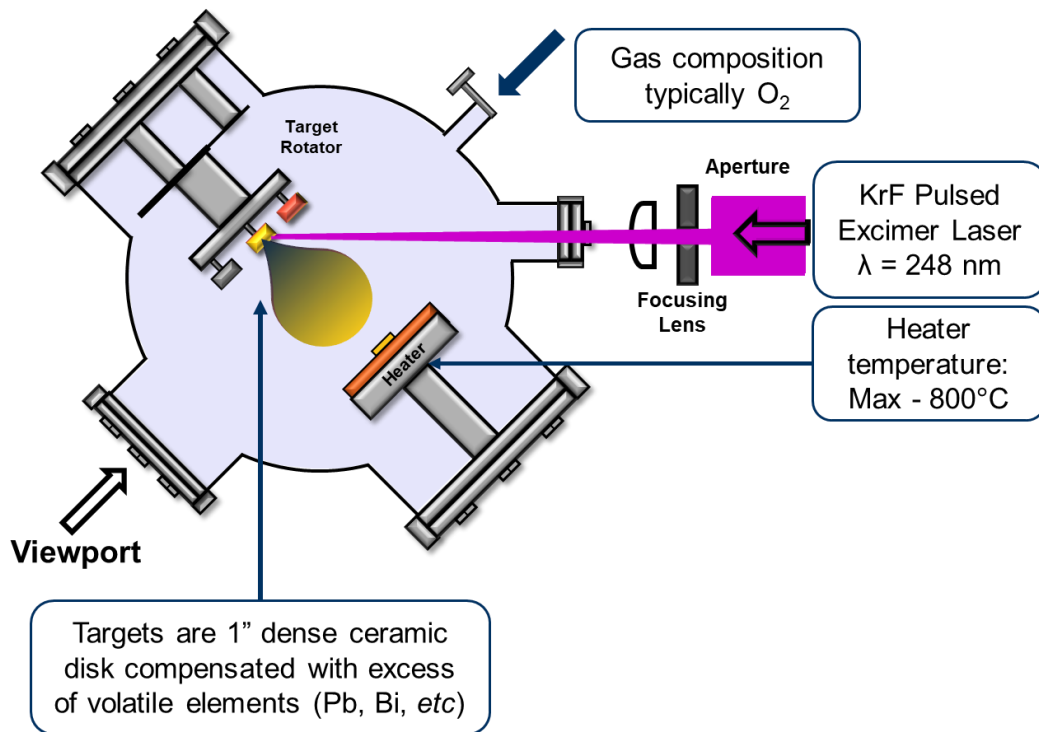


Fig. 2.1 Schematic of the PLD system used for the deposition of thin films studied in this dissertation.

desired composition. The energy of the focused incident laser is absorbed by the target which creates a molten layer (*i.e.*, Knudsen layer) and subsequently vaporizes the material on the target top surface. The high energy density laser beam incident on the target surface leads to the formation of a plasma plume [68]. The plasma plume contains highly energetic molecules, neutral atoms, ions, electrons, particulates, and molten globules, and rapidly expands away from the target, and transfers the ablated material from target to a heated substrate (generally maintained at 400-900°C). This ablation process typically takes place in a vacuum chamber in the presence of a background gas such as oxygen, argon, or a mix of such gases in a desired proportion. The growth of oxide materials is often carried out in an oxygen ambient with pressures in the range of 1-500 mTorr.

There are numerous interactions involved in the ablation process including interactions between laser and target material, the laser and the resulting plasma plume, species within the plasma, and the plasma plume with the background gas. These multiple interactions have a considerable impact on the composition and energy of the species in the plume [68]. There are many "controllable" parameters involved in the pulsed-laser deposition process, such as substrate temperature, laser-pulse repetition rate, laser fluence, background gas composition, growth pressure, target-substrate distance, deposition angle, etc. which affect such interactions, and in turn, have a marked impact on the growth rate, growth mode, stoichiometry, and structure of the synthesized thin films.

In this work, a KrF excimer laser with a wavelength of 248 nm (LPX 305, Coherent) was used. All depositions were performed using an on-axis geometry with a target-to-substrate distance of ≈ 5.5 cm. A schematic of the pulsed-laser deposition setup used in this work is provided (Fig. 2.1). The vacuum chamber includes a target holder/rotator on one side and a substrate heater on the other. Targets were sanded every time before being mounted on the target holder and were set to rotate and raster during the growth to maintain an even ablation process across the surface. The substrates were sonicated for five minutes each in acetone and isopropanol in ultrasonicate bath, and then mounted on the heater using silver paint (Leitsilber 200 silver paint, Ted Pella, Inc.), and cured for fifteen minutes at 80°C. After mounting the targets and substrates, the chamber was pumped down to a base pressure $\sim 1 \times 10^{-6}$ Torr. A leak valve along with a partially open gate valve connected to turbo pump was then used to fill the chamber with oxygen gas (99.995% pure) to set the desired dynamic growth pressure. The substrates were heated to the growth temperature at a ramp rate of 20°C min⁻¹. Prior to deposition, the targets were pre-ablated to ensure that the target surface reached a steady state chemical composition for ablation process. Following the growth, the chamber was filled with oxygen to promote complete oxidation of the grown thin films. The films were then cooled down to room temperature at a rate of 10°C min⁻¹ in a static oxygen pressure of ≈ 700 Torr.

2.2 Characterization of Ferroelectric Thin-Film Heterostructures

2.2.1 X-ray Diffraction

After the synthesis of the ferroelectric thin-films heterostructure, structural characterization was carried out using X-ray diffraction. X-ray studies for this dissertation were performed using a Panalytical X'Pert3 diffractometer with copper K_α radiation with a wavelength of 1.54 Å. X-ray diffraction is a non-destructive characterization technique which relies on the elastic scattering of X-ray photons by the electrons of the atoms in a periodic lattice. During the measurement, an

incident beam of monochromatic X-rays is focused on a crystalline material. The diffraction process involves the constructive and destructive interference of X-rays scattered from the crystal planes. The scattered X-rays that are in phase give rise to a constructive interference according to Bragg's law [69]:

$$n\lambda = 2d \sin\theta \quad (1)$$

where n is an integer called the order of reflection, λ is the wavelength of X-rays, d is the out-of-plane spacing between the crystal planes, and θ is the angle between the incident beam and the normal to the reflecting lattice planes. The θ angle of potential diffraction peaks depends on the size and shape of the material unit cell. The intensities of the diffracted waves depend on the kind and arrangement of atoms in the crystal structure [70].

One of the most widely used X-ray diffraction methods for thin-film heterostructure is the ω - 2θ scan [70] which measures the Bragg diffraction of thin-film heterostructures (Fig. 2.2). The incident angle, ω , is defined between the X-ray source and the thin-film sample, whereas the diffracted angle, 2θ , is defined between the incident beam and detector (Fig. 1.x). The ω - 2θ scan is a coupled scan in which both angles ω and θ vary constantly but stay linked such that:

$$\omega = \frac{1}{2} \times 2\theta. \quad (2)$$

This measurement allows for the assessment of phase, structure, and strain condition of the films, where the in-plane misfit strain can impact the out-of-plane spacing d through the Poisson's ratio and thus causes a peak shift. Another commonly implemented X-ray diffraction technique that provides the most complete structural information in thin-film heterostructures is the reciprocal space map (RSM), which is performed such that the Bragg diffraction is mapped in a confined area of reciprocal space. This method collects a number of ω - 2θ coupled scans [70], where each coupled scan is measured with a slightly different ω -offset such that $2\theta = 2\omega + \text{offset}$. RSMs are usually performed as symmetric scans (or on-axis scans) which probe the diffraction from planes parallel to the film surface, or asymmetric scans (or off-axis scans) which probe the diffraction from planes tilted from the film surface. In the study of ferroelectric thin-film heterostructures, symmetric RSMs are usually used to separate domain structures with different lattice tilts and to understand polar vortex periodicity. While asymmetric RSMs are usually used to analyze the epitaxial nature and the in-plane domains characterization.

2.2.2 Atomic Force Microscopy

The topographical study of the thin-film heterostructures was carried out using an atomic force microscope (AFM) using a MFP-3D microscope from Asylum Research (now Oxford). All topography measurements were carried out using silicon tips (Tap300Al-G BudgetSensor AFM)

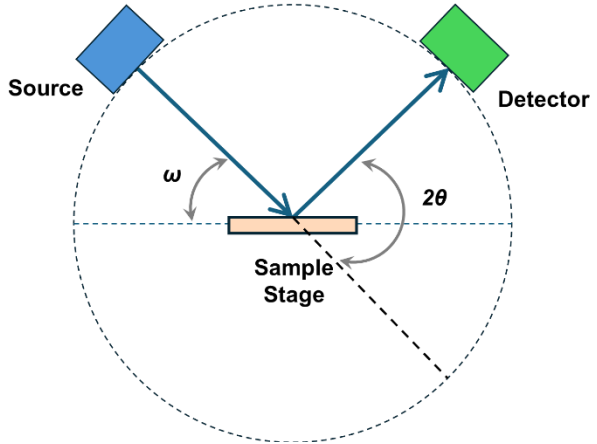


Fig. 2.2 Schematic of geometry for XRD. The incident and scattered X-rays are symmetric around the plane normal during a symmetric θ - 2θ measurement.

with a force constant of 40 Nm^{-1} at a resonance frequency of $\approx 300 \text{ kHz}$ using the AC Air Topography mode (non-contact tapping mode). AFM probes the tip-sample force where the feedback loop maintains a constant force by constantly changing the z-position of the tip when

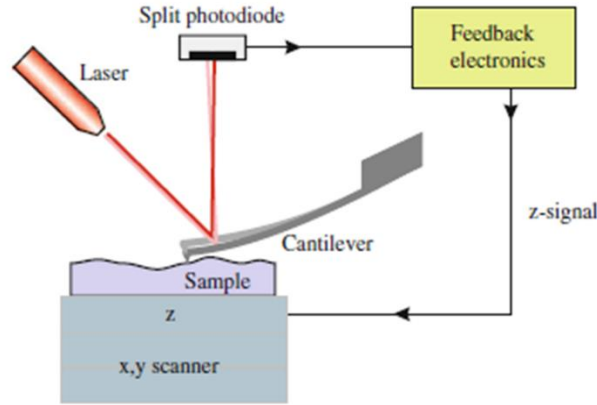


Fig. 2.3 The schematic of experimental set-up of atomic force microscope.

scanning on a surface [70] (Fig. 2.3). As a result, topographical information and the film roughness can be extracted from the corresponding z-position change. AFM is usually operated in static contact mode or dynamic tapping mode. In static contact mode, the tip-sample force is represented as the change of the cantilever bending, while in dynamic tapping mode, the tip-sample force is represented as the amplitude change of the cantilever oscillation.

2.2.3 Piezoresponse Force Microscopy

Piezoresponse force microscopy (PFM) is a scanning probe microscopy (SPM)-based method used to understand polar materials at the nanoscale and pole the selective region with applied voltage. Using a SPM setup, a PFM tip (a conductive AFM tip) is brought into contact with the surface of a piezoelectric/ferroelectric material and the piezoelectric response of the surface is detected as a function of the tip deflection during application of an AC bias to the tip. The cantilever displacement in response can be detected by the photodiode which is processed by a lock-in-amplifier to extract the phase and amplitude information of the surface oscillation. In this method, the tip follows the local deformation of the sample surface that takes place directly at the apex of the tip, driven by the alternating voltage applied to it. The forces acting on the tip can be resolved into 3-components, F_{ver} , F_{lat} , and F_{long} that manifest as a vertical deflection, lateral torsion, and buckling, respectively, of the cantilever tip (Fig. 2.4). The phase of the electromechanical response of the surface returns information on the polarization direction directly below the tip area. For domains with polarization pointing normal to the surface for the material, the application of a positive tip bias results in the expansion of the sample and the surface oscillations are in phase with the tip voltage. On the other hand, for domains with downward (into the face of the sample) polarization, the response is 180° phase shifted. The vertical displacement of the cantilever gives rise to out-of-plane or the vertical PFM contrast and details about the vertical direction of the polarization. In the same manner, torsion of the cantilever or the lateral deflection in the detector can be measured, thus allowing for determination of the in-plane or the lateral piezoresponse. In addition, PFM tool can also be used to engineer polarization by applying a local DC bias by a PFM tip which can induce local polarization switching. This methodology is called PFM lithography

which is used to create a desired domain pattern by selectively switching certain areas of ferroelectric films.

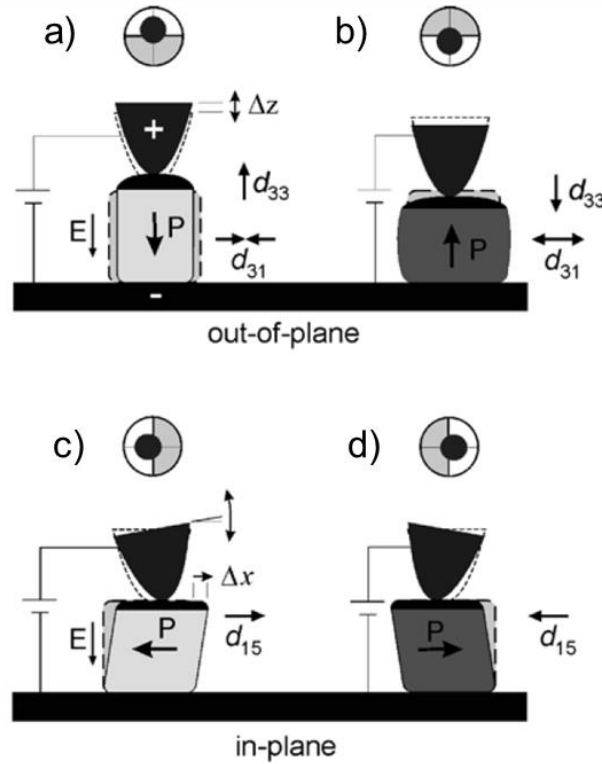


Fig. 2.4 The fundamental principle of piezoresponse force microscopy (PFM). a) and b) The vertical PFM probes the polarization component which is parallel or anti-parallel to the applied electric field which leads to the lifting or contraction of the cantilever via the d_{33} effect. c) and d) The lateral PFM probes the horizontal polarization component which leads to a shear movement of the sample and thus a torsion deformation of the cantilever via the d_{15} effect [260].

2.3 Processing of Ferroelectric Thin-Film Heterostructures

2.3.1 Out-of-plane Parallel-Plate Capacitor Device Fabrication

The electrical properties for heterostructures were studied with symmetric SrRuO_3 films serving as the top and bottom electrodes (Fig. 2.5a). Following the growth of the pertinent active (typically ferroelectric) layer, capacitor structures were fabricated via photolithography and wet etching. A photoresist layer of OCG 825 35CS-FUJIFILM Electronic Materials was spin-coated on the heterostructures using a KW-4A, Chemat Technology spin-coater with a spin speed of 1000 rpm for 10 s, followed by 6000 rpm for 40 s (Fig. 2.5b). The heterostructures were then heated to 95 °C for 120 s using a hot plate. Next, the heterostructures were exposed to ultraviolet light through a Hybrid Technology Group, Inc. photomask in a mask-alignment system for 120 s (Fig. 2.5c). After the exposure, the heterostructures were developed in a 1:1 water and Microposit developer concentrate from Rohm and Haas Electronic Materials LLC for 40 s (Fig. 2.5d). The samples were then washed thoroughly with water to remove any remaining developer solution (Fig. 2.5e). The top SrRuO_3 layer was then selectively wet-etched by an NaIO_4 aqueous solution (0.1 mol L^{-1}) to realize circular capacitor array of circles with diameters of 25 μm and 50 μm (Fig. 2.5f). The

remaining photoresist was then washed with acetone to expose top SrRuO_3 in circular capacitor form (Fig. 2.5g).

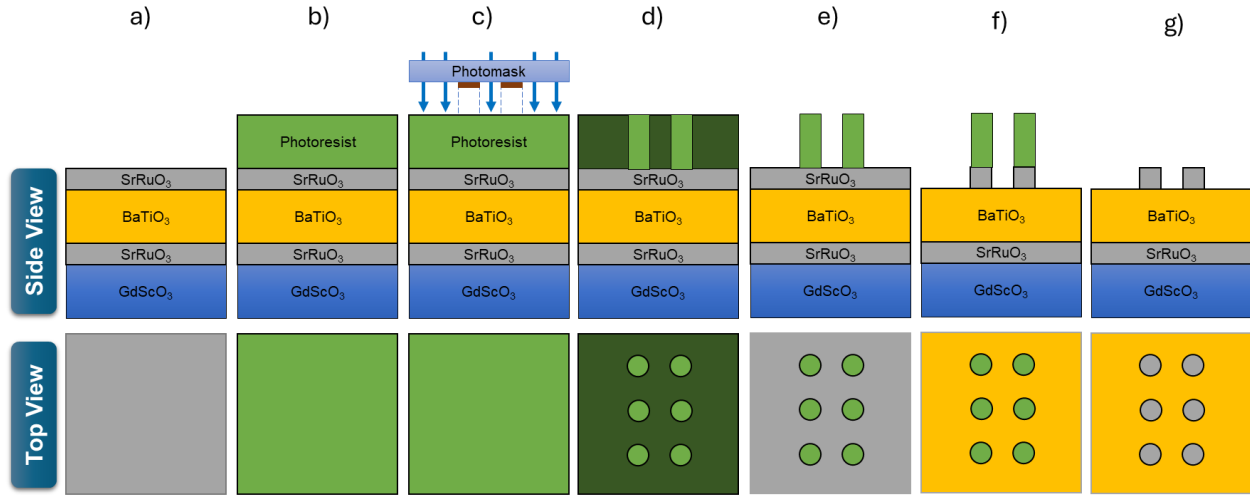


Fig. 2.5 Microfabrication process for capacitor device fabrication. a) Tri-layer sample. b) Spin coating of photoresist. c) Photolithography into circular capacitor shape. d) Photoresist after exposure. e) Photoresist development. f) Wet etching of SrRuO_3 in 0.1M NaIO_4 solution outside the circles to form top electrodes. g) Removal of photoresist in acetone.

2.3.2 In-plane Interdigitated Electrode Device Fabrication

Ferroelectric properties of the in-plane polarized ferroelectrics were studied using in-plane device structures. These structures were patterned via UV lithography using a Heidelberg MLA150 Maskless Aligner in the Berkeley Marvell NanoLab using AZ MiR 701 Photoresist. For these devices, interdigitated electrodes (IDE) with a finger length were $120\ \mu\text{m}$ and finger spacings of $5\ \mu\text{m}$ were used (Fig. 2.6). After patterning, a layer of $\sim 5\ \text{nm}$ of titanium (which is used as an adhesion layer) and a layer of $\sim 80\ \text{nm}$ of platinum was deposited at room temperature via DC magnetron sputtering with base pressure of $\sim 10^{-8}$ Torr. Titanium and platinum were sputtered at 20 W and 15 W, respectively, under argon pressures of 3.3 mTorr and 7.0 mTorr, with $1.7\ \text{nm min}^{-1}$ and $8.7\ \text{nm min}^{-1}$ growth rates. The additional metal deposited outside the primary device

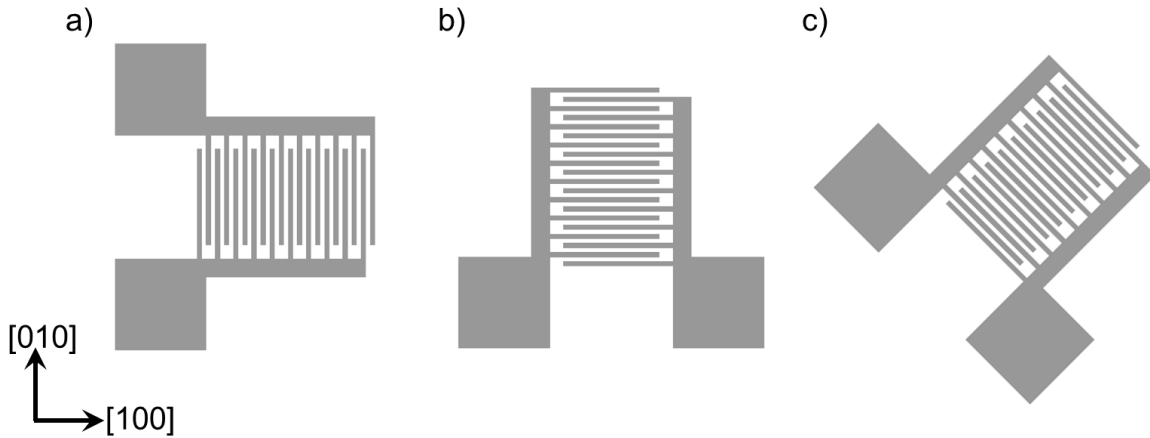


Fig. 2.6 Schematics of various device geometries. a) 0° device geometry, b) 90° device geometry, and c) 45° device geometry.

structure was then lifted off via an approximately five-hour soak in 1-methyl-2-pyrrolidone (NMP) at 85°C which was maintained using a hot plate.

2.3.3 Hall-bar Device Fabrication

FEFET device fabrication is divided into three steps based on the constituent three mask layers involved in the process. These devices are based on Hall-bar device geometry with six terminals. Starting with trilayer samples of the form $\sim X\text{-}Y$ unit cells $\text{SrRuO}_3/100\text{ nm BaTiO}_3/10\text{ nm SrRuO}_3$

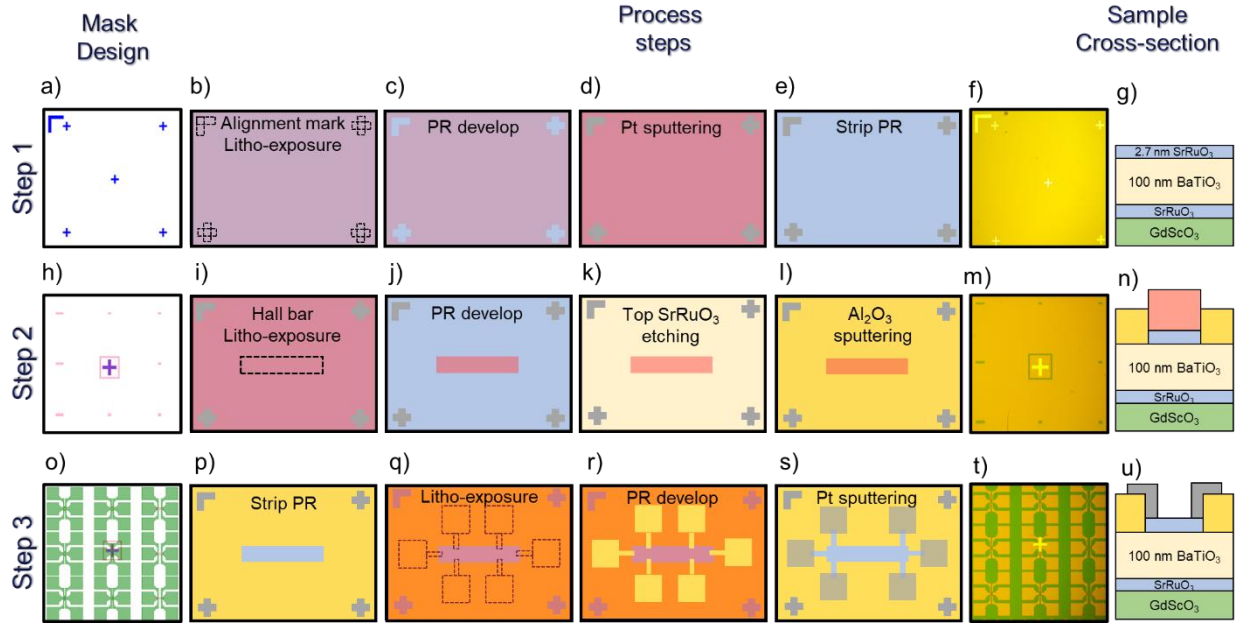


Fig. 2.7 Microfabrication process for Hall-bar devices. a) Mask layer 1 consisting of alignment marks. b) Spin coating of photoresist and photolithography exposure. c) Photoresist development. d) Pt metal sputtering. e) Remaining photoresist stripped using acetone. f) Final image of Pt alignment marks. g) Cross section of the sample after step 1 completion. h) Mask layer 1 consisting of alignment marks. i) Spin coating of photoresist and photolithography exposure of hall bars. j) Photoresist development step. k) Ion milling of external SrRuO_3 beyond defined hall bars. l) Insulating Al_2O_3 layer sputtering. m) Final image after Pt alignment marks and hall bar lithographic step. n) Cross section of the sample after step 2 completion. o) Mask layer 3 consisting of alignment Pt contact pad. p) Removal of photoresist in acetone. q) Spin coating of photoresist and photolithographic exposure. r) Pt contact pads area after development step. s) Final device. Photoresist was removed in acetone after deposition of Pt. t) Optical microscope image of an actual sample after completion of all steps. u) Cross section of the sample after all steps completion.

grown on GdScO_3 (110) substrate, step 1 consists of the fabrication of platinum alignment marks (Fig. 2.7a), which are essential for the next two steps of the alignment process. Then, the photoresist was spin-coated, exposed, and developed (Fig. 2.7b and c), like the previously discussed capacitor-making process. Next, platinum was sputtered (Fig. 2.7d) along with a titanium seed layer for better adhesion. Finally, the external platinum on the photoresist was stripped with acetone (Fig. 2.7e) to achieve platinum alignment marks on the bare samples (Fig. 2.7f and g).

Step 2 involves patterning Hall bars (Fig. 2.7h). Similar lithographic steps were carried out as previously discussed (Fig. 2.7i and j), but this time by taking reference with respect to the deposited platinum alignment marks. Then, the sample was ion-milled (Nanoquest, Intlvac Thin Film Corp.) at a beam voltage of 300 V, acceleration voltage of 45 V, and beam current of 5 mA to the top of the BaTiO_3 surface (using a SIMS detector) to isolate the SrRuO_3 Hall bars on the

sample's top surface (Fig. 2.7k). After confirming the removal of the external SrRuO₃ outside the Hall-bar patterns by inspection of surface conductivity by a multimeter, the samples are transferred to an Al₂O₃ sputtering step (Fig. 2.7l). Here, Al₂O₃ functions as an insulating layer between the BaTiO₃ and platinum contact pads. ~200 nm of Al₂O₃ is sputtered to get suitable isolation thickness between the BaTiO₃ and platinum contact pads (Fig. 2.7l-n). After this step, the photoresist pattern defining the Hall bars was stripped using acetone to expose the top SrRuO₃ for the next step (Fig. 2.7o and p).

The last step involves patterning the platinum contact pads (Fig. 2.7o). Again, lithographic process steps like that of step 1 were carried out (Fig. 2.7q and r), but this time again by carefully aligning with the Hall bar patterns defined at previous steps and with the help of previously defined platinum-alignment marks. Next, platinum was sputtered (Fig. 2.7s) along with a titanium seed layer for better adhesion. Again, the external platinum on the photoresist-defined pattern area was stripped away using the acetone to get the final six terminal Hall-bar devices (Fig. 2.3t and u).

2.4 Electrical Characterization

In this Section I emphasize basic electrical characterization such as dielectric and ferroelectric property measurements of ferroelectrics heterostructures which are commonly used in this work. Firstly, all these measurements are carried out on capacitor structures in both out-of-plane direction in parallel-plate-type devices and in the in-plane direction with interdigitated electrode (IDE) devices or in both as for the Hall-bar devices. The details of how to fabricate capacitor structures with conductive oxide electrodes, IDEs and Hall-bar based FEFET devices are discussed in the previous section.

2.4.1 Dielectric Measurements

The complex dielectric permittivity of ferroelectric heterostructures measured in the out-of-plane geometry can be probed as a function of applied frequency, background DC electric field, AC excitation field, and temperature, providing a multitude of information about the material. In this work, dielectric and loss tangent measurements were performed using an E4990A Impedance Analyzer (Keysight Technologies). The dielectric susceptibility of the material was measured in a parallel plate capacitor geometry, with the application of small AC voltage in the out-of-plane direction to measure both real and imaginary impedance parameters which in turn can generate dielectric capacitance and loss tangent ($\tan \delta$) values. The out-of-plane component of the dielectric constant or relative permittivity (ϵ_r) can be calculated from the capacitance value (C):

$$\epsilon_r = \frac{Cd}{\epsilon_0 A}. \quad (3)$$

The AC excitation voltage was picked such that it was safely in the reversible switching regime of the material and excluded the dielectric non-linearities due to the irreversible extrinsic contributions. At larger electric fields, due to the irreversible domain-wall motion in the material and switching effects, the response is no longer field-independent. This reversible regime was identified via Rayleigh measurements which probe the dielectric constant as a function of AC excitation voltage at a given frequency [61].

2.4.2 Ferroelectric Hysteresis Loop Measurements

The experimental confirmation of ferroelectricity is commonly demonstrated through the polarization-electric field (P - E) hysteresis loop. This plot showcases the integrated switching current versus the applied electric field, illustrating the hysteresis and saturation behaviors associated with switching between the different domain states. Ferroelectric polarization-electric

field hysteresis loops were obtained by applying an external bipolar triangular voltage profile (Fig. 2.8) to the capacitor heterostructures at various frequencies (0.1-100 kHz). All measurements were performed using a Precision Multiferroic Tester (Radiant Technologies, Inc.) which measures the total change in the charge of the ferroelectric capacitors in response to the voltage profile which also includes leakage and dielectric contributions from the samples. The polarization values were then calculated by dividing the measured change of the charge by the area of the capacitor. Characteristic switching values of the capacitor sample such as saturation polarization, remanent polarization, and coercive field are extracted from the collected hysteresis loops. In the case of asymmetric ferroelectric hysteresis loops, average values were reported along with an electrical imprint value:

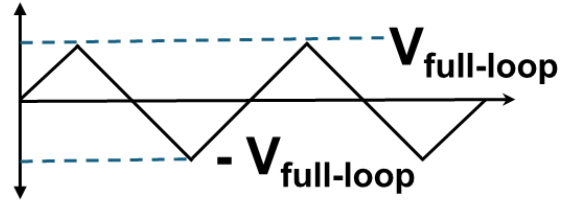


Fig. 2.8 The voltage profile used in this work for ferroelectric hysteresis-loop measurements.

$$E_{c_{avg}} = \frac{|E_{c+}| + |E_{c-}|}{2} \quad (4)$$

$$P_{s_{avg}} = \frac{|P_{s+}| + |P_{s-}|}{2} \quad (5)$$

$$P_{r_{avg}} = \frac{|P_{r+}| + |P_{r-}|}{2} \quad (6)$$

$$E_{imprint} = |E_{c+}| - |E_{c-}| \quad (7)$$

2.4.3 Ferroelectric Hysteresis Loop Measurements for In-plane Devices

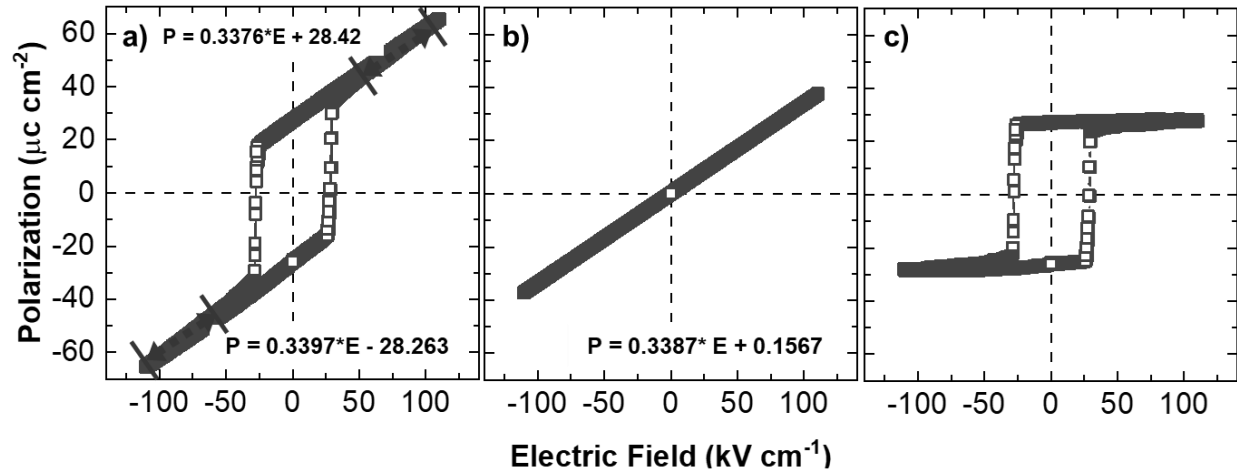


Fig. 2.9 a) Polarization vs. electric field hysteresis (P vs. E) loops measured at 1kHz frequency. The linear fitting method was used on higher positive and negative electric field regions to estimate the dielectric background. b) Based on the linear fitting from part one, the equation of a line is calculated using the average of slope and intercept values displaying dielectric background. c) The equation of the line calculated in part two is subtracted from part one to get the ferroelectric only switching contribution.

Polarization-electric field hysteresis loops for in-plane polarized ferroelectric materials was measured using a Precision Multiferroic Tester (Radiant Technologies, Inc.) using IDEs. The hysteresis loop measurements were performed at 1 kHz with a double bipolar waveform at the required voltage amplitude depending on the material's switching field requirements. To contact the sample electrodes, tungsten probe tips (model 7-B, The Micromanipulator Company) with a point radius of 0.5 μm were used. Polarization-electric field hysteresis loops were captured for a given sample (for example, Fig. 2.9a). Due to the device geometry, the hysteresis loops included a ferroelectric switching signal and a dielectric background signal. Linear fitting was done at both ends at the high-field region (positive and negative), where the signal predominantly comes from the dielectric background (Fig. 2.9b). The equation of a single line is then calculated (Fig. 2.9b) by taking an average of the slope and linear intercept of previously assessed two linearly fitted lines at the high-field regions (positive and negative). This linear equation is then subtracted from the raw hysteresis loop data to get switched polarization-only data (Fig. 2.9c).

2.4.4 Positive-Up-Negative-Down (PUND) Measurement

A pulse-switching measurement used in this study is the so-called positive-up-negative-down (PUND) method which probes the change of polarization as a function of pulse amplitude (voltage) at a constant applied pulse width. The polarization switching behavior and long-term reliability of ferroelectric capacitors are assessed through pulsed testing using PUND techniques. PUND measurements are instrumental in quantifying both the total switchable polarization and the remnant polarization in ferroelectric capacitors. These measurements serve as the foundation for reliability testing and fatigue assessment in applications such as memory and other long-term switching applications. A conventional PUND pulse sequence was used in these measurements (Fig. 2.10). Each measurement cycle is made up of five pulses comprising one preset pulse and four reading pulses with specific voltages and widths. A large preset voltage is applied at the beginning of each cycle to pre-pole the in-plane domain architecture to the negative direction; no measurement is performed for this pulse. The pulse width is kept constant ($t = 1\text{ ms}$ and 4 ms in this work), while the pulse voltage is increased by 0.5 V for each consecutive cycle. The second pulse switches the in-plane domains to the positive direction and measures the amount of switched polarization. The third pulse is an exact replica of the second pulse, which is used to read the non-remanent part of polarization along with the dielectric background, which dissipates during the delay time after the second pulse. The fourth and fifth pulses mirror the second and third, and switch the capacitor to the negative direction and read both the switched and non-switched polarization, respectively. The delay time between all the pulses

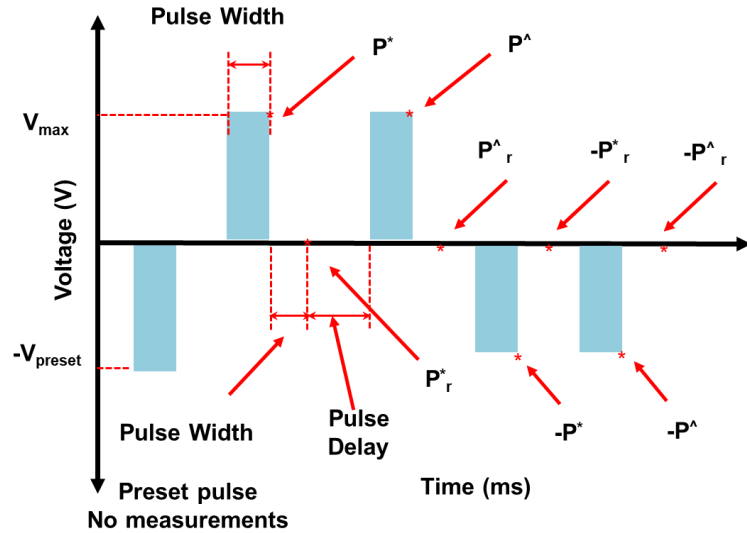


Fig. 2.10 The pulse sequence used for the conventional positive-up-negative-down (PUND) measurements.

used in these measurements (Fig. 2.10). Each measurement cycle is made up of five pulses comprising one preset pulse and four reading pulses with specific voltages and widths. A large preset voltage is applied at the beginning of each cycle to pre-pole the in-plane domain architecture to the negative direction; no measurement is performed for this pulse. The pulse width is kept constant ($t = 1\text{ ms}$ and 4 ms in this work), while the pulse voltage is increased by 0.5 V for each consecutive cycle. The second pulse switches the in-plane domains to the positive direction and measures the amount of switched polarization. The third pulse is an exact replica of the second pulse, which is used to read the non-remanent part of polarization along with the dielectric background, which dissipates during the delay time after the second pulse. The fourth and fifth pulses mirror the second and third, and switch the capacitor to the negative direction and read both the switched and non-switched polarization, respectively. The delay time between all the pulses

was set to $t = 100$ ms to let the in-plane domain structures backswitch (if required). These measurements produce $\pm P^*$, $\pm P_r^*$, $\pm P^\wedge$ and $\pm P_r^\wedge$ and $\Delta P = P^* - P^\wedge$, $\Delta P_r = P_r^* - P_r^\wedge$, $-\Delta P = -P^* - (-P^\wedge)$ and $-\Delta P_r = -P_r^* - (-P_r^\wedge)$. Here, the asterisk (*) represents the total of remanent and non-remnant polarization components and r represents the remanent polarization component only. $+P^*$ ($-P^*$) is measured at the end of the second (fourth) pulse when the voltage is on, and $+P_r^*$ ($-P_r^*$) is measured after a certain amount of delay time (100 ms) when the voltage is off after the second (fourth) pulse. $+P^\wedge$ ($-P^\wedge$) is measured at the end of the third (fifth) pulse when the voltage is on, and $+P_r^\wedge$ ($-P_r^\wedge$) is measured after a certain amount of delay time (100 ms) when the voltage is off after the third (fifth) pulse. These four terms (ΔP , $-\Delta P$, ΔP_r , $-\Delta P_r$) defined here are four different calculations of the remanent polarization only and have produced very similar results.

2.4.5 Retention Measurements

Retention measurements were used to probe the stability of the written polarization states and long-term reliability of the ferroelectric memory state. Retention refers to the gradual reduction in the

remanent polarization of a ferroelectric material over time. This phenomenon is often intensified by fluctuations in temperature or exposure to strong external fields. From a device standpoint, retention can be defined as the device's capability to maintain a specific electric signal level for a period following the initial write operation. The retention pulse sequence was used to measure the variation of remanent polarization as a function of delay time (Fig. 2.11). The retention measurements were performed using a Precision Multiferroic Tester (Radiant Technologies, Inc.). Like the PUND measurements, a large preset voltage is applied at the beginning of each cycle to pre-pole the in-plane domain structures to negative direction; no measurement is performed for this pulse (Fig. 2.11). Each polarization state is first accessed using an appropriate pulse width and voltage which were extracted from the previously shown PUND measurements. The system is then held at zero voltage for a specific retention time. In this case, starting with 2 ms retention time and then doubling for each successive cycle. After each writing cycle and the retention wait period, a reading pulse and non-switching pulse is subsequently applied to analyze the retention behavior of the switched polarization. A similar process was repeated on the negative side to get characteristics of the retention behavior on the negative side of the switched polarization.

2.4.6 Fatigue Measurement

Polarization fatigue occurs when the switchable ferroelectric polarization decreases due to repetitive electrical cycling, making it one of the primary failure mechanisms in ferroelectric films.

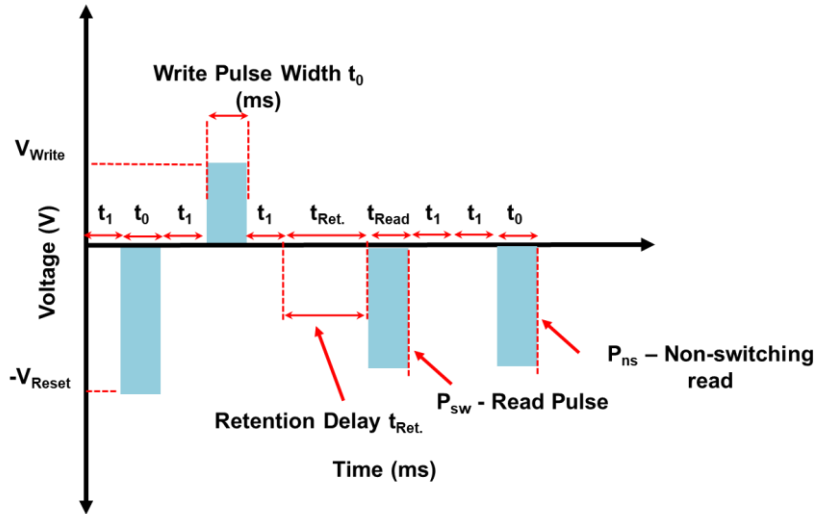


Fig. 2.11 The pulse sequence used to study the switching behavior of multistate heterostructures as a function of different pulse voltages with constant pulse width.

Historically, it has been seen that ferroelectric capacitors with elemental metal electrodes

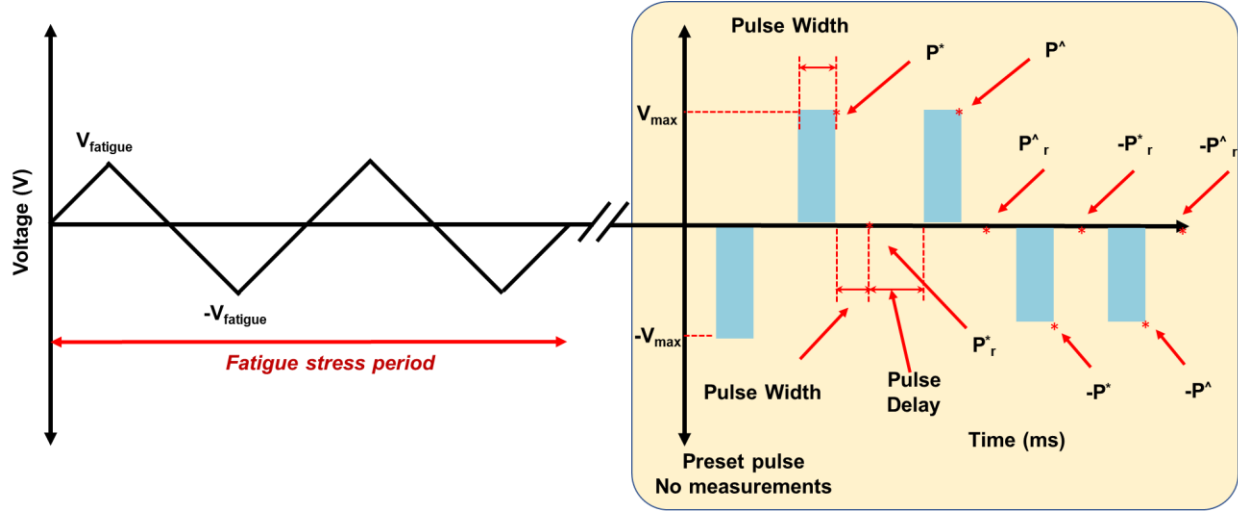


Fig. 2.12 The pulse sequence used for the fatigue measurement.

experience substantial fatigue. However, replacing elemental metals with oxide metals has been shown to enhance fatigue resistance [71–73]. This improvement is attributed to oxide metals mitigating oxygen vacancy accumulation at the metal-ferroelectric interface, a key factor contributing to fatigue. The fatigue measurements were performed using a Precision Multiferroic Tester (Radiant Technologies, Inc.). The fatigue measurement pulse sequence consists of a large number of triangular waveforms with a voltage amplitude large enough to completely switch the system at 1 MHz, followed by the PUND measurement (Fig. 2.12). In this measurement, the fatigue cycles were applied to the in-plane device to switch the in-plane domains as many as $\sim 10^9$ cycles. The fatigue cycles were interrupted regularly by PUND measurement pulses, which monitor the variation of the remanent polarization as a function of write cycles with the known combination of pulse voltage and width. Combination of pulse voltage and pulse width is applied to imitate the writing of various multistate polarization values for a large number of fatigue cycles. Consequently, these measurements produce $\pm P^*$, $\pm P_r^*$, $\pm P^A$ and $\pm P_r^A$ and $\Delta P = P^* - P^A$, $\Delta P_r = P_r^* - P_r^A$, $-\Delta P = -P^* - (-P^A)$, and $-\Delta P_r = -P_r^* - (-P_r^A)$ as explained previously in the section on the PUND measurements. These four terms (ΔP , $-\Delta P$, ΔP_r , $-\Delta P_r$) defined here are four different calculations of the remanent polarization only and have again produced very similar results.

2.5 Electromechanical response measurements

2.5.1 Laser Doppler Vibrometry

To study the electromechanical response of the heterostructures, a non-contact single-beam laser Doppler vibrometer (VibroOne, PolyTech GmbH) integrated with a Precision Ferroelectric

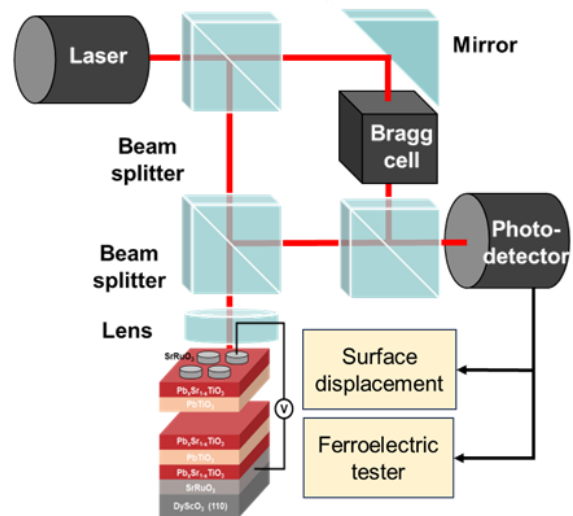


Fig. 2.13 Schematic showing the basic measurement principle in a laser Doppler vibrometer setup.

Tester (Radiant Technologies) was employed (Fig. 2.13). A 1.5- μm -diameter laser spot (HeNe laser with a wavelength of 633 nm) was focused vertically on the top surface of the capacitor structure. To contact the sample electrodes, tungsten probe tips (model 7-A, The Micromanipulator Company) with a point radius of 0.35 μm were used. A triangular electric field wave with a frequency of 3 kHz was applied across the capacitor, and the resulting electromechanical response (*i.e.*, the surface displacement) of the superlattices were measured by the Doppler shift of the backscattered laser beam, with a sensitivity of ~ 2 pm. The electromechanical strain value was defined as the ratio of the surface displacement to the thickness of the superlattice films, which was calculated as the average of values in 25 repeated measurements. During the measurement, the superlattices were glued on a rigid glass substrate, and the electrode areas were as small as 50 μm , so as to minimize the potential for substrate bending that may contribute to the measured response.

2.6 FEFET Testing Protocols

2.6.1 Volatile Testing

In the volatile testing, the gate voltage was kept on during the channel resistance measurement. This is a quick testing approach to get the on/off ratio of FEFET devices in volatile testing conditions. For this evaluation, fully fabricated three-terminal devices comprising ground, source, and drain ports are employed (Fig. 2.14a). Two Keithley 2400 sourcemeters are utilized for this testing procedure (Fig. 2.14b). The constant low magnitude V_{DS} (drain-to-source voltage) such as 30 mV is applied, while the V_{GS} (gate-to-source voltage) is varied between -1 volt and 1 volt in increments of 0.1 volt (Fig. 2.14c). The I_{DS} vs. V_{GS} is measured at fixed V_{DS} to get the on/off ratio of FEFET devices.

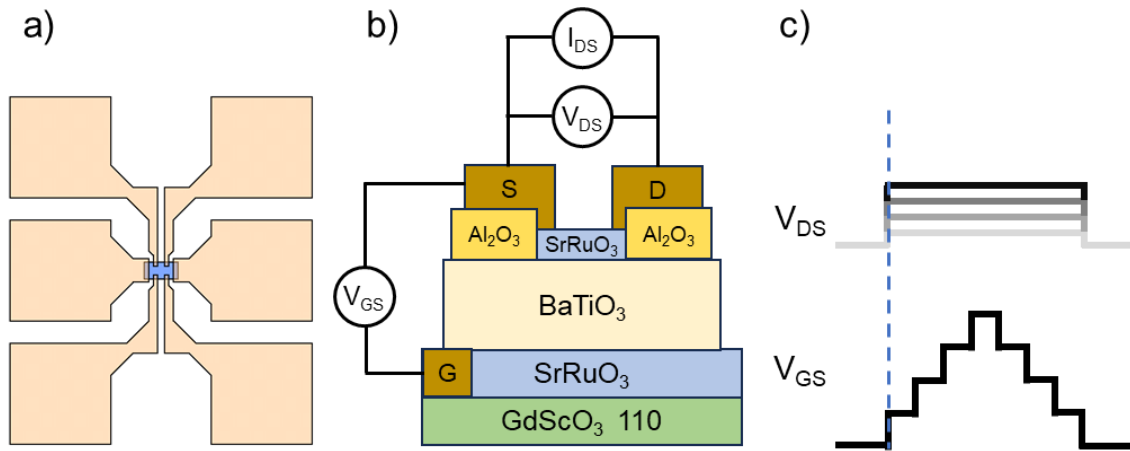


Fig. 2.14 a) Schematic of the FeFET device in the hall bar geometry. b) Schematic cross section illustrations of the FeFET device under test. c) V_{DS} and V_{GS} profile schematic used for testing procedure.

2.6.2 Non-volatile Testing

In a non-volatile type of testing, the gate voltage is applied but then removed during the channel resistance measurement after the delay period to see the effect of any switching transients to die down. To assess how this ferroelectric back-switching behavior impacts the on/off ratio of FEFET devices (Fig. 2.15a), non-volatile testing procedure is conducted. Like the volatile case, two Keithley 2400 sourcemeters are utilized for this testing procedure (Fig. 2.15b). The V_{GS} (gate-to-

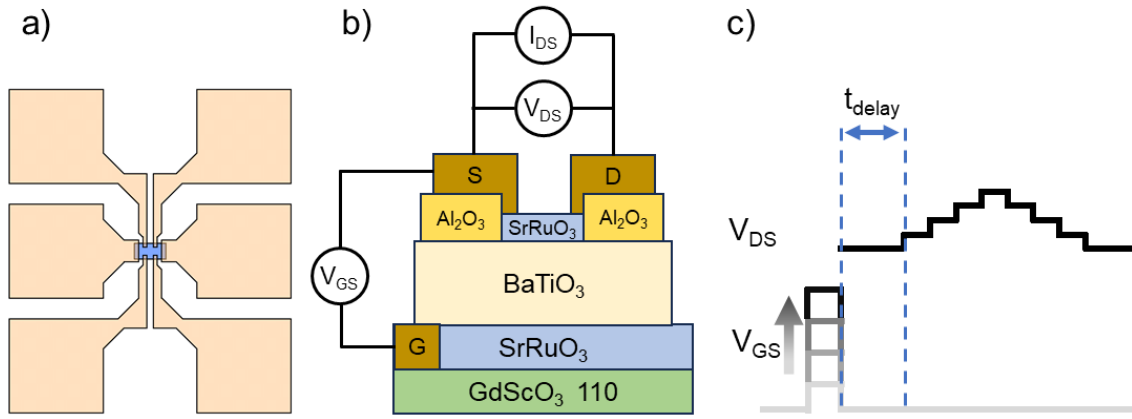


Fig. 2.15 a) Schematic of the FeFET device in the hall bar geometry. b) Schematic cross section illustrations of the FeFET device under test. c) V_{DS} and V_{GS} profile schematic used for non-volatile testing procedure.

source voltage) is varied between -1 volt and 1 volt in increments of 0.1 volt, while the V_{DS} (drain-to-source voltage) ranges from -20 mV to 20 mV in steps of 1 mV (Fig 2.15c). Unlike volatile testing, in non-volatile testing, I_{DS} (drain current) is recorded as a function of V_{DS} after a ~100 ms delay upon applying V_{GS} to allow any ferroelectric back-switching to occur. This delay ensures that the channel resistance is measured in accordance with the non-volatile nature of ferroelectric switching. Specifically, V_{GS} is turned off during the I_{DS} vs. V_{DS} measurement period to maintain the ferroelectric material in its equilibrium state following the application of a specific poling voltage of V_{GS} .

2.6.3 Gate-to-source Current (I_{GS}) Measurement During Volatile Testing

The on/off ratio of FEFET devices is assessed using a multi-modal approach to enhance comprehension of device functionality (Fig. 2.16a). Two Keithley 2400 sourcemeters are utilized for testing purposes (Fig. 2.16b). V_{GS} (gate-to-source voltage) is applied across the ground and source ports, ranging from -1 volt to 1 volt in increments of 0.1 volt (Fig. 2.16c). Simultaneously, V_{DS} (drain-to-source voltage) is applied between the drain and source ports, spanning from -20 mV to 20 mV in steps of 1 mV. During this testing procedure, I_{DS} (drain current) is recorded as a function of V_{DS} at each fixed V_{GS} to gauge channel resistance in relation to the volatile nature of

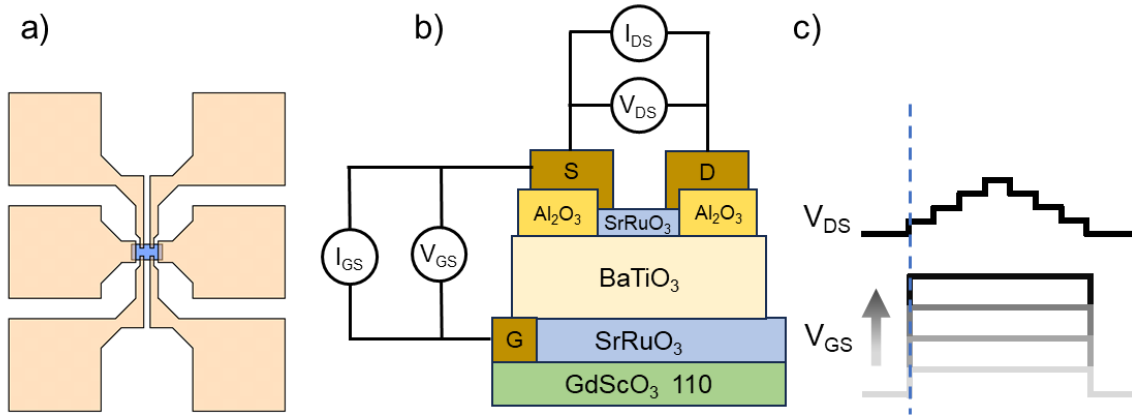


Fig. 2.16 a) Schematic of the FeFET device in the hall bar geometry. b) Schematic cross section illustrations of the FeFET device under test. c) V_{DS} and V_{GS} profile schematic used for volatile testing procedure.

ferroelectric switching. Specifically, V_{GS} remains in the active state throughout the I_{DS} vs V_{DS} measurement to maintain the ferroelectric material in a poled state. At the same time, I_{GS} (leakage current) is also recorded as a function of V_{DS} at each fixed V_{GS} to gauge the leakage performance of the devices in the out-of-plane direction and to ensure that the previously measured I_{DS} (drain current) has least contribution coming from the any form of leakage current from the bottom gate side.

CHAPTER 3

Strain-driven Mixed-phase Domain Architectures and Topological Transitions in $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

The potential for creating hierarchical domain structures, or mixtures of energetically degenerate phases with distinct patterns that can be modified continually, in ferroelectric thin films offers a pathway to control their mesoscale structure beyond lattice-mismatch strain with a substrate. In this chapter, I show how varying the strontium content provides deterministic strain-driven control of hierarchical domain structures in $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ solid solution thin films wherein two types, c/a and a_1/a_2 , of nanodomains can coexist. Combining phase-field simulations, epitaxial thin-film growth, and detailed structural, domain, and physical-property characterization, it is observed that the system undergoes a gradual transformation (with increasing strontium content) from droplet-like a_1/a_2 domains in a c/a domain matrix, to a connected-labyrinth geometry of c/a domains, to a disconnected labyrinth structure of the same, and, finally, to droplet-like c/a domains in an a_1/a_2 domain matrix. A relationship between the different mixed-phase modulation patterns and its topological nature is established. Annealing the connected-labyrinth structure leads to domain coarsening forming distinctive regions of parallel c/a and a_1/a_2 domain stripes, offering additional design flexibility. Finally, it is found that the connected-labyrinth domain patterns exhibit the highest dielectric permittivity.

3.1 Introduction

A diverse set of material classes, ranging from liquid crystals [74] to polymers [75–77] to metallic alloys [78] to ferroic materials [79] display self-assembled patterns and textures of domains. Formation of these patterns can be viewed as a manifestation of modulated phases. Despite the wide range of materials noted here and their widely varying microscopic structural details and interaction types and strengths, there are certain patterns and textures universally observed in materials, including stripes and droplets (or “bubbles”). Depending on the system, the characteristic length, or period, of these patterns can vary from a few nanometers (as in directed self-assembly of block copolymers in nanolithography) [77] to a few microns (as in ripple patterns of alternating superconducting and normal regions in type-I superconductors) [80] to centimeters (as in convective roll patterns in CO₂ gas undergoing a Rayleigh-Benard instability) [81]. It is the presence of multiple competing interaction forces that gives rise to such spatial inhomogeneities in otherwise uniform ground states. Such modulations can also arise in other order parameters, such as magnetization in films of rare-earth garnets and polarization in ferroelectric films. For example, in thin plates of barium scandium ferrite, application of a magnetic field has been shown to transform the stripe domain state into a periodic array of magnetic bubbles/skyrmions due to the interaction between the long-range magnetodipolar force, Dzyaloshinskii-Moriya interaction, and exchange interactions [82].

Ferroelectric materials also provide a rich design space for tuning material structure and properties by changing mechanical and electrical boundary conditions. For example, interesting modulations of polarization including polarization vortices [53], skyrmions [83], and merons [84] can be observed as one manipulates the energy balance with the boundary conditions. More generally, when grown as films on an appropriate crystalline substrate, ferroelectric materials can accommodate lattice-mismatch stress by forming various patterns of ferroelastic domains.[85] In the case of a tetragonal ferroelectric such as PbTiO₃ grown on *RE*ScO₃ substrates (where *RE* = Dy, Gd, Tb, Sc, Nd) [86], different types of 90° domain configurations form, either so-called *c/a* (wherein the polar axis alternates from being aligned along the out-of-plane and in-plane directions from domain to domain) or *a₁/a₂* (wherein the polar axis is always aligned in the plane of the film, but alternates between being aligned along the [100] or [010]) domains can be achieved depending on the strain imposed by the substrate [87]. Furthermore, these domain structures, when controlled to have similar energies, can produce coexisting mixed-phase polarization structures [45]. Such coexisting structures have been shown to exhibit facile interconversion between polarization states upon application of mechanical [88] and electrical [89] stimuli. Besides substrate-induced strain control of domains, compositional control of systems has also been used to realize intricate domain modulations. For example, in single crystals of the (1–*x*)BiFeO₃-(*x*)PbTiO₃ system, researchers have shown a complex hierarchical structure of alternating *a-a* and *a-c* domain bands with *x* = 0.2 and stripe-type 109° twin domains with *x* = 0.6 [90]. In compositionally graded PbZr_{1–*x*}Ti_{*x*}O₃ heterostructures, researchers have demonstrated the effectiveness of chemistry-driven strain gradients in stabilizing highly susceptible needle-like ferroelastic domains producing a locally enhanced piezoresponse [91]. Finally, other similar chemistry-controlled ferroelectric heterostructures have shown rich property modulation such as unique hysteresis response [92], temperature-stable dielectric permittivity [93], and enhanced pyroelectricity [94].

Not only can such phase competition lead to the creation of different kinds of hierarchical domain patterns wherein the constituent phases exist in specific ratios (as dictated by the boundary conditions), but these mixed-phase structures can evolve via different pathways that exhibit similarities to topological processes observed in porous media [95] and polymers [96]. Such

topologically non-trivial phases in ferroelectric domains [97], as in labyrinth and bubble domains in $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$, have recently been shown experimentally and controlled via temperature [98], electric field [99], mechanical stress [100], and/or electrical boundary conditions [101]. This begs the question if similar topologically distinct phases can be readily tuned in thin films and what the implications of such control of hierarchical, mixed-phase domains structure means for property evolution?

In this chapter, moving beyond simple lattice-mismatch strain with different substrates, I demonstrate that chemistry, namely strontium content in $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ solid solutions, is a powerful approach to attain deterministic control of hierarchical-domain structures. To do this I combine phase-field simulations, epitaxial thin-film growth, and detailed structural, domain, and physical-property characterization to explore $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0-0.3$) films grown on DyScO_3 (110) substrates where it is possible to produce continually tunable hierarchical, mixed-phase domain structures wherein c/a and a_1/a_2 nanodomains coexist. Chemical alloying allows for more precise control of the system than using different substrates and, thus, allows for the production of mixed-phase domain structures that exhibit a gradual transformation of the domain morphology from (with increasing strontium content) small isolated a_1/a_2 domains in a c/a domain matrix (henceforth called droplet-like using the language of the field) [102], to connected-labyrinth c/a domains, to a disconnected labyrinth structure of the same, and, finally, to droplet-like c/a domains in an a_1/a_2 domain matrix. This domain evolution is then studied for its topological nature, using lessons from work on porous media [95]. This analysis provides additional understanding of the phase-separation kinetics [103] where I explore not only the phase-fraction evolution, but the evolution of domain connectivity which is important in controlling the overall domain structure. Among the topologically unique structures observed, the connected-labyrinth pattern (which exhibits an array of interesting pattern defects) is annealed and I probe the defect-annihilation process that accompanies the conversion of a disordered structure into another topologically distinct structure with aligned domain stripes of c/a and a_1/a_2 domains. Finally, the implications of this control of the domain architectures for materials properties are tested by measuring the dielectric response wherein it is found that the materials exhibiting connected-labyrinth patterns, which have the greatest normalized domain-boundary perimeter, also exhibit the highest dielectric permittivity and maximum extrinsic contribution to the same. All told, this offers a nuanced approach to the design of domain-structure architectures and access to a broader range of properties than lattice-mismatch strain alone.

3.2 Structural Analysis

3.2.1 GLD and Phase-field Simulations-based Phase Diagram

To understand the evolution of phases and domain structures in the multi-dimensional design space, a detailed thermodynamic description (based on a Ginzburg-Landau-Devonshire (GLD) formalism) [46] of dense polydomain states in $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films was developed to calculate the phase diagram of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ epitaxial thin films as a function of misfit strain, temperature, and chemistry (x). Previously, the phase diagram for $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ films on DyScO_3 (110) substrates was calculated considering only monodomain configurations [35]; however, such monodomain states are unlikely except in very thin films since domains are expected to form to lower the free energy of the system [104]. Here, different possible mono- and poly-domain states were considered while comparing the energy levels and stability regions of various thermodynamically stable phases in the misfit strain-temperature phase diagram for various $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$.

$x\text{Sr}_x\text{TiO}_3$ compositions (from $x = 0$ to 0.5 at intervals of $x = 0.05$) to generate a 3D phase diagram (Fig. 3.1). As expected, different strain values stabilize polarizations along different directions and domain structures because of the competition among various energy terms. For large compressive strains, the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system is predicted to be monodomain c (polarization is fully out-of-plane oriented). Under slightly tensile strain, one expects c/a domain formation. At large tensile strains, the a_1/a_2 phase is stabilized (polarization is fully in-plane oriented). Individual strain-temperature phase diagrams for $x = 0.00, 0.10, 0.20, 0.30, 0.40$, and 0.50 are also provided (Fig. 3.2).

While the GLD formalism provides a starting point to understand the expected domain structures, it fails to address regions of potential mixed-phase coexistence as have been observed in related systems [5,45]. To further explore the potential for mixed-phase coexistence, we performed phase-field simulations in collaboration with Dr. J. A. Zorn, Dr. B.

Wang, and Prof. L.-Q. Chen at the Pennsylvania State University with a particular focus on intermediate strain states (-0.2% to 1%) wherein a mixed-phase domain architecture was expected. In this range, strain accommodation is achieved via formation of a mixture of c/a - and a_1/a_2 -domain structures (yellow areas, Fig. 3.1). Formation of these mixed-phase regions can be understood as a decomposition of the material into two distinct domain structures with different strain states (specifically the c/a domains have an in-plane strain $\approx 0.1\%$ and the a_1/a_2 domains have an in-plane strain $\approx 2\%$) in an appropriate proportion so that the overall strain balances to the net in-plane biaxial strain (≈ 0.2 - 0.8%) imposed from the substrate. In this region, any change in epitaxial strain can be accommodated by changing the relative fractions of c/a and a_1/a_2 domains. At the same time, increasing the strontium content results in a systematic decrease in the Curie temperature because of the decrease in the tetragonality of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ unit cell, also in agreement with previous reports [35]. All told, this offers an alternative pathway to control the domain architectures. Specifically, one can take a single substrate (here I have chosen growth on DyScO_3 (110) substrates ($a_{\text{pc}} = 3.949 \text{ \AA}$) because it provides an apt starting point with the formation of pure c/a domains with $x = 0$) and propose to vary the strontium composition to provide finer control of the misfit strain and more controllable access to the different hierarchical domain structures (dashed plane, Fig. 3.1).

In turn, one can produce a dedicated phase diagram (now in strontium content (x) and temperature space) representing growth on DyScO_3 (110) substrates (Fig. 3.3) by combining the GLD and phase-field simulations. As expected, starting with small strontium content ($x \lesssim 0.1$) one

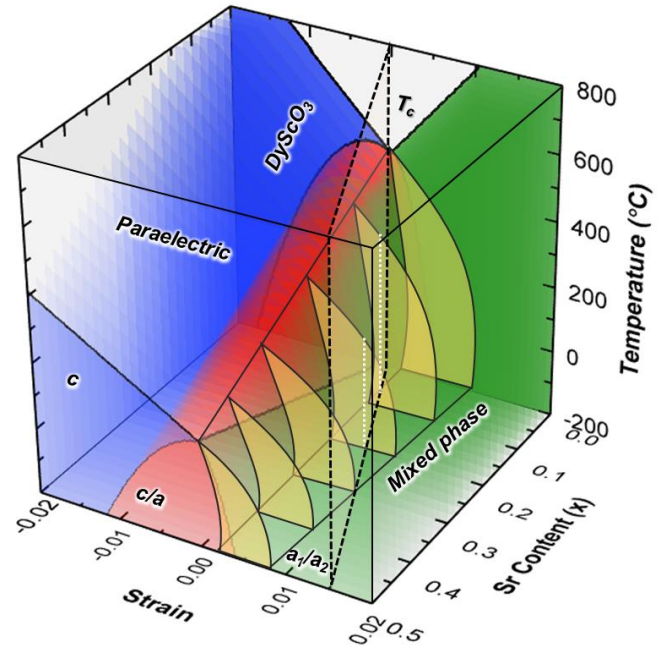


Fig. 3.1 Analytical phenomenological modeling-based temperature-strain-strontium content (x) 3D-phase diagram illustrating the stability regimes for paraelectric, c , c/a , and a_1/a_2 domain structures for $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films. The mixed-phase domain region where c/a and a_1/a_2 domains coexist is calculated by phase-field simulations and is shown in the yellow color at $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 . Strain position of the DyScO_3 (110) is schematically shown as a plane.

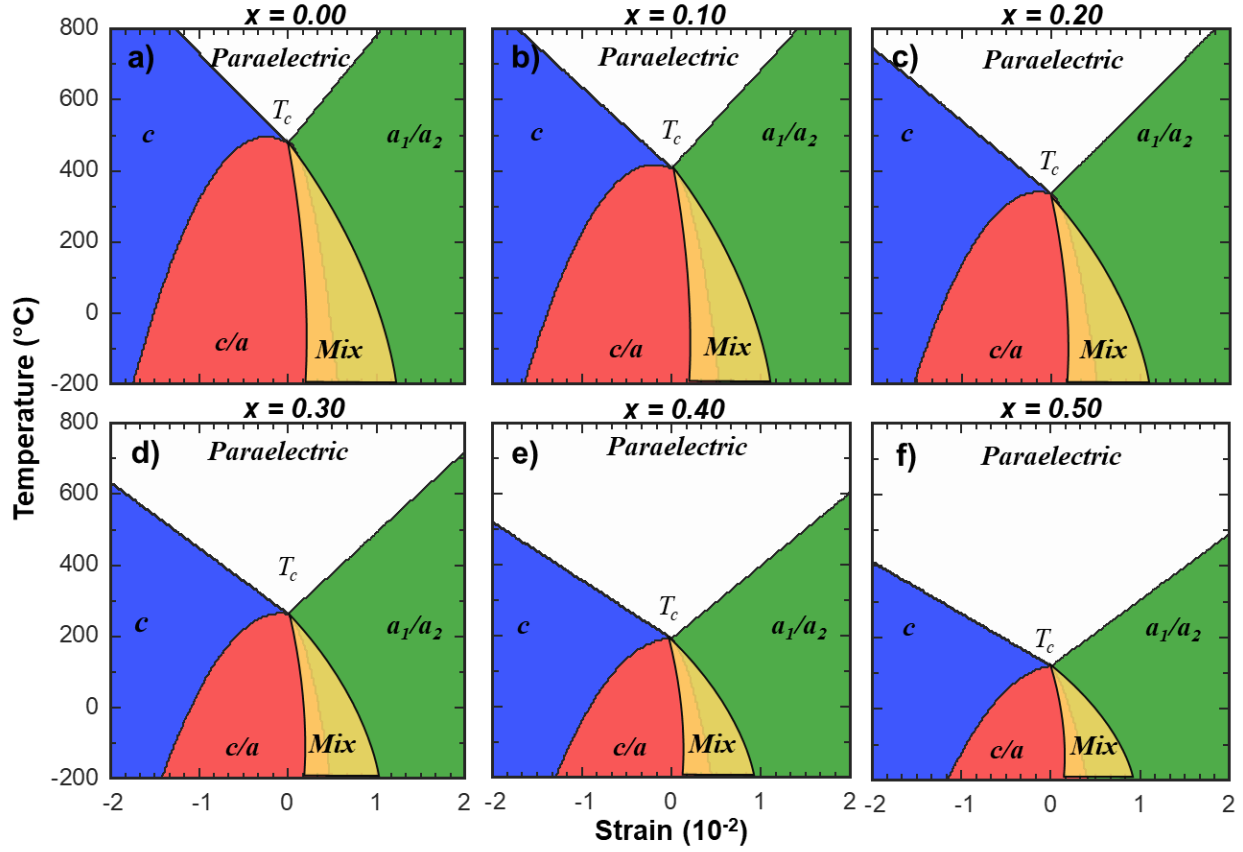


Fig. 3.2 Analytical phenomenological GLD modeling-based temperature-strain phase diagram for $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films with compositions a) $x = 0.0$, b) $x = 0.1$, c) $x = 0.2$, d) $x = 0.3$, e) $x = 0.4$, and f) $x = 0.5$. The different colors correspond to different stability regimes for paraelectric, c , c/a , and a_1/a_2 domain regions. The yellow areas represent the region where coexisting c/a and a_1/a_2 domain structures are expected to form a mixed-phase region under equilibrium calculated using phase-field simulations.

can expect c/a -domain structures and then, upon increasing the strontium content, it will first pass through a mixed-phase regime ($0.1 \lesssim x \lesssim 0.3$) before finally entering the a_1/a_2 regime ($x \gtrsim 0.3$).

Upon closer inspection, at room temperature and going from lower to higher strontium content, the mixed-phase regime undergoes a gradual transition (Fig. 3.4). At $x = 0.15$ the system exhibits small droplets of a_1/a_2 domains inside a c/a -domain matrix (Fig. 3.4a). As the strontium content increases, corresponding to a decrease in the pseudocubic lattice parameter of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ and thus more tensile strain, more in-plane-oriented domains appear resulting in the formation of a connected-labyrinth structure of c/a domains at $x = 0.19$ (Fig. 3.4b) and a disconnected-labyrinth structure at $x = 0.21$ (Fig. 3.4c). Finally, as the strontium content increases further, for example to $x = 0.275$, a_1/a_2 domains grow at the

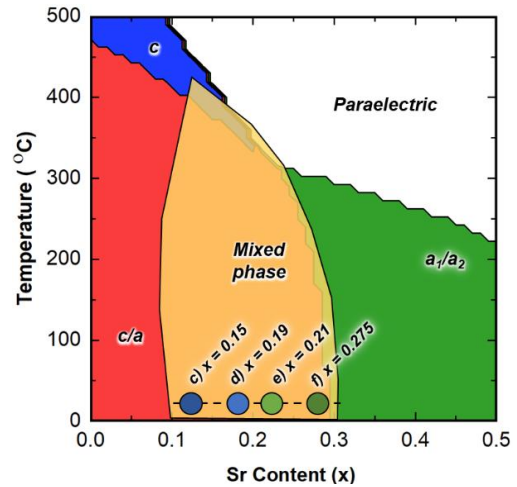


Fig. 3.3 Analytical phenomenological modeling-based temperature-strontium content (x) phase diagram of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin film on DyScO_3 (110) substrate. The mixed-phase region was calculated using phase-field simulations and is shown in yellow.

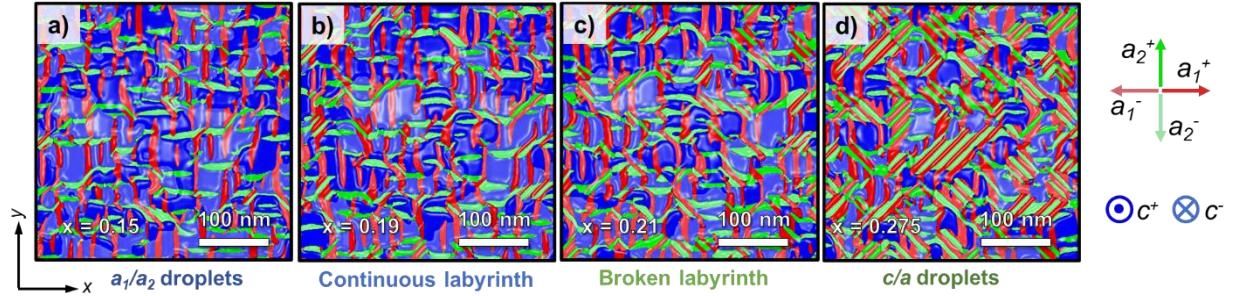


Fig. 3.4 The mixed-phase region shows a gradual transition in the domain architecture as a function of strontium content (x) such as from a) small droplets of a_1/a_2 domains inside a c/a domain matrix at $x = 0.15$, to b) a connected-labyrinth structure of c/a domains at $x = 0.19$, to c) a disconnected-labyrinth structure at $x = 0.21$, and finally to d) c/a droplets in an a_1/a_2 matrix at $x = 0.275$.

expense of the c/a -domain regions forming c/a droplets in an a_1/a_2 matrix (Fig. 3.4d). Previously, similar mixed-phase domain architectures were observed for PbTiO_3 thin film grown on GdScO_3 (110) substrates [45], but there was no demonstration of further modulation. Only if the strain can be tuned continuously, as can be done herein with the variable strontium content with one fixed substrate, can one access the phase-field predicted mixed-phase architectures and/or properties which occur only for a narrow range of strain values and with a fine step size of the compositional variation.

3.2.2 X-ray Diffraction Studies

To test the predictions, I synthesized a composition series of 100-nm-thick $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films with $x = 0, 0.06, 0.17, 0.20, 0.23, 0.25, 0.27$, and 0.30 on DyScO_3 (110) substrates via pulsed-laser deposition. Following the growth, detailed structural studies were completed via X-ray diffraction to probe the evolution of the crystal structure (Fig. 3.5) of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films. High-quality, fully epitaxial solid-solution films were obtained for all compositions studied herein. The $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0-0.3$) 002-diffraction peaks, in all cases, appear to shift to higher θ - 2θ values with increasing strontium content (corresponding to a reduction of the out-of-plane lattice parameter) along with the appearance of the 200-diffraction peak (Fig. 3.5). This is consistent with what is expected for isovalent substitution of a smaller-sized Sr^{2+} cation (144 pm) at the Pb^{2+} (149 pm) site. Coexistence of both the 002- and 200-diffraction peaks observed in the composition range $x = 0.06-0.27$ points to the formation of mixed-phase domain architectures. At $x = 0.30$, only a single (strong) peak corresponding to the 200-diffraction peak is

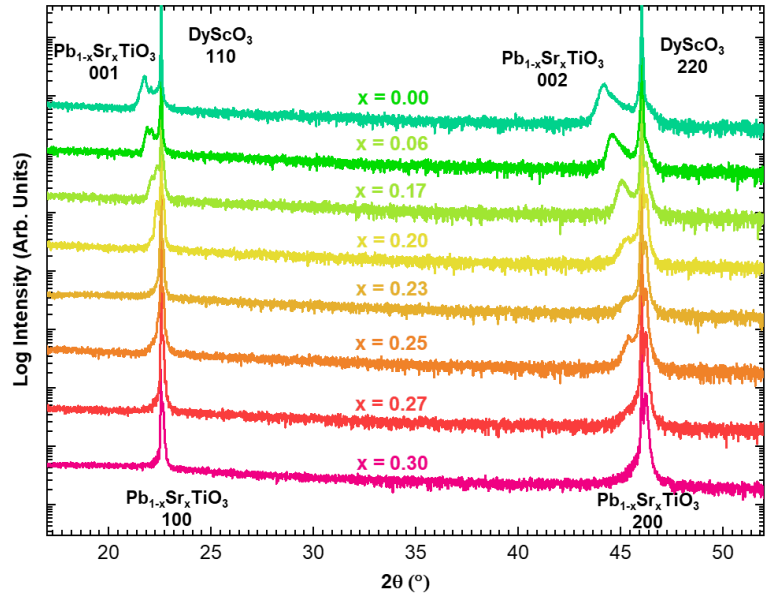


Fig. 3.5 Wide-angle θ - 2θ X-ray diffraction scans for 100-nm-thick $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films grown on DyScO_3 (110) substrate, from top to bottom, $x = 0, 0.06, 0.17, 0.20, 0.23, 0.25, 0.27$, and 0.30 .

observed, indicating single-phase a_1/a_2 domains.

3.2.3 Domain Structures in $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

Examination of the surface topography using atomic force microscopy (AFM) reveals systematic evolution of the hierarchical-domain structures [45] (Fig. 3.6a-d) in agreement with both the phase-field simulations and the X-ray diffraction. Two distinct areas are observed in each topography image: the areas with elevated topography (bright in the images) are the c/a -domain regions and the lower-lying regions (dark in the images) are the a_1/a_2 -domain regions. These hierarchical domain structures show four broad categories of morphology based on the distribution and connectivity of the c/a domains across intermediate strontium compositions ($0.06 \leq x \leq 0.27$). Starting with $x = 0.06$ heterostructures (Fig. 3.6a), a predominantly c/a domain structure with small droplet-shaped a_1/a_2 regions are observed. Upon increasing the strontium content to $x = 0.17$ (Fig. 3.6b), what is called a connected-labyrinth structure of the c/a domains is observed. To accommodate the increased strain induced by the presence of additional strontium, the individual a_1/a_2 -droplet regions elongate (and increase in volume fraction) and create a connected labyrinthine pattern of c/a domains. Further increasing the strontium content to $x = 0.25$ results in the formation of a broken-labyrinth structure of the c/a domains (Fig. 3.6c). Instead of reducing the c/a domain stripe width, the structure prefers to break down into smaller length scale c/a domain stripes to accommodate an increased a_1/a_2 -domain fraction. Finally, when $x = 0.27$ (Fig. 3.6d), the majority phase is now the a_1/a_2 -domain structure with sparsely dispersed c/a -domain droplets; essentially an inverse replica of the $x = 0.06$ heterostructures where there were droplets of a_1/a_2 domains in a c/a matrix.

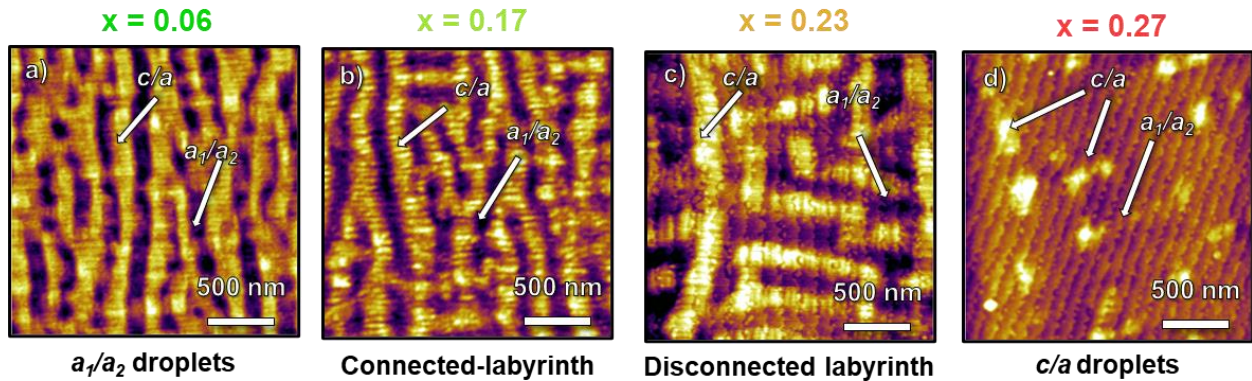


Fig. 3.6 AFM topography images of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films showing a) a_1/a_2 droplets in a c/a matrix for $x = 0.06$ heterostructures, b) a connected-labyrinth structure for $x = 0.17$ heterostructures, c) a disconnected-labyrinth structure for $x = 0.23$ heterostructures, and d) c/a droplets in an a_1/a_2 matrix for $x = 0.27$ heterostructures.

3.2.4 Reciprocal Space Mapping (RSM) Studies

Further understanding of the hierarchical domain architectures can be obtained by studying different features in X-ray reciprocal space mapping (RSM) studies. While RSMs for heterostructures of all compositions studied herein are provided (Fig. 3.7), here, for brevity, I use an RSM about the 220_O-diffraction condition of the DyScO_3 substrate for an $x = 0.20$ heterostructure to explain the pertinent features (Fig. 3.8a). The RSM reveals film peaks corresponding to 002-oriented c domains as well as two versions of in-plane polarized a domains: (1) an untilted variant (arising from the classic a_1/a_2 structure) and (2) a tilted variant (arising from the a domains in the c/a structure). The lattice matching between the c and a domains in the c/a

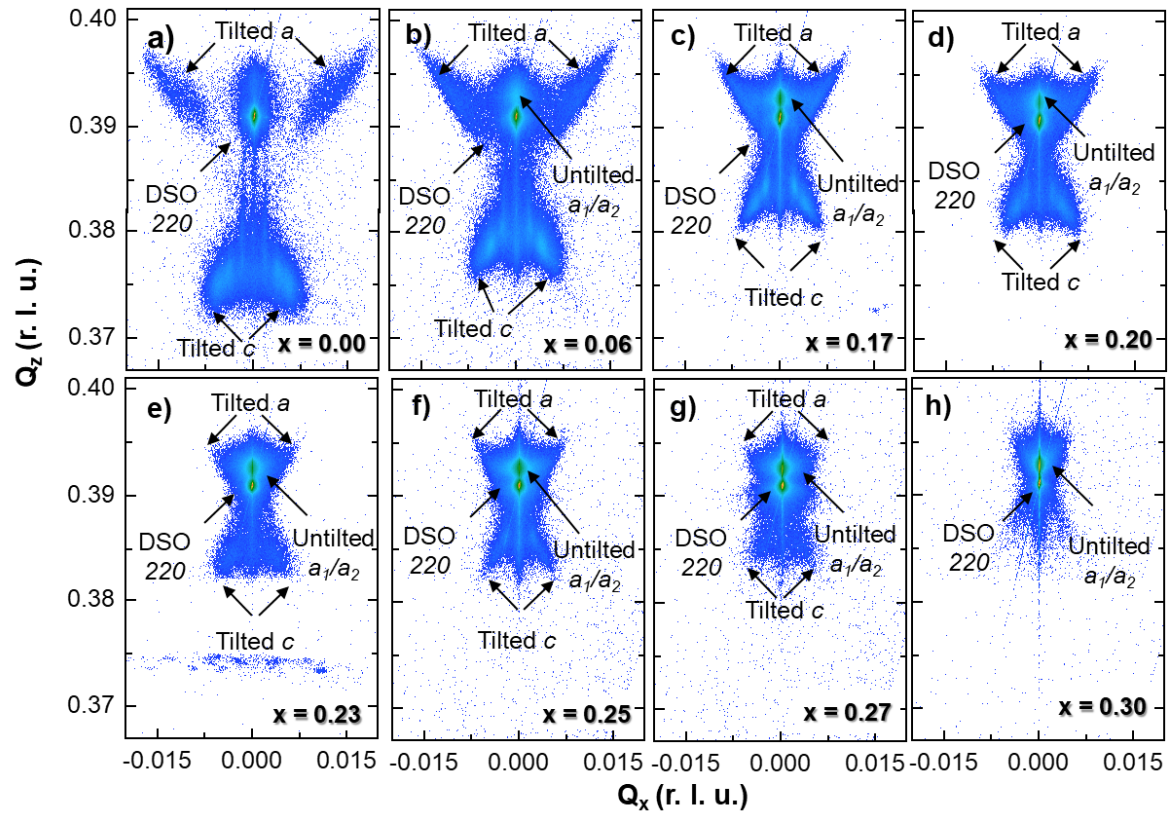


Fig. 3.7 2D reciprocal space mapping (RSM) studies about the 220_o-diffraction peak of the DyScO₃ (110) substrates showing the 002- and 200-diffraction peaks of Pb_{1-x}Sr_xTiO₃ thin films corresponding to the tilted *c* and tilted/untilted *a* domain variant for a) *x* = 0, b) *x* = 0.06, c) *x* = 0.17, d) *x* = 0.20, e) *x* = 0.23, f) *x* = 0.25, g) *x* = 0.27, and h) *x* = 0.30.

domains involves the tilt of the individual *c* and *a* domains such that the coherent boundary between them lies on a {101}. A schematic of such a *c/a* domain structure (Fig. 3.8b) shows this domain-tilting phenomenon where the tilt angles θ_c and θ_a refer to the tilts of the *c* and *a* domains, respectively, relative to the film normal [001] and an a total characteristic angle $\theta_{ca} = \theta_c + \theta_a$ is defined to provide a single metric to describe the structure. These tilt angles are extracted for

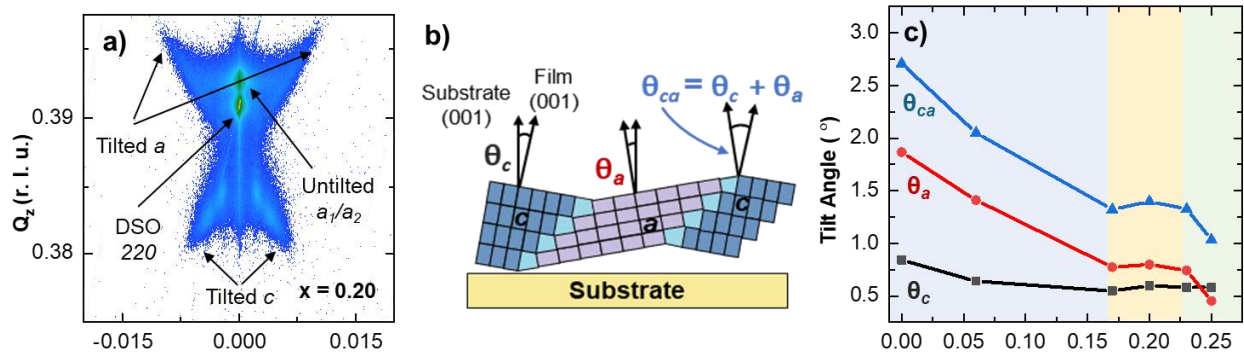


Fig. 3.8 a) RSM about the 220-diffraction peak of the DyScO₃ (110) substrate revealing 002- and 200-diffraction peaks for the Pb_{1-x}Sr_xTiO₃ thin films corresponding to the tilted *c* and tilted/untilted *a* domain variants, respectively, for an *x* = 0.20 heterostructure. b) Schematic of the domain tilting phenomenon observed in the *c/a* domain stripes with characteristic angles defined. c) Measured tilt angles for the *c* and *a* domains and the net tilt angle between them as a function of film composition.

heterostructures of composition $x = 0.00, 0.06, 0.17, 0.20, 0.23$, and 0.25 (Fig. 3.8c) and it is found that as the strontium content increases, the tilt angles decrease continuously for lower strontium contents ($0 < x < 0.17$) before leveling off at intermediate strontium contents ($0.17 < x < 0.23$; where domains exist in connected- and broken-labyrinth patterns) and then ultimately decreasing further as the strontium content increases further ($x > 0.23$). The angle θ_{ca} depends on the ratio of the long and short unit cell lengths [105]. Thus, a net decrease in θ_{ca} can be explained by the reduction in the out-of-plane lattice parameter that corresponds with increasing strontium content. Consequently, this can also provide an effective tool to tune tilt angle θ_{ca} in a controlled manner which could impact both the dielectric response and polarization switching processes [106].

3.3 Topological Transitions in $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

3.3.1 Background on Topological Transitions

One interesting observation is that, upon increasing the strontium content, instead of just enlarging the isolated a_1/a_2 droplets observed at $x = 0.06$, the system self-assembles into a new structure (the connected-labyrinth pattern of c/a domains) at $x = 0.17$. Such changes in the domain structure are similar to effects observed in polymer blends [107] and porous media [108] where the topology of the structures changes from “bubbles” to “cylinders” to “bicontinuous networks” to “lamellar structures” upon changing the relative concentration of the two constituents and/or temperature [109]. In these cases, as is seen here in the ferroelectric-domain structures, the result is that not only does the phase fraction of the secondary phase change, but also how that phase is arranged within the primary phase changes. In turn, taking lessons from these other fields of study, I have applied analysis approaches developed therein [110–112] to the domain structures observed herein. In particular, I translate ideas of topology (a branch of mathematics that offers a means to characterize the shape of data objects) [112] including the so-called Euler characteristic (EC) which is a topologically invariant number that describes a topological space’s shape or structure regardless of the way it is bent or stretched without breaking,[113] to explore these domain structures. The EC has seen limited applications in engineering, but has been used to describe porous media [114] and fluids within them [95], where the topological characteristics of the porous media calculated by EC, together with the pore size distribution, provide a good projection of the effective hydraulic properties and transport [115]. Recently, similar topological characterization has been applied to ferroelectrics to identify the transition from a labyrinth pattern (formed via a suspected spinodal decomposition) to a bubble-domain pattern (formed via nucleation) induced via applied electric field in $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ by effectively using the phase fraction and percolation threshold of the minority phase [97]. In that regard, EC can provide a robust descriptor of phase distribution and connectivity without being affected by the size and shapes of various domains, information which is missing in many statistical descriptors [110].

3.3.2 Topological Transitions Using Phase-field Simulations and Real-space Imaging

Here, it was observed that upon increasing the strontium content in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films, the mixed-phase domain structure undergoes a gradual transformation as observed via phase-field simulations (Fig. 3.4) and AFM topography (Fig. 3.6). To show the similarity in the experimental and simulation results and support our analysis, I provide three types of information for a selection of compositions studied herein (*i.e.*, experimental $x = 0.06, 0.17, 0.23$, and 0.27 ; Fig. 3.9a-d, respectively): 1) an AFM topography image, 2) a phase-field simulation (scaled to a similar length scale as the AFM image), and 3) a binarized image of the corresponding AFM and phase-field data wherein the white and black colors correspond to the c/a and a_1/a_2 regions, respectively, and are

used for the subsequent topological analyses. As expected, the phase-field simulations and experimental data show similar trends in the evolution of the hierarchical-domain structures, albeit with an offset in terms of the chemistry. This difference in chemistry is explained by the fact that the phenomenological thermodynamic potential used in this work may overestimate the stability of the *c/a*-domain regions as well as provide slight variations of the Curie-temperature values for different compositions of strontium [116,117]. Additionally, there are varying reports on the compositions and temperatures at which the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ crystal becomes cubic [32,118,119] which also plays a factor in directly translating the chemistries between simulation and experiment. Considering these numerical and experimental constraints, I believe such differences between the two curves are inconsequential to the main conclusions of the present study and the trends of the data and resulting structures are found to be identical.

3.3.3 Euler Characteristics

Focusing now on the binarized images, the EC number χ is calculated as the total number of objects (*i.e.*, the distinct number of *c/a*-domain regions) minus the total number of holes (*i.e.*, distinct number of *a₁/a₂*-domain regions). This simple approach, however, has the challenge that there can be both different total numbers of objects/holes in the various AFM images and the numbers would depend on image size. Thus, to assure the production of comparable numbers, I defined a normalized EC number χ_N , which is defined as the average number of discrete topological features that the morphology supports relative to total number of features as defined as:

$$\chi_N = \frac{(\text{Number of Objects } (O) - \text{Number of Holes } (H))}{(\text{Number of Objects } (O) + \text{Number of Holes } (H))}$$

This characterization approach is, thus, independent of the domain size, domain numbers, domain-boundary roughness, and shape of the domain-wall patterns.

3.3.4 Euler Characteristics of Experimental and Simulated Domain Structures

The evolution of χ_N (with respect to the *c/a*-domain structure) was determined for various $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films (Fig. 3.10a) as a function of strontium content for the microstructure produced

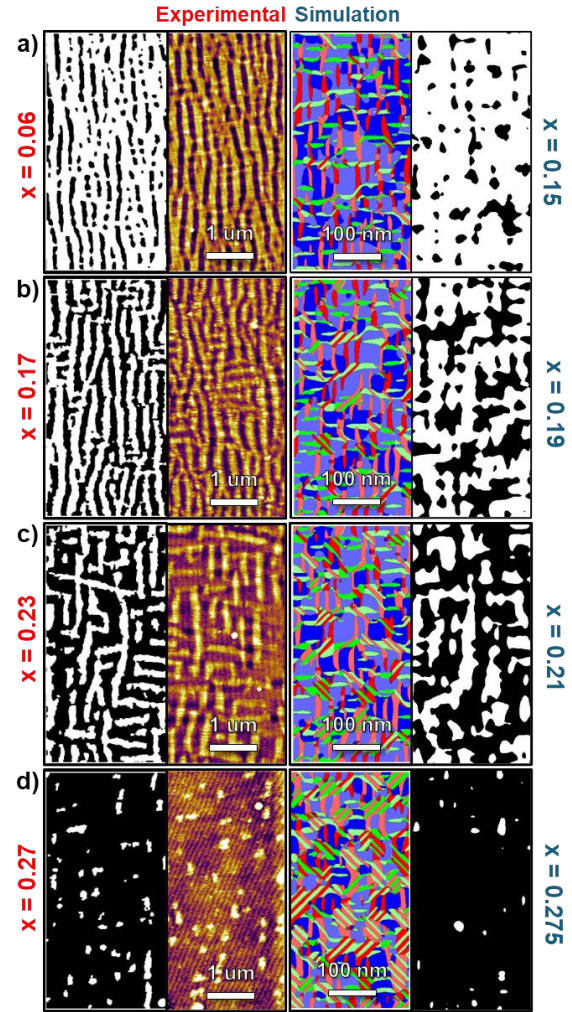


Fig. 3.9 From left to right, a binarized image used for analysis based on the experimental AFM data, the AFM topography image, the corresponding phase-field simulation, and a binarized image used for analysis based on the phase-field simulation for $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films with a) $x = 0.06$, b) $x = 0.17$, c) $x = 0.23$, and d) $x = 0.27$ (experimental x values noted here, but corresponding phase-field x values are noted on the figure).

by both phase-field simulations and the AFM data. As noted, there is a slight difference between the evolution of χ_N for the phase-field simulation and experimental strontium content values.

Upon stepping through the piecewise fitted curve of χ_N , one can find that at a local minimum, it has “holes” throughout the area (*i.e.*, a_1/a_2 droplets as in the $x = 0.06$ heterostructures). When it passes through a saddle point, multiple objects are joined to form connected-labyrinth structures of c/a domains (as in the $x = 0.17$ heterostructure). And, at a local maximum, the majority objects scattered without any holes inside them (as in the c/a droplets in $x = 0.27$ heterostructures). It has been widely observed that the logarithm density of the EC, $\log(|\chi|)$ (*i.e.*, the Euler entropy), shows singular behavior around a thermodynamic phase transition in theoretical models [120,121] as well as around the zeros of the EC [122–126]. This has led to the introduction of topological phase transitions as the loci of such critical points of the EC [127], where there is a large component (objects or holes) transition in the neighborhood [128]. Thus, the location of different topological transitions occurring as the system evolves from pure c/a domains to pure a_1/a_2 domains via the mixed-phase region can be inferred by taking the derivative (Fig. 3.10b) of the piecewise fitted curve of χ_N and the extrema of these derivatives are used to demarcate different characteristic zones, the boundaries between which represent the geometric growth or decay in the domain numbers [97]. The different regions including: 1) pure c/a domains, 2) a_1/a_2 droplets in a c/a matrix, 3) connected-labyrinth structure of c/a domains, 4) broken-labyrinth structure of c/a domains, 5) c/a droplets in an a_1/a_2 matrix, and 6) pure a_1/a_2 domains can be identified using this method. This approach provides novel insight into the strain-field tuning of domain structures and ferroelectric topological nanostructures and helps open the door for the new field of “topological strain-field engineering” [129] and “topological defectronics” [130,131].

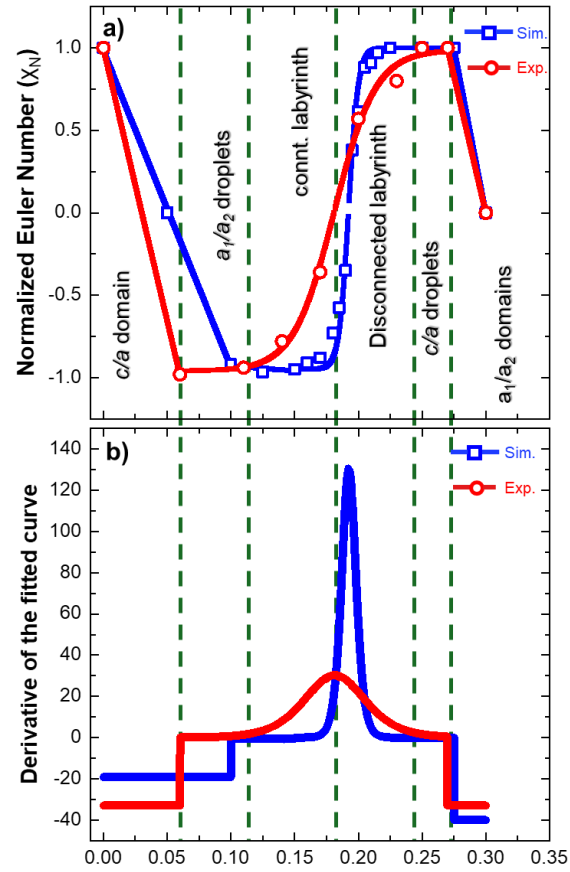


Fig. 3.10 a) Calculated normalized Euler characteristic (χ_N) vs. strontium content (x) for the experimental part (red circles) and phase-field generated (blue squares). b) Derivative of the part-wise fitted curve of the normalized Euler characteristic (χ_N) for the experimental and simulated data. Extrema of the derivative of the experimental curve (red line) are used to demarcate various topological regions observed in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films.

3.4 Thermal Annealing of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

3.4.1 Domain Straightening in Continuous-labyrinth Structure

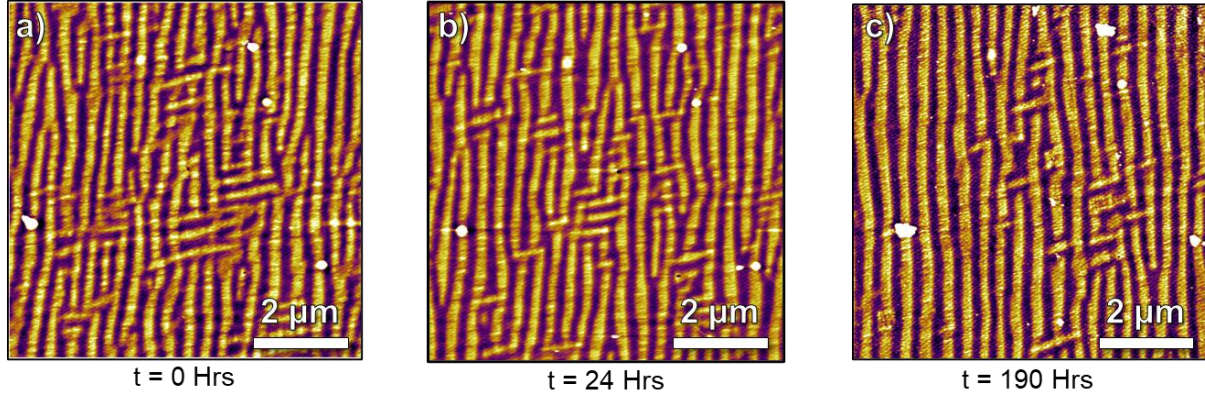


Fig. 3.11 AFM topography images of 100-nm-thick $\text{Pb}_{0.83}\text{Sr}_{0.17}\text{TiO}_3$ thin films grown on DyScO_3 (110) substrates in the a) as-grown state and the same area after annealing at 270°C for b) 24 hours and c) 190 hours.

Building from these observations, I focused specifically on the continuous-labyrinth structure which showed local ordering up to a certain finite length and also exhibited the most types of pattern defects in its as-grown state. Upon annealing, such labyrinth patterns have shown transformation into parallel-stripe patterns in ferroelectrics [98]; a behavior which is analogous to the inverse-transition phenomenon observed in magnetic films [132,133] and explained via topological-defect annihilation. In that regard, to study to what extent this potentially metastable continuous-labyrinth morphology is kinetically constrained, I performed a series of annealing experiments wherein, briefly, samples were annealed to 270°C for increasing lengths of time (12-190 hours) and then cooled to room temperature where I completed AFM imaging to explore the evolution of the domain structures in the same region (Fig. 3.11a-c). The realignment to the unidirectional stripe domain pattern starts after just a few hours (Fig. 3.11b). The same area, after 190 hr of annealing (Fig. 3.11c), shows distinct c/a - and a_1/a_2 -domain stripe ordering (along the vertical direction).

The macroscopic nature of this ordering is confirmed by RSM studies

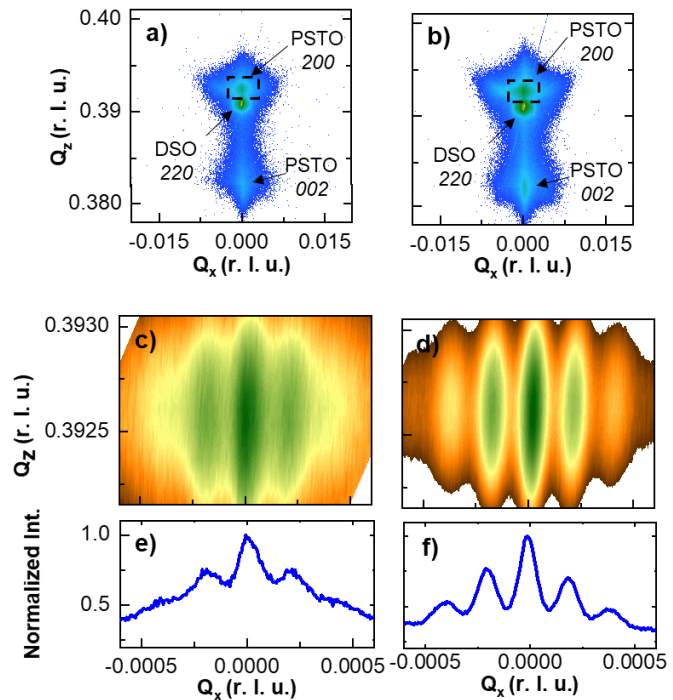


Fig. 3.12 Reciprocal Space Mapping (RSM) about the 220_o -diffraction peak of the DyScO_3 (110) substrate showing the 002- and 200-diffraction peak of $\text{Pb}_{0.83}\text{Sr}_{0.17}\text{TiO}_3$ thin films a) before annealing and b) after 190 Hrs. of annealing at 270°C . Box shows the location of a domain which is selected for zoom in scan to detect changes in satellite peaks intensity due to periodicity enhancement. c) Zoom in RSM scan around a domain location showing satellite periodicity peak arising from alternating stripes of c/a and a_1/a_2 domains in the as-grown sample. d) Zoom in RSM scan around the a domain location showing considerable enhancement in the satellite peaks due to the large-scale domain realignment occurring during the extended annealing process. Normalized intensity at the position at $Q_z = 0.3926$ for e) before annealing and f) after annealing process exhibiting apparent enhancement in stripe ordering during the annealing process.

(Fig. 3.12). The ordering distance measured from AFM topography (~ 400 nm) matches well with the distance calculated from the satellite ordering peaks (~ 390 nm) in the RSM studies. It should also be noted that the overall phase fraction of the c/a domains and the shared perimeter between the c/a - and a_1/a_2 -domain remains constant over successive annealing cycles (Fig. 3.13a). There are no structural changes in the $\text{Pb}_{0.83}\text{Sr}_{0.17}\text{TiO}_3$ thin film with increasing annealing time (Fig. 3.13b). Finally, there is a change in the normalized EC, representing the realignment of connected labyrinth structure to the stripe domains (Fig. 3.13c).

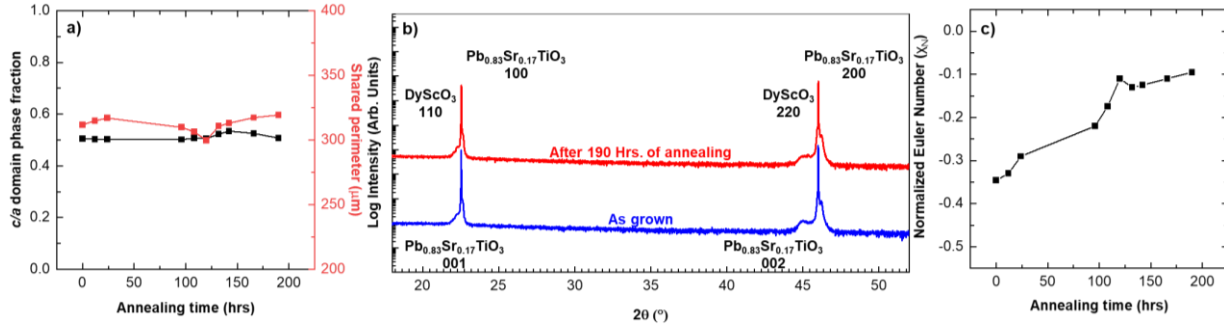


Fig. 3.13 a) Domain fraction of c/a domains as a function of annealing duration. b) Room-temperature wide-angle θ - 2θ X-ray diffraction scans for as-grown and after 190 Hrs. of annealing. c) Normalized Euler Number as a function of annealing time.

3.4.2 Phase-field Confirmation of Domain Straightening

The phase-field simulations (Fig. 3.14) show a similar domain stripe reordering phenomenon upon short (Fig. 3.14a) and long (Fig. 3.14b) annealing process. It is seen that at an annealing temperature of 277°C (550 K), the domain structure consists predominantly of a_1/a_2 twin structures (Fig. 3.15a-d). This agrees with the phase diagrams described earlier (Fig. 3.3), where the high-temperature phase at intermediate strontium content is close to the mixed-phase and a_1/a_2 polydomain boundary. Upon cooling, however, c domains begin to form and create c/a regions

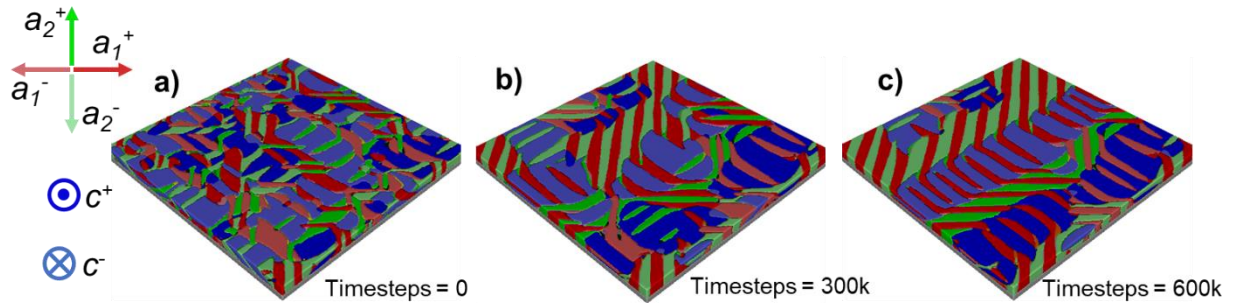


Fig. 3.14 Phase-field simulations showing similar domain alignment phenomenon in the connected-labyrinth structure for the a) as-grown state and after annealing for b) 300k and c) 600k timesteps.

that lead to the formation of regularly arranged stripe domains (Fig. 3.15d). Again, the phase fractions of the a_1/a_2 and c/a regions remain essentially constant throughout the annealing cycles (Fig. 3.15e). This realignment process (Fig. 3.16a-e) also leads to the overall lowering of the energy of the system (Fig. 3.16f) as the energy difference between the as-grown state and the longest (600k timesteps) annealed sample changes by nearly 9%. The advantage of phase-field modeling over experimental methods is the ability to record the magnitude of each energy

contribution (Fig. 3.16g-j) to the resulting structure. Investigating this further, it is found that much of the energy difference comes from the bulk Landau energy (Fig. 3.16h) followed by the short-range gradient contribution (Fig. 3.16j). This can be reasoned for the domain realignment. The resulting domain structure is nearly uniform in one of the lateral directions and only varies in other lateral direction, which will decrease this energy contribution. This global free energy minimization allows us to visualize the complex reorganization within different types of labyrinthine patterns [134] as compared to as-grown glass-like kinetically arrested state [135]. This energy lowering process is accompanied by the realignment of the domain structure leading to the stripe-like domain pattern.

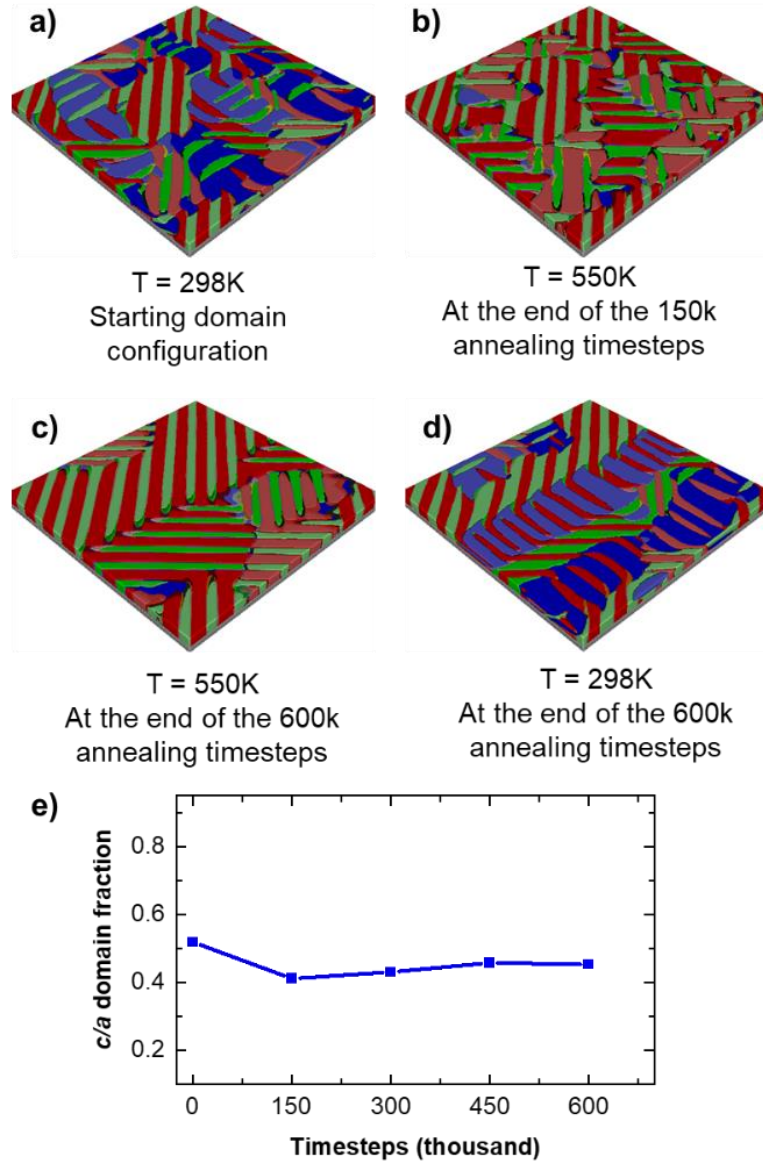


Fig. 3.15 Temperature-dependent evolution of hierarchical domain architectures during different annealing cycle stages. Corresponding domain architecture of a) initial domains at $T = 298\text{ K}$, b) at the end of 150k annealing timesteps with $T = 550\text{ K}$, c) at the end of the 600k annealing timesteps with $T = 550\text{ K}$, and d) after the 600k annealing timesteps at $T = 298\text{ K}$. e) Corresponding phase fraction of c/a domains is tracked throughout the annealing process.

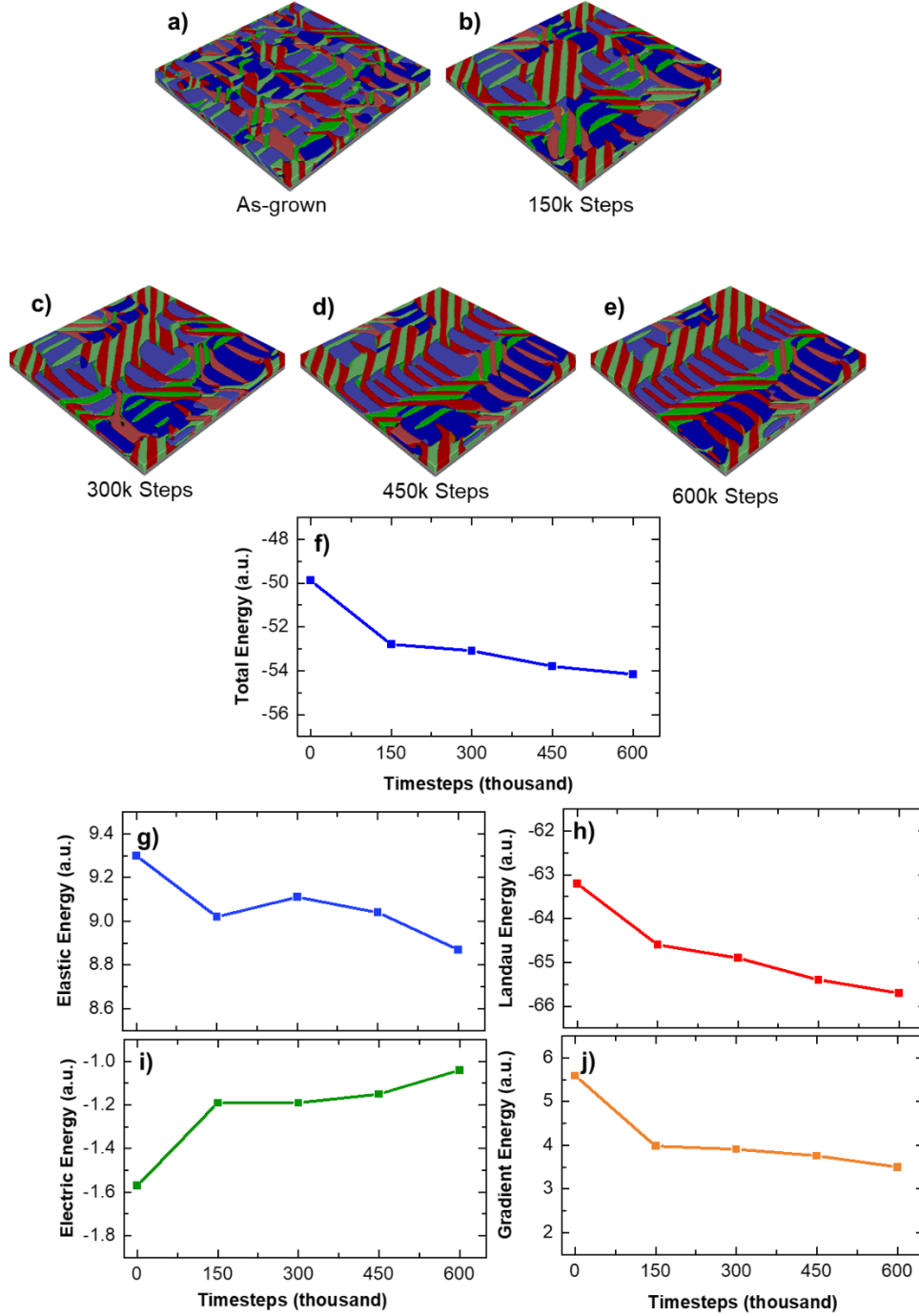


Fig. 3.16 Time-dependent evolution of hierarchical domain architectures during annealing wherein a domain coarsening and straightening increases with annealing time. The corresponding domain architecture at 300 K of a) as-grown film and after b) 150k, (c) 300k, (d) 450k, and e) 600k steps displaying increasing realignment of c/a and a_1/a_2 domain stripes in a hierarchical domain structure. f) Energy of domain structure as a function of simulation steps (equivalent to annealing time). Points at 150k, 300k, 450k, and 600k timesteps showing an increasing annealing period and corresponding energy lowering. g) elastic, h) Landau, i) electric, and j) gradient energy contributions to the total energy computed from phase-field studies during different annealing cycles after 150k, 300k, 450k, and 600k timesteps (equivalent to annealing time).

3.4.3 Topological Defect Characterization in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

This ordering process can be further understood by analysis of the pattern-defect densities as a function of annealing time. For that, I identified different types of elementary and composite defects during the annealing process. Among these multiple defects, threefold junctions (Fig. 3.17a) and stripe-endpoints (convex disclinations, Fig. 3.17b) are identified as primary defects, like those previously defined for defects in liquid crystals [136]. Further, they combine within themselves to form multiple other types of composite defects [137]. For example, by combining two threefold junctions it is possible to form a saddle defect (*i.e.*, a fourfold defect; Fig. 3.17c) and by combining a threefold junction and stripe endpoint it is possible to produce a handle defect (Fig. 3.17d). Further observation revealed other types of defects, namely isolated stripe segments (Fig. 3.17e), dots (Fig. 3.17f), target skyrmions (Fig. 3.17g) [138], and dislocation-style defects.

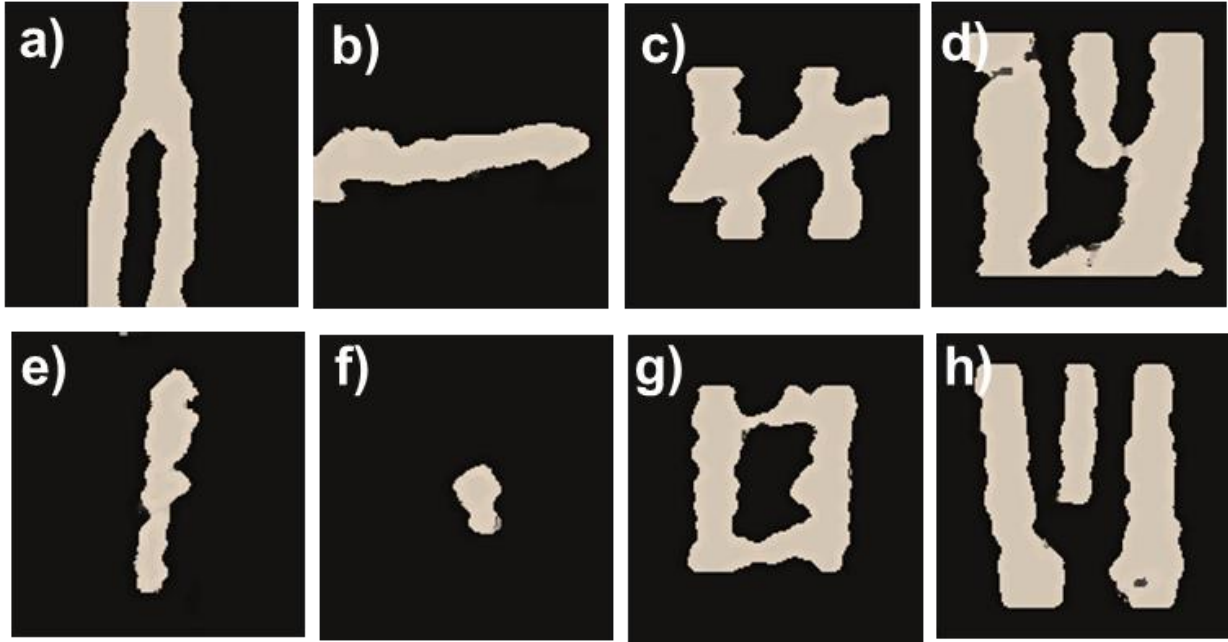


Fig. 3.17 Various types of defects are observed in the $\text{Pb}_{0.83}\text{Sr}_{0.17}\text{TiO}_3$ thin films such as a) threefold junctions, b) stripe end-points, c) fourfold junctions (saddle points), d) handle defects, e) disconnected stripes, f) droplets, g) target skyrmions, and h) dislocations.

3.4.4 Topological Defect Annihilation in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

Examination reveals that the density of type-1 (d_{type1} ; *e.g.*, fourfold and threefold junctions) and type-2 (d_{type2} ; *e.g.*, stripe endpoints) defects shows a steady decrease as a function of annealing time (Fig. 3.18). In the early stages of annealing, the majority type-1 defects annihilate. Thus, junctions can be seen as the weak links of the connected-labyrinth structure as they are first to disappear during the annealing process. In the later stages of annealing, the density of type-2 defects also decreases significantly. This reduction in defect densities can be understood as a recombination and annihilation of defects [136,139], where, for example, a pair of concave and convex disclinations can combine leading to the unidirectional stripe domain with new periodicity. Such control via annealing over the self-assembly of domain patterns provides additional knob, beyond conventional domain engineering [140] and domain wall [141] based methodologies, to manipulate domain structure morphologies.

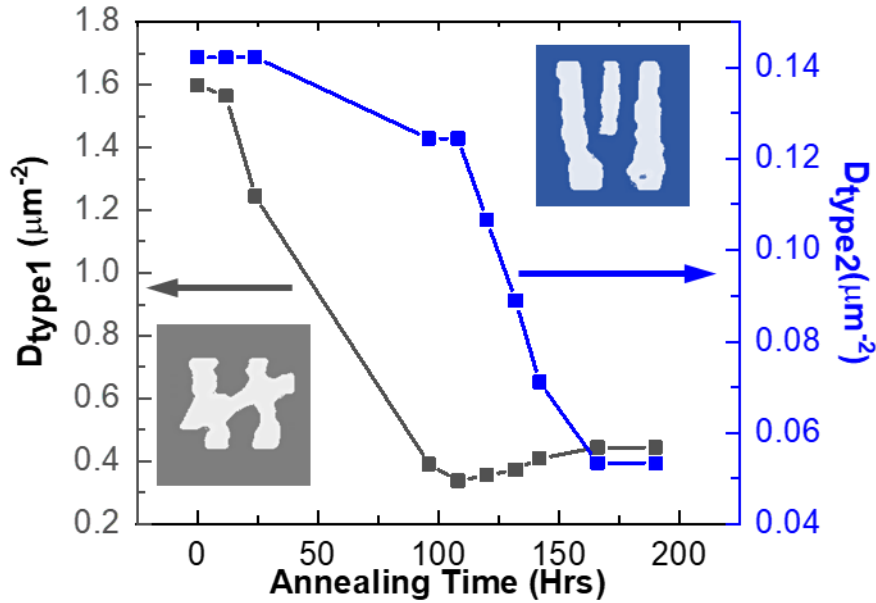


Fig. 3.18 The defect densities of three- and four-fold junctions (d_{type1}) and the stripe end-points (d_{type2}) as a function of annealing time. The insets show the dislocation and four-fold defect types.

3.5 Dielectric Properties of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

3.5.1 Total Dielectric Response of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

Thus far I have demonstrated an exacting and extensive pathway to control domain structures in ferroelectrics. This is of particular interest since it is well known that domain structures can greatly impact the evolution of properties (*e.g.*, dielectric [142,143], piezoelectric [144], pyroelectric [94,145], etc.) in ferroelectrics. To study the effect of our ability to continually manipulate the domain structures on the properties, dielectric constant (ϵ_r) was measured. To do this, 30 nm SrRuO_3 /100 nm $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.00, 0.06, 0.17, 0.20$, and 0.30)/30 nm $\text{SrRuO}_3/\text{DyScO}_3$ (110) heterostructures were fabricated into capacitor structures. Firstly, polarization-electric field hysteresis loops (reported at 10 kHz) were measured and, as anticipated, the largest saturated polarization (P_s) values were observed for the $x = 0.00$ heterostructures, while the $x = 0.30$ heterostructures exhibited the lowest (Fig. 3.19).

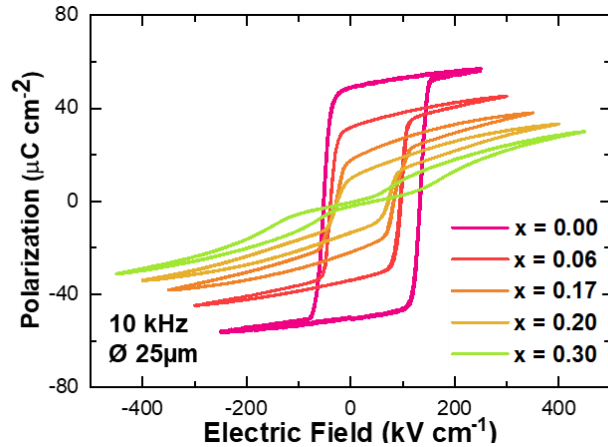


Fig. 3.19 Room temperature ferroelectric hysteresis response the various $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films measured at 10 kHz.

3.5.2 Interdomain Perimeter Calculation in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

As the strontium content is increased, there is a systematic increase in the a_1/a_2 -domain fraction in the mixed-phase domains which manifests as an overall increase in the out-of-plane dielectric response (Fig. 3.20); as ϵ_r is higher for a domains than for the c domains in the measured geometry [146]. With this trend, ϵ_r can be seen reaching a maximum value in the connected-labyrinth ($x = 0.17$) heterostructures, suggesting additional new domain boundaries are forming between the c/a and a_1/a_2 domains (henceforth referred to as the inter-domain boundaries; Fig. 3.21 Fig. 3.22a) and potentially affecting the net dielectric response largely by introducing added extrinsic contributions [142,147] over the regular higher contribution introduced by increasing the overall a_1/a_2 -domain fraction. To understand this potential effect, I extracted the shared perimeter between the c/a and a_1/a_2 domains from the AFM images and then normalized by the area of the majority domain variant to calculate a so-called

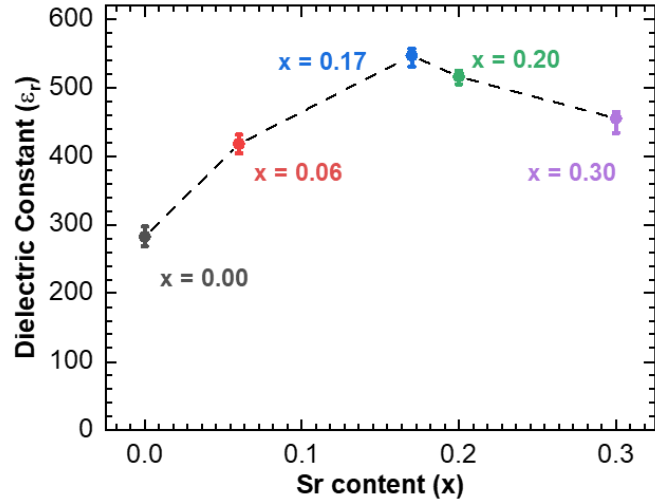


Fig. 3.20 Dielectric permittivity (ϵ_r) as a function of strontium content (x).

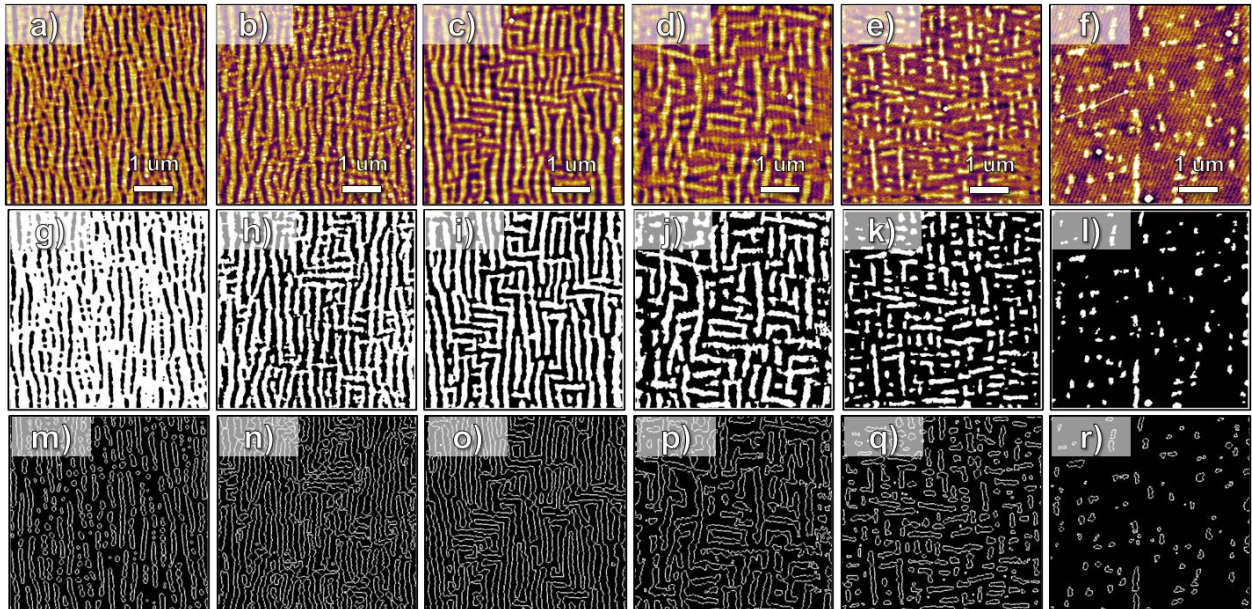


Fig. 3.21 AFM topography images of 100-nm-thick $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin film grown on DyScO_3 (110) substrate with a) $x = 0.06$, b) $x = 0.17$, c) $x = 0.20$, d) $x = 0.23$, e) $x = 0.25$, and f) $x = 0.27$. The images are $5 \times 5 \mu\text{m}^2$. The bright region shows c/a domain region and dark region describes a_1/a_2 domain area. These images are converted into black and white contrast for MATLAB based image processing methods. Corresponding compositions are g) $x = 0.06$, h) $x = 0.17$, i) $x = 0.20$, j) $x = 0.23$, k) $x = 0.25$, and l) $x = 0.27$. The shared perimeter between c/a and a_1/a_2 domain area identified for m) $x = 0.06$, n) $x = 0.17$, o) $x = 0.20$, p) $x = 0.23$, q) $x = 0.25$, and r) $x = 0.27$.

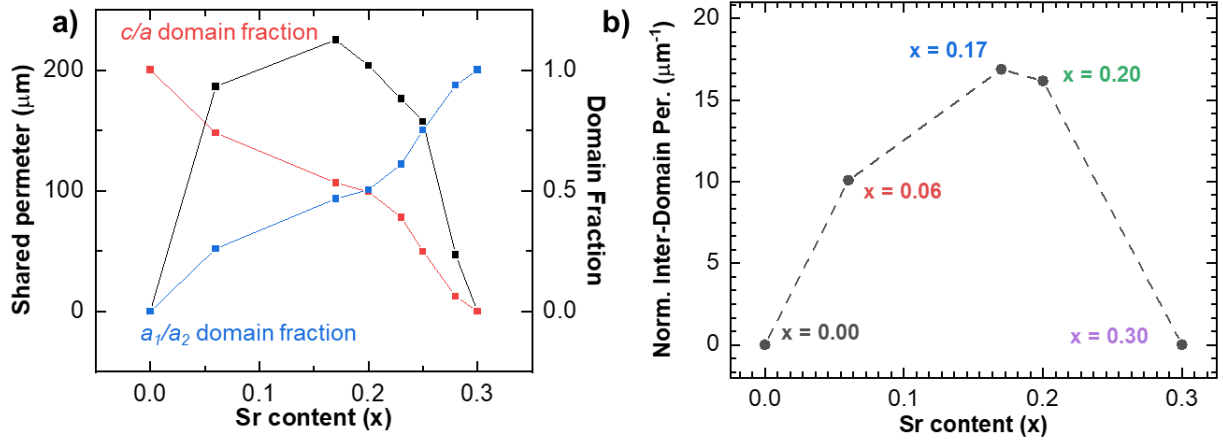


Fig. 3.22 a) Domain fraction of a_1/a_2 and c/a domains as a fraction of strontium content (x) in 100-nm-thick $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films grown on DyScO_3 (110) substrates. A shared perimeter between a_1/a_2 and c/a domain is derived from AFM images for each strontium content for an image size of $5 \times 5 \mu\text{m}^2$. b) Shared perimeter between c/a and a_1/a_2 domains normalized by majority phase as a function of strontium content (x).

normalized inter-domain perimeter (Fig. 3.22b). This value also reaches its maximum value at $x = 0.17$, the same composition at which ϵ_r is maximized. This indicates a connection between the inter-domain boundaries and the dielectric response.

3.5.3 Intrinsic and Extrinsic Dielectric Contributions in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

This can be taken one step further since the total contribution to ϵ_r can be divided into multiple sources, including *intrinsic* (arising from the polarization within a ferroelectric domains) and *extrinsic* (arising from the movement of domain walls) contributions. To quantify these contributions, the dielectric permittivity was measured as a function of frequency between 5-1000 kHz at different applied background dc electric fields. The applied background dc electric field can suppress the extrinsic contributions and allows for quantitative measurement of the intrinsic

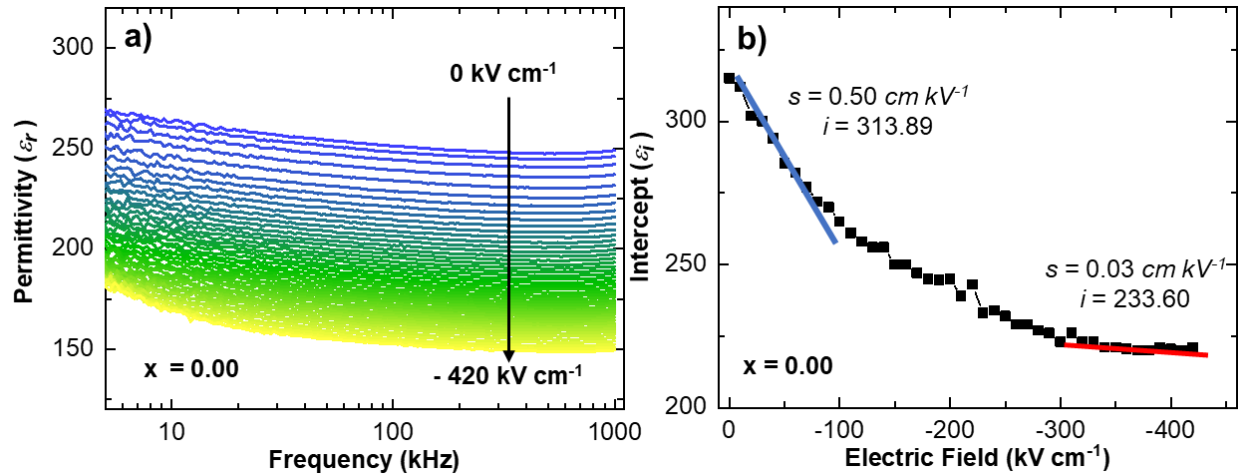


Fig. 3.23 a) Dielectric permittivity as a function frequency measured at different applied background dc electric fields for $x = 0.00$ heterostructure. b) Intercepts obtained from a linear logarithmic fit of the dielectric permittivity–frequency plot at various applied background dc electric fields are plotted as a function of the applied dc electric fields for $x = 0.00$ heterostructure.

response [148]. By fitting the frequency (f) dependence of the permittivity with each applied background dc electric field to the equation $\varepsilon = \varepsilon_i - \alpha \log f$, the dc biased dependence of the zero-field dielectric constant intercept (ε_i) and slope (α) can be calculated. The magnitude of the dielectric constant decreases as the applied background dc electric field is increased from 0 to -420 kV cm^{-1} (shown here, as an example, for an $x = 0$ heterostructure; (Fig. 3.23a)). ε_i is then obtained from a linear logarithmic fit of the dielectric permittivity-frequency data at different applied background dc electric fields. These intercepts are then plotted as a function of applied background dc field to obtain values of the zero-field intercept and slope for two distinct regions (again, shown here for an $x = 0$ heterostructure as an example; (Fig. 3.23b)). The low-field regime comprises the combined *intrinsic* and *extrinsic* contributions (fitted with blue line), and the high-field regime is indicative of the intrinsic response (fitted with red line). Similar analysis was done for other compositions (Fig. 3.24a). As one moves from low to higher strontium content ($0 \leq x \leq 0.3$), while the overall dielectric response (intrinsic and extrinsic contributions) is maximum at $x = 0.17$, the intrinsic contribution is found to increase systematically with strontium content as expected from the increasing a_1/a_2 domain fraction. The maximum value at $x = 0.17$, in turn, arises from the fact that this composition has the largest extrinsic contribution ($\sim 38\%$ of the overall response). This is in comparison to the $x = 0$ (pure c/a -domain structure) and $x = 0.3$ (pure a_1/a_2 -domain structure) heterostructures where the extrinsic contribution makes up only 26% and 0% of the overall response. The presence of the mixed-phase structures and the inter-domain boundaries (as for the $x = 0.06, 0.17$, and 0.2 heterostructures) results in larger extrinsic contributions and higher overall responses.

To further examine the impact of inter-domain boundaries on the properties, I performed phase-field simulations and calculated the dielectric constant (k_{33}) for a mixed-phase $\text{Pb}_{0.8125}\text{Sr}_{0.1875}\text{TiO}_3$ thin film (Fig. 3.24b). I could see the enhanced dielectric coefficient (k_{33}) at the inter-domain boundaries signifying increased activity. This is qualitatively like what is seen in the experimental work of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ solid solutions for dielectric permittivity. These results signify that the distinct topological structures engineered so far in various material systems ranging

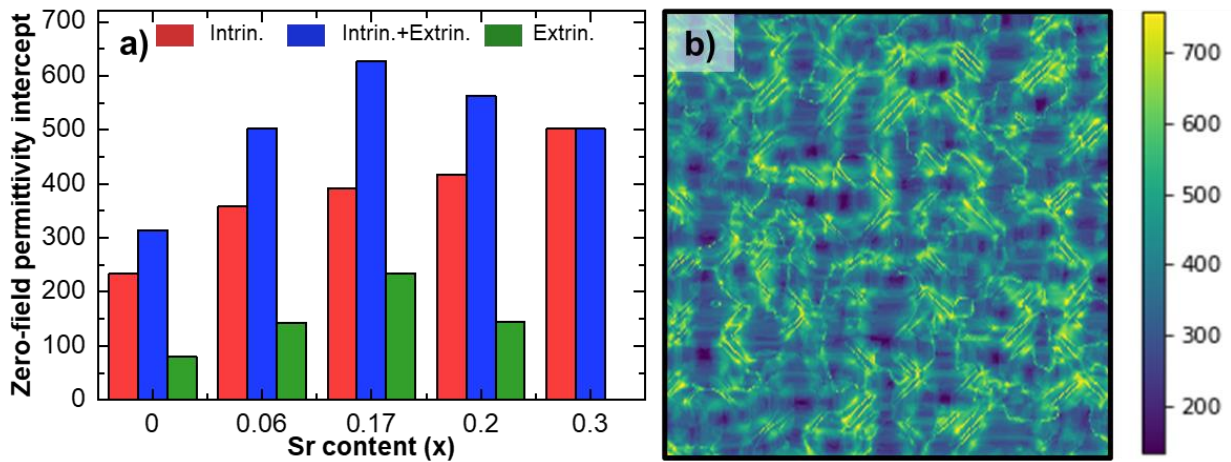


Fig. 3.24 a) Zero-field permittivity intercept of Intrinsic-only, combined intrinsic-extrinsic contribution, and the difference between them (extrinsic-only contribution) is plotted as a function of strontium content (x). b) Phase-field simulations for permittivity coefficient (k_{33}) for mixed-phase $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin film with $x = 0.1875$.

from polymers [75,76] to liquid crystals [74], can also be engineered in ferroelectric systems to enhance their functional properties.

3.6 Conclusion

All told, by combining epitaxial thin-film growth and various characterization methods with phase-field simulations, I have systematically investigated the evolution of complex, mixed-phase domain structures in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system as a function of strontium content. Unlike simple lattice-mismatch strain, the combination of strain, chemistry, and annealing provide for a fine level of control of the domain patterns, phase fractions, domain-wall length, etc. In turn, these structures have been analyzed for their topological nature and using approaches adapted from other fields, I identify a number of topological transitions across these different patterns. Further annealing the connected-labyrinth structures results in defect annihilation and ordered of the system into parallel-stripe domain patterns of c/a and a_1/a_2 domains, thus providing additional control of the system. In turn, this control has an impact on the properties of the films. By measuring the dielectric response for the different domain structures, it is found that the highest dielectric constant and maximum extrinsic contribution to the dielectric response occur when the domains arranged in the connected-labyrinth structures.

CHAPTER 4

Exchange-interaction-like Behavior in Ferroelectric Bilayers

Interlayer coupling in materials, such as exchange interactions at the interface between an antiferromagnet and a ferromagnet, can produce exotic phenomena not present in the parent materials. While such interfacial coupling in magnetic systems has been widely studied, there is considerably less work on analogous electric counterparts (*i.e.*, akin to electrical “exchange-bias-like” or “exchange-spring-like” interactions between two polar materials) despite the likelihood that such effects could also engender new features associated with anisotropic electric dipole alignment. In this chapter, I show electric analogs of such exchange interactions along with their physical origins for bilayers of in-plane polarized $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ferroelectrics. Variation of the strontium content and thickness of the layers provides for deterministic control over the switching properties of the bilayer system resulting in phenomena analogous to an exchange-spring interaction and, leveraging added control of these interactions with an electric field, the ability to realize multistate-memory function. Such observations not only hold technological promise for ferroelectrics and multiferroics, but also extend the similarities between ferromagnetic and ferroelectric materials to include the manifestation of exchange-interaction-like phenomena.

4.1 Introduction

Coupling across interfaces is important for many fields, such as hydrodynamic coupling across fluid interfaces [149,150], coupling across interfaces in composite materials with layers having different mechanical properties [151,152], magnetoelectric coupling in heterostructures consisting of magnetic and piezoelectric materials [153,154], and exchange interactions at interfaces between ferromagnets and antiferromagnets [155]. Among these, the interface coupling phenomena in multilayer magnetic systems, wherein there can be strong interactions between a ferromagnet and an adjacent ferromagnetic or antiferromagnetic layer, have been widely studied and utilized [156]. Exchange bias (or exchange anisotropy), in particular, is one of the most extensively studied phenomena [157,158]. It describes the situation wherein the magnetic response of a ferromagnetic layer is shifted away from zero magnetic field, resulting from an exchange interaction with an adjacent antiferromagnet layer [156]. This effect was essential for realizing devices such as magnetic read-write heads [159] and magnetic random access memory [160]. Other related phenomena include exchange-spring magnets (ESM) which are achieved by coupling hard and soft ferromagnets such that the hard magnet provides high anisotropy and coercive fields, while the soft magnet enhances the magnetic moment [161]. In such exchange springs, the soft magnet rotates back into alignment with the hard magnet when the applied field is removed; hence the analogy to a spring. The possibility of designing synthetic magnets for specific applications is, thus, intimately related to the ability to induce and tune the couplings between the individual magnetic layers.

On the other hand, considerably less work has been done on anisotropic dipole interactions across the interface between different ferroelectric materials and the range of resulting ferroelectric responses that are possible are still not fully explored and understood. It should be noted, of course, that an exchange interaction (in the rigorous sense as defined in magnetic systems) is not possible in ferroelectrics, but analogous coupling between layers via dipolar (electrostatic and potentially elastic) interactions could arise. This said, effects that appear similar to “exchange bias” have been observed in ferroelectrics in the form of hysteresis loops that are shifted along the electric field (voltage) axis due to the presence of an “internal-bias field” [162]. In general, however, such effects are not due to interfacial coupling, but instead can arise for many other reasons. For example, it is not uncommon to have preferentially aligned defect dipoles which pin the polarization of the ferroelectric in a given direction, effectively biasing the loop in one direction [163–166]. Compositional (or strain) gradients across the material can also produce similar effects [91,92] due to voltage offset induced by flexoelectric coupling between the polarization and strain gradient [167,168]. The observed hysteresis loops [91] are similar to that of a soft ferromagnet in an ESM system [161]. Beyond these examples there are other things that can give rise to built-in bias fields in ferroelectrics, including the presence of asymmetric electrodes [169] wherein different work functions produce asymmetric band bending at the different interfaces, interfacial Schottky effects caused by polarization-dependent band bending [170], charge trapping at electrode interfaces [171], and surface polar absorbates [172] leading to preferential polarization pinning. A recent study of $\text{BaTiO}_3/\text{PrScO}_3$ (110)₀ heterostructures also showed anisotropic (shifted) ferroelectric hysteresis loops arising from anisotropic strain, monoclinic distortions induced by interfacial oxygen octahedral coupling, and interfacial electrostatic potential stabilized, single-variant in-plane polarized BaTiO_3 [173]. Finally, “exchange-spring-like” effects have been studied via phase-field approaches in ferroelectric BaTiO_3 -dielectric SrTiO_3 superlattices wherein constricted hysteresis loops due to dipole-dipole interactions have been observed [174]. For these instances the analogy to magnetic exchange interactions (which is based on cross-interface

coupling) does not extend very far. Researchers have, however, also explored multilayer ferroelectric heterostructures in an attempt to manipulate their properties. For example, in bilayers based on the $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ system, heterostructures composed of tetragonal $x = 0.3$ and rhombohedral $x = 0.7$ layers showed enhanced piezoelectric behavior due to increased ferroelastic-domain activity [175] and deterministic reorientation of ferroelastic domain walls [176]. Bilayers formed from tetragonal $x = 0.2$ and $x = 0.8$ layers exhibited tunable structural, dielectric, and ferroelectric properties upon altering the order of the films [92]. Such examples demonstrate the potential for coupling ferroelectric layers across interfaces, but fall short of observations that are truly analogous to exchange-bias or exchange-spring effects. This begs the question of whether such interface-related phenomena observed in magnetism can be realized and tuned in ferroelectric-ferroelectric thin films multilayers?

With consideration to interface-controlled effects, in-plane ferroelectrics could provide a unique opportunity wherein the polarization lies parallel to the substrate surface. For $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$, prior work (Chapter 3) has illustrated the range of in-plane domain structures that can be produced in this system, including the formation of in-plane ferroelectric superdomains [36] and the field-induced dynamics of which have been explored using an automated experimental approach (FerroBOT [177]) [178]. Similar in-plane domains in BaTiO_3 system have been studied for their high-speed collective switching velocities [179]. Here, I demonstrate purely in-plane polarized bilayer ferroelectric heterostructures based on $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ [49] grown on DyScO_3 (110) substrates where it is possible to realize phenomena analogous to magnetic exchange bias and exchange-spring effects in a purely polar system. This is achieved by deterministic control of the coercive field of the individual layers by controlling both the strontium content and the thickness of the individual layers to induce “hard” (high coercivity) and “soft” (low coercivity) versions of the material. In turn, an array of interlayer lattice-polarization couplings are observed, including exchange-spring-like function and ferroelectric bias, which is further tunable via application of electric fields, such that it is possible to create stable multistate switching in the in-plane direction. Such observations not only hold technological promise for ferroelectric and multiferroic devices, but also extend the similarities between ferromagnetic and ferroelectric materials to include the manifestation of exchange-interaction-like phenomena.

4.2 Structural Analysis

4.2.1 X-ray Diffraction Studies

To study the potential for interlayer coupling phenomena, a model system that provides the right combination of properties is required. Here, a compositional series of 100-nm-thick $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films with $x = 0.4, 0.6$, and 0.8 was synthesized on DyScO_3 (110) substrates via pulsed-laser deposition. Following the growth, structural studies were completed via X-ray diffraction to probe the evolution of the crystal structure of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ films (Fig. 4.1a). High-quality, fully epitaxial solid-solution films were obtained for all compositions studied herein. In all cases, the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ 200-diffraction peaks appear to shift to higher 2θ values (Fig. 4.1b) with increasing strontium content (corresponding to a reduction of the out-of-plane lattice parameter). This is consistent with what is expected for the isovalent substitution of a smaller-sized Sr^{2+} cation (144 pm) at the Pb^{2+} cation (149 pm) site. Note that there is no peak corresponding to the c domain (*i.e.*, the 001- and 002-diffraction peaks) for these $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ films in such compositions as they are fully in-plane polarized domain structures and, therefore, such peaks will not appear in symmetric θ - 2θ line scans.

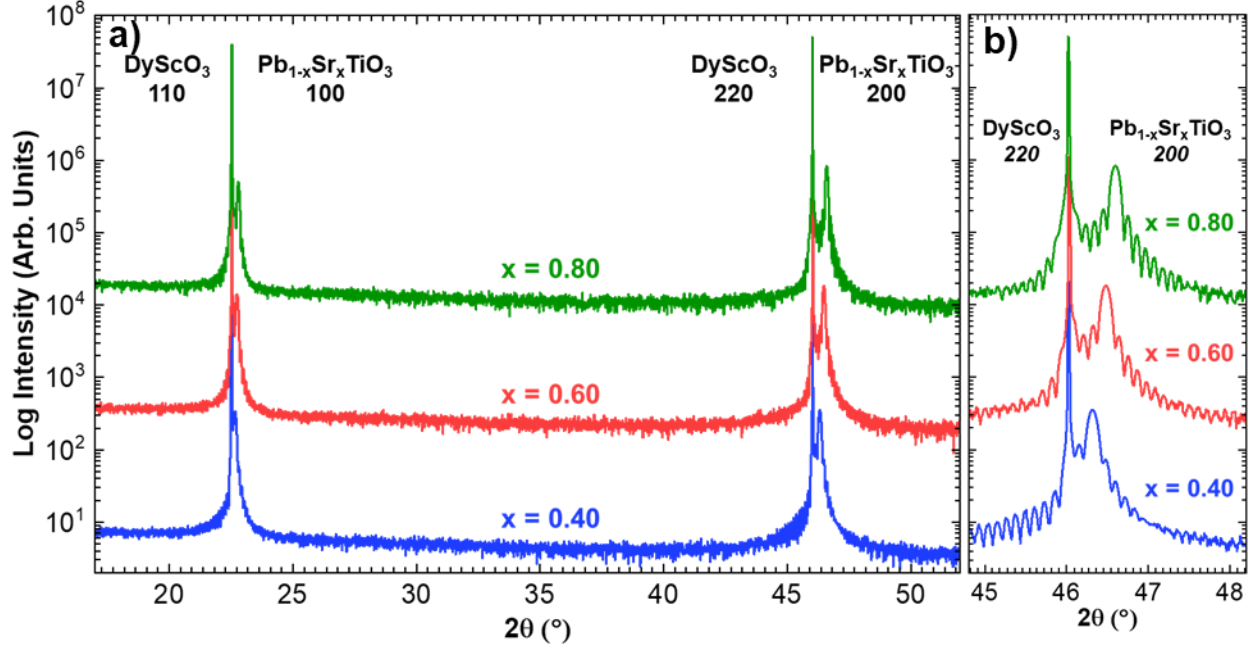


Fig. 4.1 a) Wide-angle θ - 2θ X-ray diffraction scans for 100-nm-thick $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films grown on DyScO_3 (110) substrate. From top to bottom, $\text{Pb}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ (green), $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ (red), and $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (blue). b) Zoom-in scan around 220 diffraction condition of DyScO_3 (110) substrate.

4.2.2 Reciprocal Space Mapping Studies

Further details about the materials, including the domain structure, can be obtained by exploring various features in X-ray reciprocal space mapping (RSM) studies. Here, considering the observation of only the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ 200-diffraction peak, asymmetric RSM studies about the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ 310-diffraction condition were completed for all films. The asymmetric RSM studies (Fig. 4.2) reveal a film peak corresponding to the 310-diffraction condition of the in-plane polarized domains that has the same Q_x as the DyScO_3 332_o-diffraction peak indicating that the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ films grow coherently strained with the underlying substrate. Also, distinct ordering peaks are visible along the $[h00]$ and at the same Q_z position for all $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films. For example, in the case of $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (Fig. 4.2c), such peaks indicate the systematic long-range ordering of stripe-like, in-plane domains with a periodicity of ~ 55 nm. Further asymmetric RSM

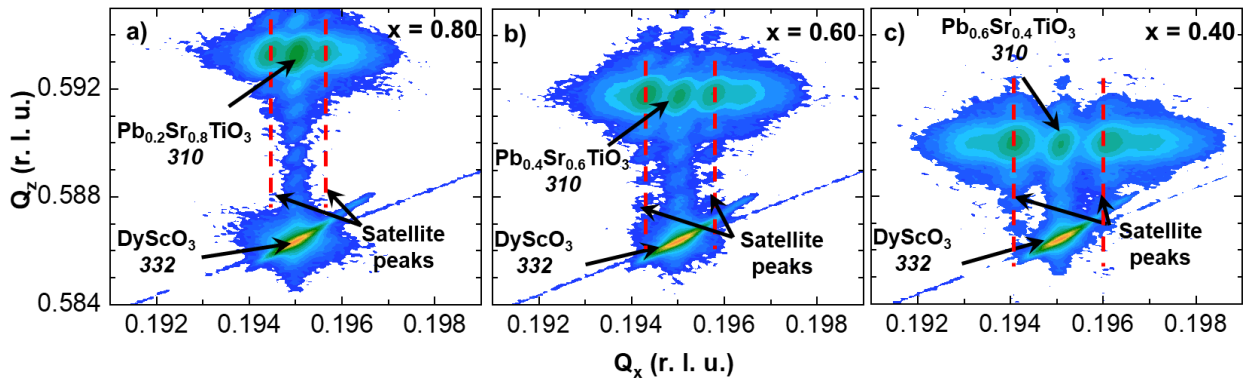


Fig. 4.2 2D reciprocal space mapping (RSM) about the 332_o-diffraction peak of DyScO_3 (110) with a pair of vertical dashed red lines representing domain periodicity satellite peaks for the 100-nm-thick a) $\text{Pb}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$, b) $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ and, c) $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$.

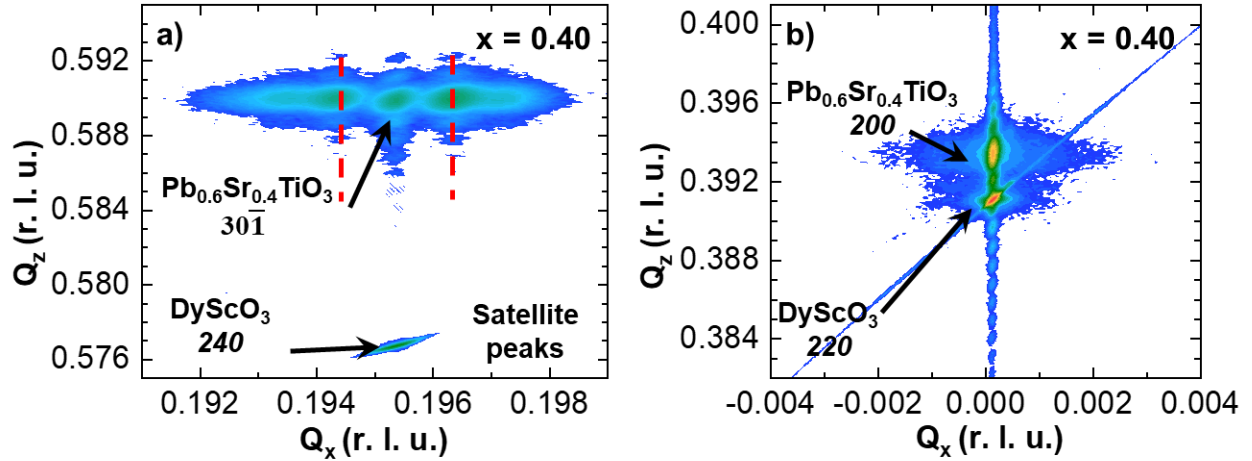


Fig. 4.3 a) 2D reciprocal space mapping (RSM) about the 240_o-diffraction peak of the DyScO₃ (110) with a pair of vertical dashed red lines indicating the positions of the domain periodicity reflections originating from in-plane Pb_{1-x}Sr_xTiO₃ domains and b) Similar RSM about the 220_o-diffraction peak of the DyScO₃ (110) where such domain periodicity satellite peaks are missing due to the absence of any regular arrangement of out-of-plane polarization in the pure in-plane domain.

studies were done about the Pb_{1-x}Sr_xTiO₃ 301̄-diffraction condition (Fig. 4.3a) to confirm that similar periodicity exists in the other perpendicular direction. Also, RSM studies about the symmetric 200-diffraction condition of the Pb_{1-x}Sr_xTiO₃ (Fig. 4.3b) demonstrate no signatures of any satellite peaks, which are usually induced by any regular out-of-plane polarization arrangements associated with the periodic domains [53]. The two possible uncharged domain structures with these types of walls are: (i) the *aa*₁/*aa*₂-phase wherein the polarization is along the base diagonals of the Pb_{1-x}Sr_xTiO₃ unit cell (Fig. 4.4a) and (ii) the *a* phase (Fig. 4.4b) with the polarization along the longer base edges of the Pb_{1-x}Sr_xTiO₃ unit cell (also called *a*₁/*a*₂ or 90° domains).

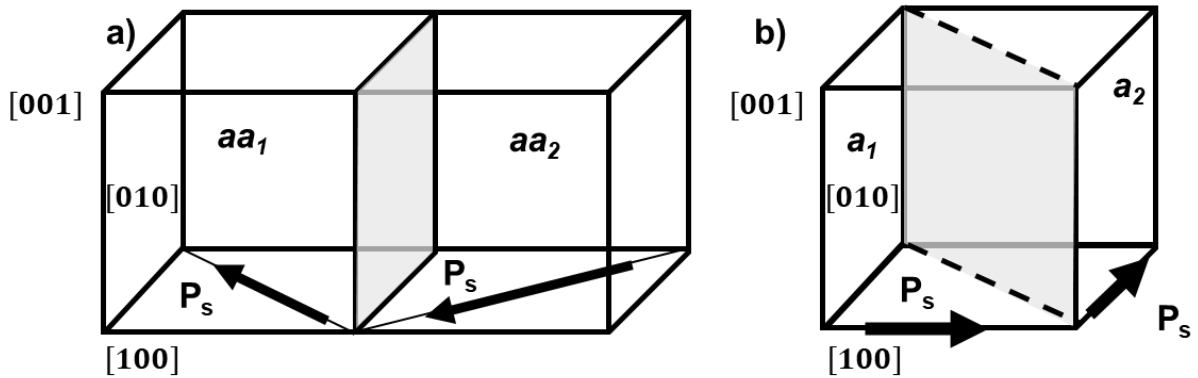


Fig. 4.4 Domain structures representation of domains separated by a domain wall predicted in the Pb_{1-x}Sr_xTiO₃ thin films. a) *aa*₁/*aa*₂ structure with polarization along [1̄10] and [11̄0] directions. b) *a*₁/*a*₂ domain structure with tetragonal symmetry and the polarization alternating along [100] and [010].

4.2.3 Domain Structures in Pb_{1-x}Sr_xTiO₃ Thin Films

To further understand the in-plane domain configuration, it was directly visualized via piezoresponse force microscopy (PFM) which, for an entirely in-plane polarized ferroelectric material, is detected by lateral PFM (L-PFM) [180]. Indeed, in-plane domains are observed in the

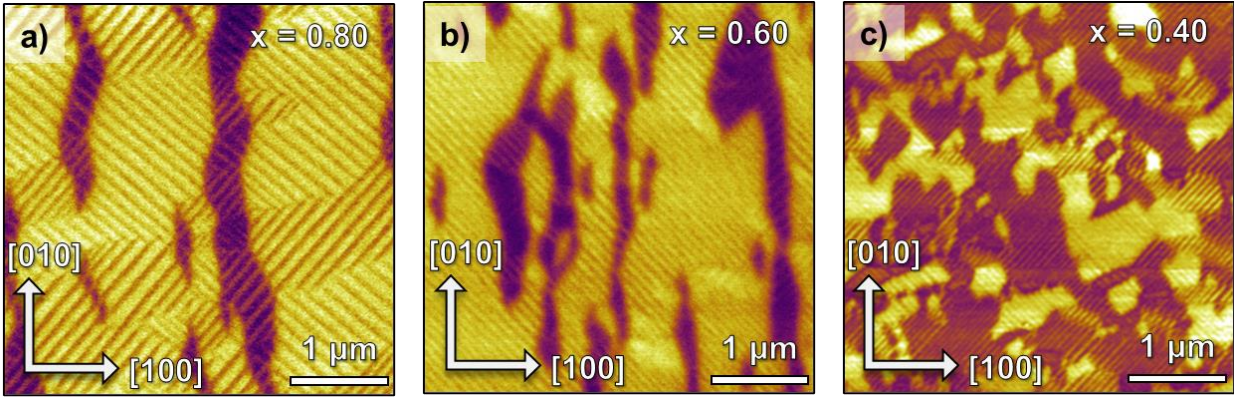


Fig. 4.5 Lateral PFM (L-PFM) images of 100 nm-thick a) $\text{Pb}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$, b) $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$, and c) $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$.

as-grown films (Fig. 4.5). The orientation of the domain walls along the $[110]$ and $[\bar{1}10]$ is consistent with an a_1/a_2 -domain structure [46]. Furthermore, the as-grown $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ films show no other surface features other than substrate terraces (Fig. 4.6a) and there is no contrast in vertical

PFM (Fig. 4.6b); further supporting the conclusion that the films are fully in-plane polarized. The periodicity of the domain structure, as measured from L-PFM (λ_{PFM}) matches well with the periodicity extracted from the ordering peaks (λ_{RSM}) in the RSM studies (Fig. 4.7). An additional noteworthy observation is that the domain

periodicity increases upon increasing the strontium content. Observation of large, single-variant regions would cause large local compressive or tensile strains. Domain formation like that seen here is an effective mechanism (that does not require the formation of interfacial misfit dislocations) to alleviate the formation of such high-strain regions by averaging the strain values in both in-plane directions. As the overall lattice parameters and tetragonality of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ unit cell decrease with increasing strontium content, the lattice mismatch with the substrate consequently reduces. Therefore, a frequent requirement for forming such in-plane domain variants in both directions to avoid excessive local strain areas decreases, leading to the

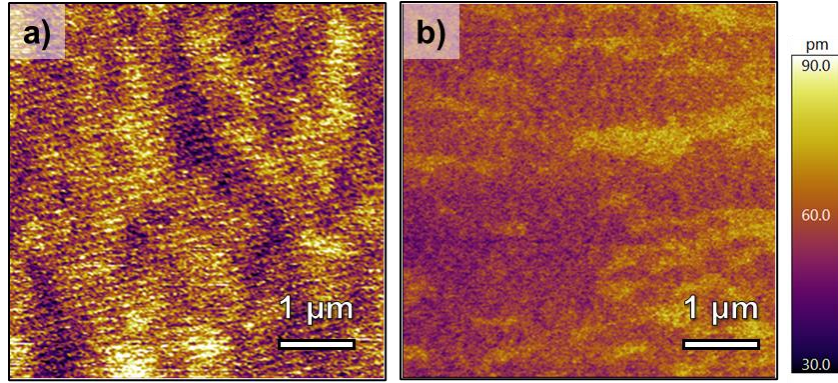


Fig. 4.6 a) AFM topography showing substrate terraces and b) Vertical PFM (V-PFM) probing the out-of-plane polarization of 100-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ thin films grown on DyScO_3 (110).

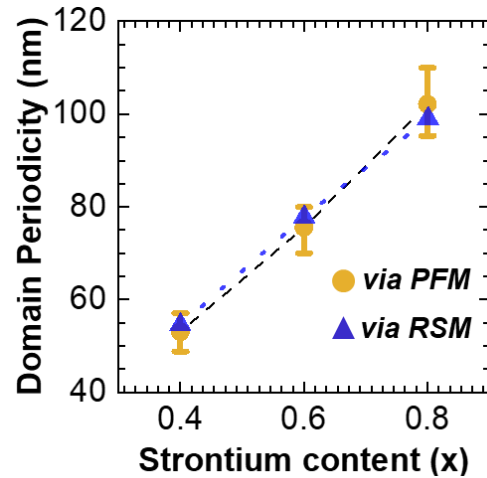


Fig. 4.7 Domain periodicity extracted from 2D-RSM and L-PFM for each composition shows a good match.

individual domain stripe size increment and overall periodicity. This provides an effective tool to tune domain periodicity other than thickness [36].

4.3 Device Orientation Dependent In-plane Switching of The $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$

4.3.1 Local Domains and Global Superdomains in $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

Moving on from static understanding of the as-grown domain structures, I used L-PFM to probe the evolution of (and pathway for) switching in these in-plane polarized films. Here, a domain naming scheme is defined such that if the polarization is along the in-plane $[100]$, $[\bar{1}00]$, $[010]$, and $[0\bar{1}0]$ those domains are referred to as a_{1+} , a_{1-} , a_{2+} , and a_{2-} domains, respectively (Fig. 4.8a). Assemblies of these small-scale a_1 and a_2 nanodomains can be further arranged in four types of “superdomains” which are related by 90° rotations (Fig. 4.8b-e). These superdomains are further categorized as type I or II for those with domain walls running along the $[110]$ or $[\bar{1}\bar{1}0]$, respectively. Additional + or – suffixes are added to these superdomain type names based on the type of a_2 domains included in the superdomain. For example, if the superdomain contains a_{2+} domains it would be the + variant and if it contained a_{2-} domains it would be the - variant. The resultant global in-plane component of polarization (blue arrow, Fig. 4.8b-e) can now be defined and can lie along the $[\bar{1}10]$ (type I+, Fig. 4.8b), $[1\bar{1}0]$ (type I-, Fig. 4.8c), $[110]$ (type II-, Fig. 4.8d), or $[\bar{1}\bar{1}0]$ (type II+, Fig. 4.8e). Like local dipoles, these superdomains can be represented as global dipoles (Fig. 4.8f). To study the dependence of applied electric field (E) direction on switching characteristics of various superdomains involving different combination of local dipoles, planar device structures were fabricated on the top surface of the films such that in-plane E can be applied along the $[100]$, $[\bar{1}00]$, $[010]$, or $[0\bar{1}0]$ (henceforth referred to as 0° devices) and the $[110]$, $[\bar{1}10]$, $[1\bar{1}0]$, or $[\bar{1}\bar{1}0]$ (henceforth referred to as 45° devices).

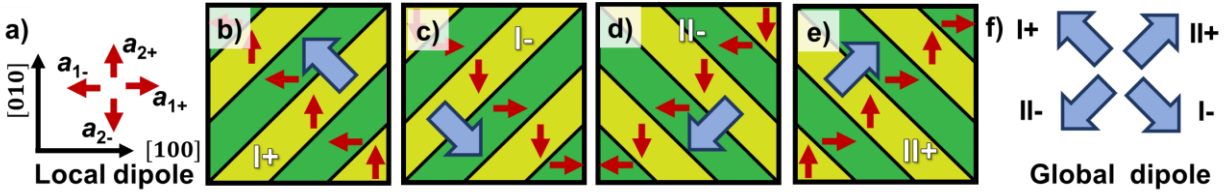


Fig. 4.8 a) Different local domains based on the in-plane directions. Different superdomain types based on the global polarization direction. b) type I+, c) type I-, d) type II- and e) type II+. f) Representation of different global dipole direction based on superdomain types.

4.3.2 Switching Characteristics of 0° Devices

When E is applied along the $[100]$ it results in the stabilization of two superdomain variants (type I- and II+, Fig. 4.9a). Stabilization of these two superdomain variants, out of the four initial variants, is based on energy minimization by alignment of the resultant global polarization direction of the superdomains with the applied E [36,178]. Upon applying the E along the $[\bar{1}00]$ on the same structure (Fig. 4.9a), the domains show characteristic switching wherein the superdomain boundaries remain essentially intact without any significant motion (Fig. 4.9b), but the superdomains themselves show characteristic switching from type II+ to I+ and I- to II- via local a_1 and a_2 domain level switching.

To further understand the nature of switching, phase-field simulations were performed in collaboration with Aiden M. Ross, Dr. J. A. Zorn, and Prof. L.-Q. Chen at the Pennsylvania State University to map the switching pathways (Fig. 4.9c) among multiple potential available routes. The domain structure with two superdomain variants (here, type II+ and I-), obtained by applying

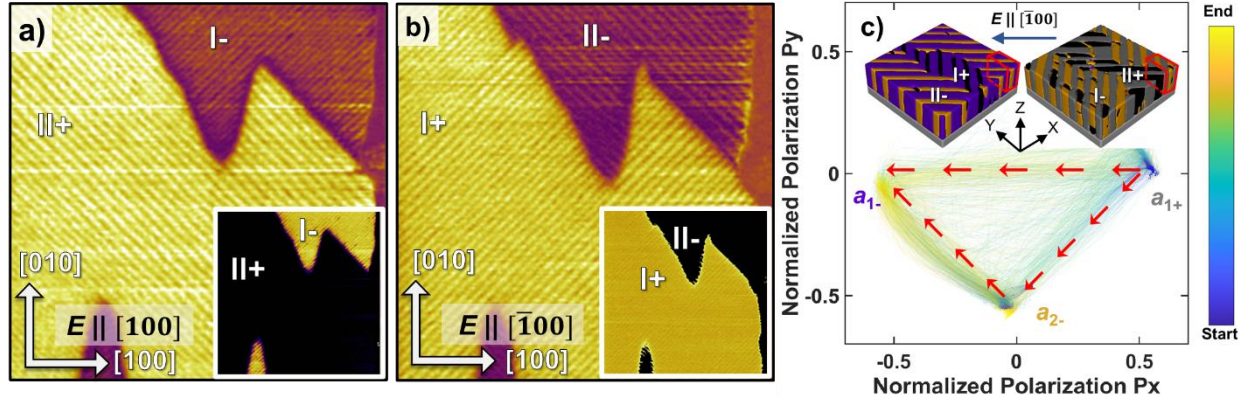


Fig. 4.9 a) L-PFM scan for a 0° device after applying E along the $[100]$ showing type-I- and -II+ superdomains. Inset showing the corresponding phase of the superdomains. b) Same area is then analyzed after applying E along the $[100]$ showing type-I+ and -II- superdomains. c) Switching pathway analyzed for a 0° device after application of E along the $[100]$ on a type-I- superdomain variant subsection (shown in red color box) showing stepwise 90° switching and 180° switching pathway.

an electric field E along the $[100]$, is used as a reference state (inset, Fig. 4.9c). Upon reverse poling by applying E along the $[100]$, the superdomains switch from type II+ to I+ and I- to II- via a nucleation-and-growth-like mechanism (Fig. 4.9c). To capture the local switching mechanism in response to the applied electric field E along the $[100]$, we focus on the polarization evolution in a small subsection of one of these superdomains (within the simulation cell, marked by the red volume within the type-I- superdomain, Fig. 4.9c), comprising two tetragonal domain variants – namely a_{1+} and a_{2-} . The phase-field simulations offer further insights about the switching pathways by providing the path each simulation cell takes (individual lines show the individual cell switching pathways and the red arrows show the overall, dominant pathways; Fig. 4.9c). There are two dominant pathways, the first is a one-step process, where a single 90° switching event causes a_{1+} domains to become a_{2-} domains or a_{2-} domains to become a_{1-} domains. The second pathway is a two-step process in which the a_{1+} domains first switch to a_{2-} domains then to a_{1-} domains. A small portion of a_{1+} domains also undergo a single 180° switching step to become a_{1-} domains and some a_{2-} domains do not undergo any switching. Thus, during this collective switching process, each unit-cell polarization responds to the applied E via one of the various switching pathways discussed above before moving to the final, elastically more compatible switched state within the superdomain boundary.

4.3.3 Switching Characteristics of 45° Devices

On the other hand, applying E along the $[110]$ leads to the stabilization of only type I- superdomains (Fig. 4.10a). This selection is again based on energy minimization of the global polarization direction of the superdomain variant with applied E [36,178]. Applying the E along the $[110]$ on the same structure after initial poling, the superdomain shows no visible signs of domain pattern changes in L-PFM amplitude (Fig. 4.10b). In reality, this superdomain variant rearranges itself via local single 90° switching events at the individual a_1 and a_2 domain level from a type-I- to a type-I+ superdomain.

As was done previously, further understanding of the nature of switching was gained via phase-field simulations for the 45° devices (Fig. 4.10). Applying E along the $[110]$ energetically favors two tetragonal domain variants (a_{1+} and a_{2+}) resulting in a single superdomain variant (type II+, Fig. 4.10a). Upon reverse poling by applying E along the $[110]$, the polarization in the two

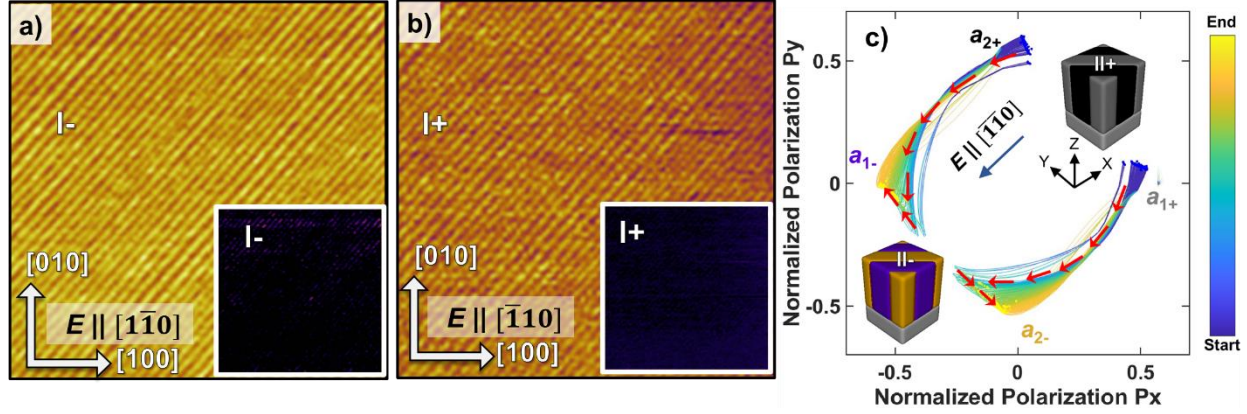


Fig. 4.10 a) L-PFM scan for a 45° device after applying E along the $[1\bar{1}0]$ showing the resulting type-I- superdomain. Inset showing the corresponding phase of the superdomains. b) The same area is then analyzed after applying E along the $[\bar{1}10]$ showing the resulting type-I+ superdomain. c) Switching pathway analyzed for a 45° device after applying E along the $[\bar{1}10]$ on a type-II+ superdomain showing a 90° switching pathway to convert it into type-II- superdomain.

tetragonal domains will attempt to equally align with the electric field, creating an equal driving force for switching. This balance of driving forces eliminates the driving force for any domain-wall motion, leading to the uniform switching along with maintenance of the local domain order in the in-plane direction. Finally, this equal driving force creates two thermodynamically degenerate states (a_{1-} and a_{2-}), stabilizing a single superdomain variant (type II-, Fig. 4.10b). The phase-field simulations provide further insight into the actual switching pathways (Fig. 4.10c) and one can plot the path each simulation cell takes during the 45° device switching, where a single 90° switching step causes a_{1+} domains to become a_{2-} domains and a_{2+} domains to become a_{1-} domains. This notably changes the orientation of the electrostrictive strain (*i.e.*, the polarization induced or coupled strain) direction of the domains by 90° . During this collective switching process, each unit-cell polarization responds to the applied E by first rotating towards the same direction (*i.e.*, parallel to the $[\bar{1}10]$) before reaching the final, elastically more compatible switched state (individual lines show the individual cell switching pathways and the red arrows show the overall, dominant pathways, Fig. 4.10c). Such robust control of in-plane domains and superdomains, guided by phase-field simulations, offers a promising perspective to design devices based on these in-plane domain structures.

4.3.4 Exchange-bias-like Behavior in The Stacked $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

The 45° devices, which produce large-scale, single-superdomain-variant ordering upon poling were used for next set of experiments. In turn, in-plane ferroelectric hysteresis loops (Fig. 4.11a) were measured for 50-nm-thick $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.4, 0.6$, and 0.8) films at 1 kHz. As-measured hysteresis loops include a background dielectric contribution which makes them appear tilted; this has been subtracted for clarity. As previously observed for related systems in the out-of-plane direction [49,181], both coercive field and remanent polarization decrease as a function of increasing strontium content. Hereafter, I transition to explore bilayer structures beginning with a 50-nm-thick $x = 0.6$ layer on top of a 50-nm-thick $x = 0.4$ layer. Under small E it is observed that only the top $x = 0.6$ film switches (Fig. 4.11b) as was determined by the switched polarization value ($\Delta P = 22 \mu\text{C cm}^{-2}$) for the first switching event. The bottom $x = 0.4$ film switches only once the electric field exceeds $\sim 60 \text{ kV cm}^{-1}$, resulting in a complete switching of the bilayer system.

The result is a two-step switching process which repeats itself under reverse poling (producing

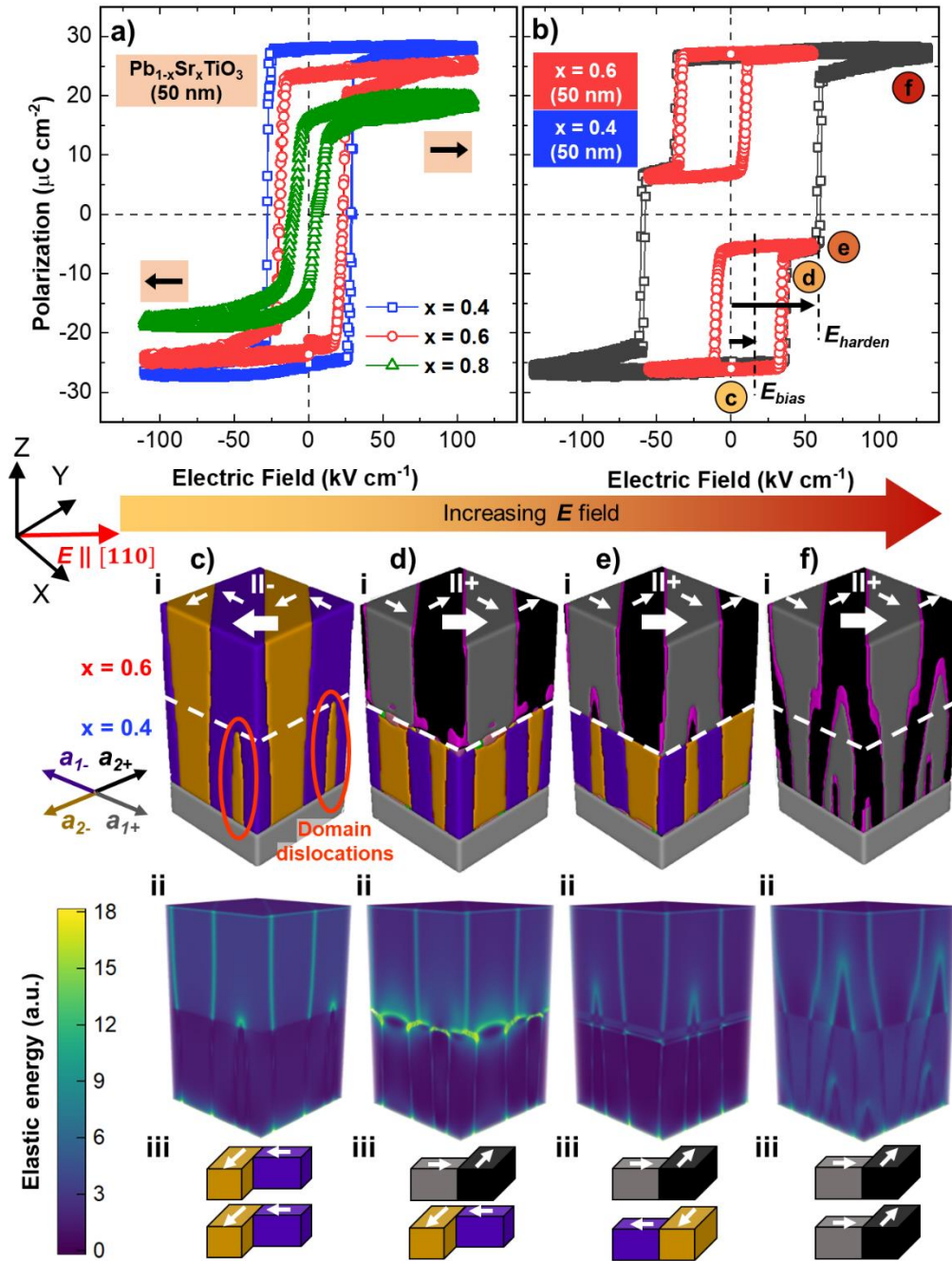


Fig. 4.11 a) Polarization-electric field hysteresis loops measured at 1 kHz frequency for a) 50-nm-thick $\text{Pb}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ (green), $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ (red), and $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (blue) heterostructures. b) Bilayer of 50-nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 50-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ exhibiting ferroelectric bias and coercivity hardening behavior with minor (red) and major (black) loops, respectively. Switching steps are further analyzed using phase-field simulations starting with c) the initial state, d) after the first switching event of the top $x = 0.6$ layer (The magenta regions at the domain wall between the a_{1+} and a_{2+} domains have polarization pointing along the $[110]$), e) after domain reshuffling in the bottom $x = 0.4$ layer, and f) after complete bilayer switching. For c)-f), i) shows the equilibrium domain structure of the bilayer system, ii) shows the corresponding elastic-energy distribution, and iii) shows a simplified version of the domain arrangement at the interface at each switching step.

four distinct polarization states). To distinguish the two switching events, the first switching event is referred to as the “minor loop” (and corresponds to the switching of the top $x = 0.6$ layer) and the second, larger switching event (corresponding to the complete switching of the bilayer system) is referred to as the “major loop”. Both minor loops (one in the first half and the other in the second half of the bipolar waveform) are highlighted to aid the reader (red loops inside the major loop which is shown in black; Fig. 4.11b). The minor loops are considerably shifted (for the bottom right side, by a bias field $E_{bias} = 14 \text{ kV cm}^{-1}$); a behavior analogous to exchange bias.

To better understand this effect, two coupling phenomena need to be considered that emerge when the ferroelectric films with in-plane polarization are placed in direct contact. The first is *dipolar coupling* which emerges from the electrostatic interaction of the polarization in the two layers and tends to align the polarization of the neighboring layers. The second is *lattice coupling*, which emerges from an elastic-energy interaction and works to form a domain of a similar type across the interface (*i.e.*, it works to maintain domain continuity across the interface between the two layers). Such domain continuity effectively lowers the strain (elastic) energy cost of having the interface. As discussed earlier, the strontium content of a given layer (and assuming a constant substrate) can be used to engineer the domain periodicity. The lattice coupling, in turn, works to evolve both layers towards a similar strain state which requires similar domain orientation and periodicity in both layers of the bilayer. The phase-field simulations provide a detailed look at the equilibrium domain structure of the bilayer heterostructure at each switching step (Fig. 4.11c-f, i) and the corresponding elastic-energy distribution for the bilayer throughout the switching process (Fig. 4.11c-f, ii). Simplified domain-stacking schematics are also provided to help illustrate the cross-interface domain continuity of the bilayers (Fig. 4.11c-f, iii). Using these three representations, one can explore the evolution of the bilayer systems under applied field.

The initial state of the bilayer is a type-II- superdomain (Fig. 4.11c, i) wherein individual a_{1-} and a_{2-} domains of the top $x = 0.6$ layer are aligned with the a_{1-} and a_{2-} domains of the bottom $x = 0.4$ layer. It is also found that the two layers have nearly matched domain periodicity, but that there are some additional small, needle-shaped domains in the bottom $x = 0.4$ layer which has intrinsically smaller domain periodicity; accommodated by dislocation-like domains or so-called “domain dislocations”. This “matched” periodicity is also captured experimentally, where the common periodicity of $\lambda_{RSM} = 56 \text{ nm}$ was observed for the bilayer structure. This periodicity is marginally higher than the intrinsic periodicity of the bottom $x = 0.4$ layer and the aforementioned “domain dislocations” form as the system tries to bridge between the elastic energy state of the two layers. Examining the elastic-energy density for the initial state (Fig. 4.11c, ii), however, reveals that while the system has found a tentative equilibrium, there is some stored elastic energy in the system, especially in the top $x = 0.6$ layer and near the interface wherein the “domain dislocations” touch the interface. All told, however, the initial state of the system sees the same kind of domains aligning across the interface (Fig. 4.11c, iii), albeit with some elastic frustration from intrinsic domain periodicity differences.

As the E is turned on and the system starts to evolve, the top $x = 0.6$ layer, which has a lower coercive field, switches first (Fig. 4.11d, i). The increasing E along the $[110]$ results in the rotation of local polarization by 90° (*i.e.*, a_{1-} (purple) and a_{2-} (dark orange) to a_{2+} (black) and a_{1+} (gray), respectively; Figure 3d, i), and the corresponding transformation of the electrostrictive strain related to the initial type-II- superdomain in the top $x = 0.6$ layer to a type-II+ superdomain. As the global dipole associated with the type-II+ superdomain aligns perfectly with applied E with these single 90° switching step, it does not need to follow other switching routes (*e.g.*, double 90° switching steps or a single 180° switching step) to achieve the same required superdomain state; a

mechanism explained previously for single-layer 45° devices. This 90° rotation of the electrostrictive strain of the top layer, however, creates elastically incompatible perpendicular electrostrictive strain at the interface since the bottom layer does not rotate yet. As the a_{1-} (a_{2-}) domains of the top $x = 0.6$ layer switch to a_{2+} (a_{1+}), the bilayer finds a new equilibrium wherein those domains interface with a_{1-} (a_{2-}) domains in the bottom $x = 0.4$ layer. This elastic incompatibility is clearly seen in the elastic-energy density (Fig. 4.11d, ii), wherein there is high elastic energy stored at the interface. This also creates additional domain walls at each of the a_1 and a_2 stripes across the interface and a 90° alignment between polarization states across the interface as can be schematically seen from the overall domain picture (Fig. 4.11d, iii). The result, therefore, is that the switching should be anisotropic and energetically expensive due to the formation of such substantial discontinuity in spontaneous strain and polarization across the interface during this first switching event, leading to an exchange-bias-like shift in the form of a higher magnitude of the positive-coercive field than that of the negative-coercive field (Fig. 4.11b). Similar behavior was observed in the reverse switching direction of the major loop (Fig. 4.11b) in the form of a higher magnitude of negative-coercive field than that of the positive one. This “ferroelectric bias” is thus tunable on both sides via an electric field compared to previously reported defect-based ferroelectric bias, where field cooling was essential to change the bias direction [166].

From the ferroelectric hysteresis loops (Fig. 4.11b) it is also evident that the coercive field of the bottom $x = 0.4$ layer is enhanced (hardened) to $E_{\text{harden}} = 60 \text{ kV cm}^{-1}$ as compared to its value in isolation ($E_c = 30 \text{ kV cm}^{-1}$). This can be understood by taking into consideration the strain mismatch at the interface (Fig. 4.11d, ii). This strain mismatch drives the reorganizing of the domain structure in the bottom $x = 0.4$ layer where the a_{1-} (purple) and a_{2-} (dark orange) domains redistribute their fraction (periodicity) and partial switch to a_{2-} (dark orange) and a_{1-} (purple), respectively, without an overall ferroelectric switch of the entire layer (Fig. 4.11e, i). This rearrangement of the domain structure in the bottom $x = 0.4$ layer works to make the system more elastically compatible and effectively lowers the elastic-energy density at the interface (Fig. 4.11e, ii). Thus, the overall domain structure of the bilayer adjusts to prefer 180° alignment of polarization across the interface thereby placing a_{1-} and a_{1+} and a_{2-} and a_{2+} domains in contact (Fig. 4.11e, iii). This domain “reshuffling” does, however, lead to an additional energy penalty resulting in the form of “coercivity hardening” before ferroelectric switching for the bottom $x = 0.4$ layer (Fig. 4.11b). Ferroelectric switching begins from the substrate side after the completion of the domain reshuffling process in the bottom $x = 0.4$ layer (Fig. 4.11e, ii). Finally, increasing E further results in the bottom $x = 0.4$ layer switching completely (Fig. 4.11f, i) without generating a high elastic-energy density at the interface (Fig. 4.11f, ii). The final configuration (as one would expect) mirrors the initial state in that the same kind of domain types are present across the interface (Fig. 4.11f, iii). Importantly, after completing the bilayer switching process, domain dislocations can be seen to remain in the bottom $x = 0.4$ layer (Fig. 4.11f, i) and their influence can be seen in the reverse switching direction of the hysteresis loop (Fig. 4.11b) with similar biasing and coercivity hardening effects. Some small extensions of existing domain dislocations for the bottom $x = 0.4$ layer into the top $x = 0.6$ layer lead to a (slightly) different elastic energy distribution for the final state (Fig. 4.11f, ii) as compared to the initial state (Fig. 4.11c, ii). The phase-field simulations not only provide an ability to watch how switching evolves in these multilayer structures, but can also be used to extract simulated versions of the ferroelectric polarization-electric field hysteresis loops which aptly recreate the two-step switching process observed experimentally. All told, such a bilayer system with strong interlayer coupling gives rise to a complex, interdependent domain-

switching process that allows one to produce effects not commonly seen in single layers alone and, in turn, opens avenues to explore device designs beyond traditional purely substrate-controlled domain engineering pathways.

4.4 Multistate Switching, Bilayer Decoupling, and Exchange-spring-like Behavior

4.4.1 Multistate Switching in the Stacked $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

With this in mind, I extended the analysis of the switching behavior of the same $x = 0.6 / x = 0.4$ bilayer system. First, I bring forward (for reference) the overall ferroelectric polarization-electric field hysteresis loop shown previously which revealed that the intermediate polarization states produced by the minor loop (*i.e.*, switching the top $x = 0.6$ layer) are stable (red loops crossing at $E = 0 \text{ kV cm}^{-1}$ with non-zero remanent polarization, Fig. 4.12). Further assessment of this data reveals that the first switching event effectively creates a stable, remanent polarization value of $\pm 6 \mu\text{C cm}^{-2}$ and complete switching of the bilayer results in a stable, remanent polarization value of $\pm 26 \mu\text{C cm}^{-2}$. As the two states have been observed in both the forward and reverse switching directions, the system exhibits four different states. Additional pulsed-switching studies (PUND) (Fig. 4.13a) were used to further interrogate the nature of these four distinct polarization states. It was found that one can independently access all four states – meaning that one can go from one state to any other state as desired. Furthermore, all four states in the bilayer heterostructures were found to be highly stable and showed minimal change in polarization with time in retention testing (Fig.

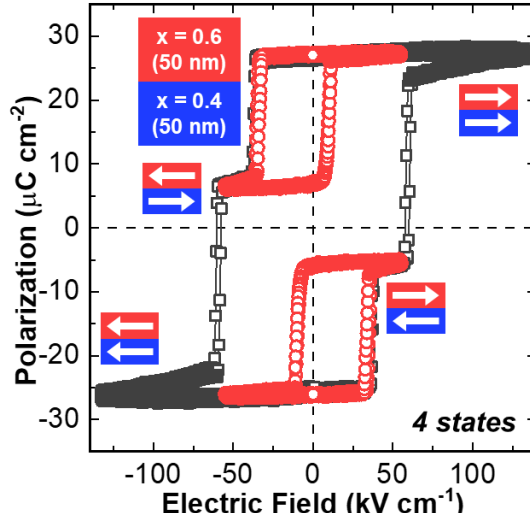


Fig. 4.12 Polarization-electric field hysteresis loops measured at 1 kHz frequency for a bilayer of 50 nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 50-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ exhibiting four states.

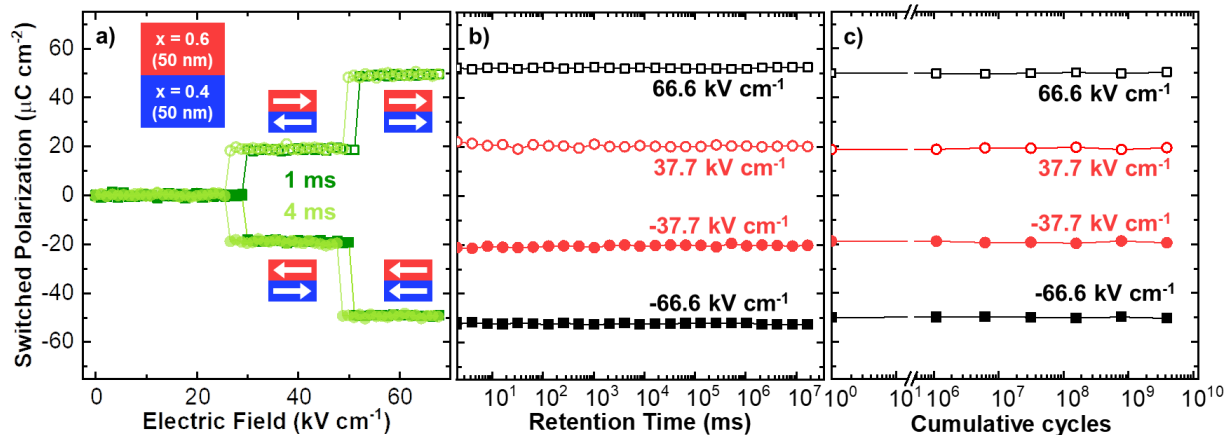


Fig. 4.13 a) The PUND studies reveal the pathway to the different polarization states at a constant pulse width of 1 ms and 4 ms as a function of different pulse voltages. b) The long-term retention and stability of the multiple polarization states. c) Stability of the multiple polarization states after long fatigue cycles.

4.13b). While the retention testing showed stability out to over five hours, other tests have shown the states to be stable for more than 200 days and, to the best of knowledge, they are stable well beyond this. Likewise, the endurance of each polarization state was also explored using a fatigue-pulse sequence, and it was found that each state could be repeatedly accessed and was easily distinguishable even after $>10^9$ write cycles (Fig. 4.13c). These results indicate several essential features required for a robust multistate operation.

4.4.2 Structural Decoupling on Dielectric Layer Insertion

To bring home the analogy with magnetic systems and confirm that these effects truly arise from cross-interface coupling, a 20-nm-thick SrTiO_3 dielectric buffer layer was added in the middle of the same heterostructure such that it is now a $x = 0.6$ / SrTiO_3 / $x = 0.4$ trilayer system. With the SrTiO_3 layer present, the minor loop showed minimal horizontal shift (~ 1.4 kV cm^{-1} ; red loops, Fig. 4.14). Additionally, the minor loops showed stable remnant polarization after the first switching event, demonstrating effective decoupling. This decoupling is also reflected in structural characterization, where each layer's domain periodicity returned to close to its original periodicity for the 50-nm-thick individual films (Fig. 4.15). The thickness of the SrTiO_3 spacer layer required to decouple the two adjoining ferroelectric layers is set by how the electric and elastic fields depend upon the polarization value of each ferroelectric layer, the magnitude of the ferroelectric proximity induced

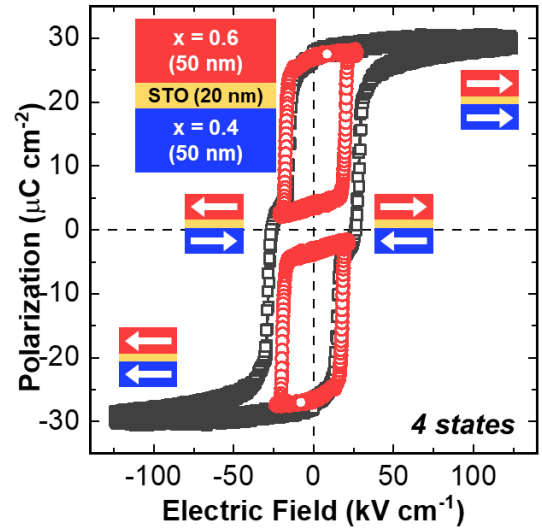


Fig. 4.14 Bilayer of 50-nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 50-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ separated by a 20-nm-thick SrTiO_3 spacer layer exhibiting lattice decoupling phenomenon.

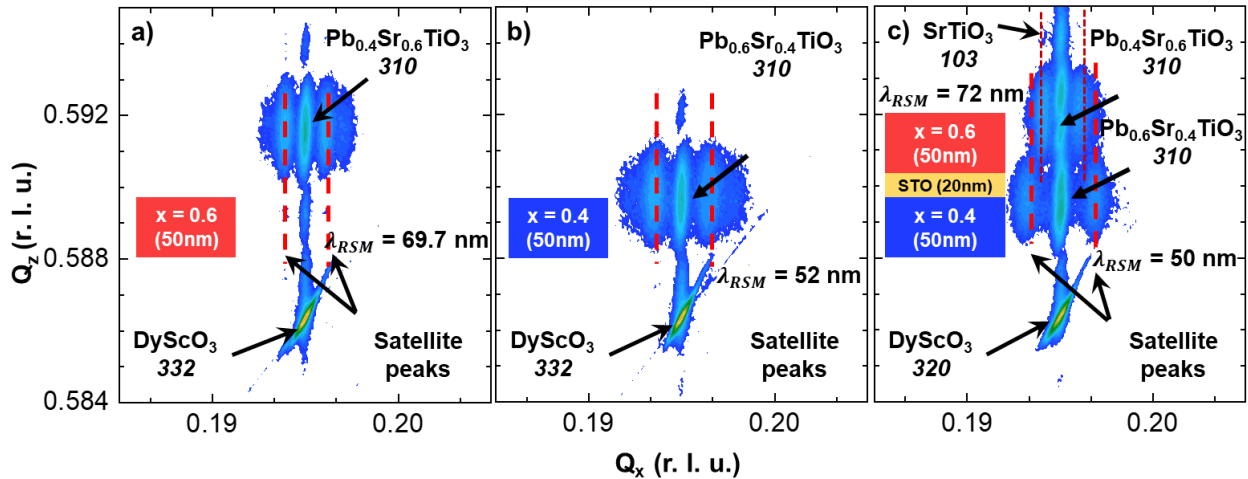


Fig. 4.15 2D reciprocal space mapping (RSM) about the 332_0 -diffraction peak of the DyScO_3 (110) with pair of vertical dashed red lines indicates the positions of the in-plane domain periodicity reflections of a) 50 nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ with the periodicity $\lambda_{\text{RSM}} = 69.7$ nm. b) 50 nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ with a periodicity of $\lambda_{\text{RSM}} = 52$ nm and, c) 50 nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 50 nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ with 20 nm-thick SrTiO_3 layer as a buffer layer. The periodicity of the $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ layer becomes 72 nm, and the periodicity of the $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ layer becomes 50 nm, close to the original periodicity of each layer with the implementation of the buffer layer.

dipole-dipole interaction strength [182], and the polarization due to substrate-induced epitaxial strain [183]. This is consistent with what has been previously observed in the order-disorder transition in superlattices exhibiting polar vortices [183] and in ferroelectric proximity effects in ferroelectric bilayers [182]. In essence, the electric and elastic fields in the SrTiO_3 layer decay with increasing distance, a distance that scales with the polarization of the adjoining ferroelectric layers and with the strain.

4.4.3 Multistate Tunability in the Stacked $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

Having established the robust nature of the multistate polarization and cross-interface coupling produced in this bilayer structures, I proceeded to use our knowledge of the individual layers to further manipulate the nature of multistate switching and to demonstrate the flexibility of such heterostructures to produce novel function. First, I explored the use of layer thickness to control the polarization value of the distinct intermediate states. For example, in a similar bilayer heterostructure but with a 75-nm-thick top $x = 0.6$ layer and a 50-nm-thick bottom $x = 0.4$ layer, it is possible to produce a minor loop in both the positive and negative half of the switching cycle that has a stable intermediate polarization value of $0 \mu\text{C cm}^{-2}$ (red loop, Fig. 4.16). Thus, here it is possible to make a three-state system (as opposed to four-states shown before). With this as an example, the flexibility of these heterostructures to produce on-demand polarization states is demonstrated. Furthermore, the $E_{\text{bias}} = 13.8 \text{ kV cm}^{-1}$ for this bilayer is essentially the same as that observed for that from the 50-nm-thick $x = 0.6$ layer on top of a 50-nm-thick $x = 0.4$ layer, suggesting that varying the thickness of the soft ferroelectric layer (here, the $x = 0.6$ layer) has little to no influence on the magnitude of E_{bias} . In turn, we also explored the use of changing the chemistry of the layers to demonstrate further control.

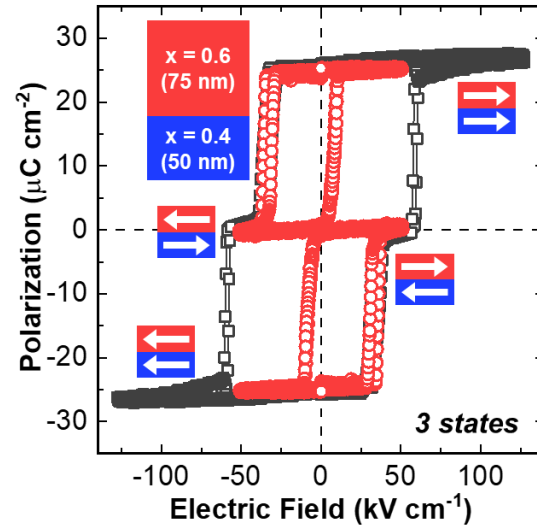


Fig. 4.16 Polarization-electric field hysteresis loops for a bilayer of 75-nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 50-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ exhibiting three distinct states.

4.4.4 Exchange-spring-like Behavior in the Stacked $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

Again, in a similar bilayer heterostructure but with a 50-nm-thick top $x = 0.8$ layer and 50-nm-thick bottom $x = 0.4$ layer, it was found that the switching of the top $x = 0.8$ layer was not stable, as captured by the minor loop displaying no remanence (green loops, Fig. 4.17). Here, $E_{\text{bias}} = 7 \text{ kV cm}^{-1}$ was observed and suggests that lowering the magnitude of the polarization of the soft ferroelectric layer (here, the $x = 0.8$ layer), which arises from the further introduction of strontium and a lowering of the tetragonality, leads to lower anisotropy during the first 90° switching event and, thus, a lower E_{bias} value. In other words, the lower the switched polarization value of the soft layer, the lower the E_{bias} value. Pulsed-switching studies for the positive side (inset, Fig. 4.17) also showed no stable remanence (dP) after the first switching event (P^*), demonstrating that the switched top $x = 0.8$ layer returns to its initial configuration, akin to a spring. After the second switching event (*i.e.*, of the bottom $x = 0.4$ layer), both layers showed stable switching without any

backswitching as captured by the hysteresis loop and also with the pulsed-switching studies. Similar behavior was observed in the negative side. This behavior is similar to the ESM concept introduced before, wherein the appropriate couples of hard and soft ferromagnets exhibit the high anisotropy and coercive fields of the hard magnet, with an enhanced magnetic moment coming from the soft magnet. In ESMs, the coupling appears below a certain critical thickness of the soft layer, leading to a simultaneous magnetization reversal process. When this critical value is exceeded, a two-step feature appears in the hysteresis loop of the system [184]. A similar kind of coupling is observed here, but in this case it is between the lattice and, in turn, polarization dipoles in two different in-plane polarized ferroelectric layers.

The hard and soft ferroelectric layers are again defined based on the coercive field of each ferroelectric. The soft, in-plane ferroelectric layer (*i.e.*, the top $x = 0.8$ layer) is pinned firmly to the hard layer (*i.e.*, the bottom $x = 0.4$ layer) at the interface. The top $x = 0.8$ layer starts switching only when the applied E exceeds the electric field denoted as the bending or nucleation field (E_N), which is same as of positive coercivity field here. Upon reducing the applied E before the second switching event (*i.e.*, that of the bottom $x = 0.4$ layer), backswitching of the soft, top $x = 0.8$ layer happens in a “springy” nature which returns it to its original state as captured by the minor loops. In ESMs, there is also a critical thickness below which the soft magnet is rigidly coupled to the hard one, and the two phases reverse at the same nucleation field resulting in a rectangular hysteresis [184]. Similar thickness-dependence is observed in the ferroelectric bilayers. For example, when a bilayer heterostructure of the form of a 40-nm-thick top $x = 0.6$ layer and a 40-nm-thick bottom $x = 0.4$ layer is probed, it is observed that the entire system switches, in a single event (Fig. 4.18), at $E = 23 \text{ kV cm}^{-1}$; which is lower than the coercive field of the bottom $x = 0.4$ layer alone ($E_c = 30 \text{ kV cm}^{-1}$) but close to that of top $x = 0.6$ layer ($E_c = 22 \text{ kV cm}^{-1}$). In essence, the bilayer can be controlled to give rise to “coercivity

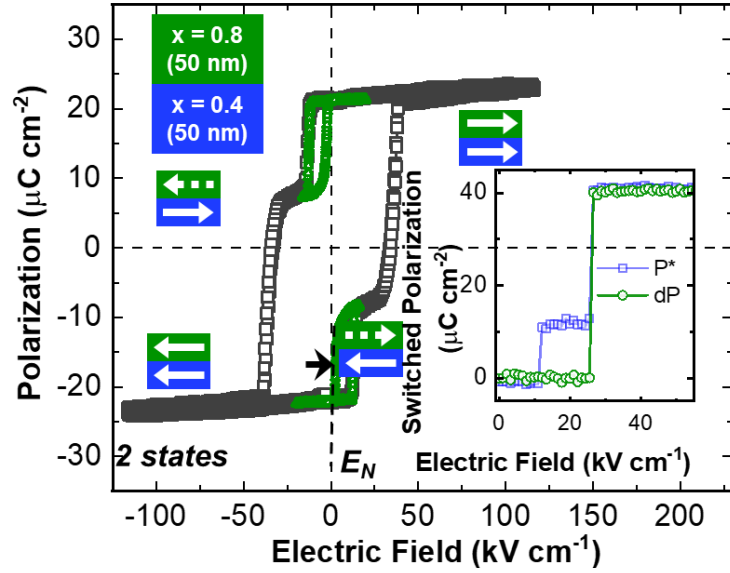


Fig. 4.17 Bilayer of 50-nm-thick $\text{Pb}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ on top of 50-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ exhibiting exchange-spring-like behavior.

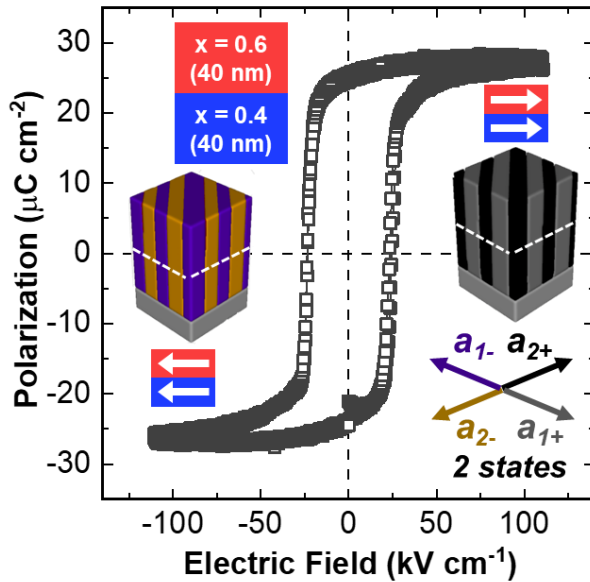


Fig. 4.18 Bilayer of 40-nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 40-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ exhibiting two states with coercivity softening of the hard layer.

softening”. As the individual layers become thinner, the domain periodicity difference between the two layers reduces [36] and the average distance from the bilayer interface becomes smaller, thus increasing the effective coupling between the films. This causes the individual a_1 and a_2 domain stripes in each layer (more) perfectly match across the interface without exhibiting any “domain dislocations” in the bottom $x = 0.4$ layer. The periodicity matching phenomenon is also captured experimentally, where the common periodicity of $\lambda_{RSM} = 50$ nm (Fig. 4.19) was observed for the bilayer structure. This, furthermore, effectively changes the bilayer switching mechanism. Simulations show that no domain reshuffling occurs in the bottom layer in the absence of domain dislocations, eliminating the kinetic pathway for multistate switching. This also creates a high elastic energy interface cost between the top, switched, soft layer and the bottom, unswitched, hard layer acting as an additional driving force to switch, thus inducing the hard layer to switch at a lower E value than the coercive field of that its isolated version of the hard layer (Fig. 4.20). This behavior is, again, similar to that observed in ESMs where the decrease of coercivity of the hard ferromagnet is explained by the propagation of the domain wall formed in the soft ferromagnet compressing against the interface and then propagating further, reducing the coercive field of the hard phase [184–186]. Thus, the geometrical arrangement of domains and polarization in the in-plane ferroelectrics offers access to a wide design space and access to phenomena largely unexplored and inaccessible in prototypical ferroelectric heterostructures made up of out-of-plane polarized domains. These findings signify that the in-plane bilayer

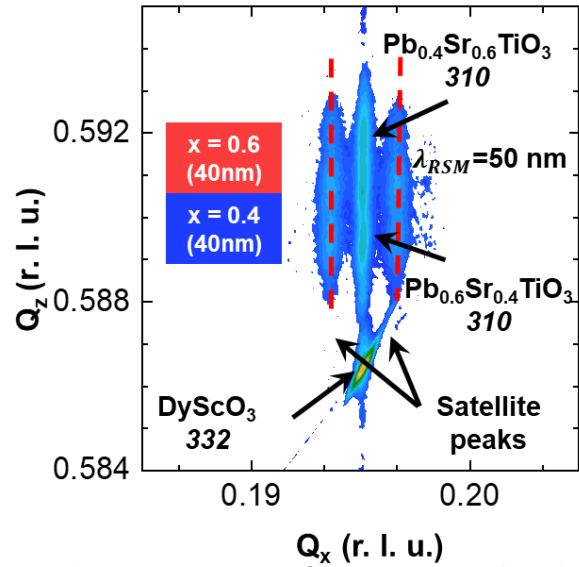


Fig. 4.19 2D reciprocal space mapping (RSM) showing the common periodicity of $\lambda_{RSM} = 50$ nm for the whole structure.

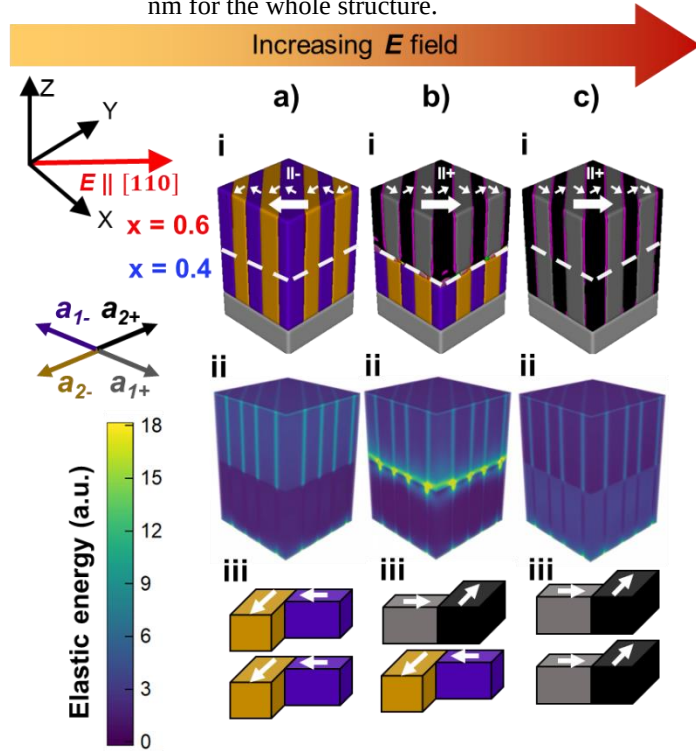


Fig. 4.20 Switching steps for bilayer with 40-nm-thick $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ on top of 40-nm-thick $\text{Pb}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ are analyzed starting with a) the initial state, b) after the first switching event of the top $x = 0.6$ layer, and after c) complete switching of the bilayer. For each a-c), the i) equilibrium domain structures of the bilayer system, ii) corresponding elastic-energy distribution, and iii) simplified version of domain arrangement at the interface at each switching step.

ferroelectrics can also be engineered in ways similar to their magnetic cousins and can exhibit effects analogous to exchange-bias and exchange-spring effects via lattice and polarization coupling.

4.5 Conclusion

All told, by combining epitaxial thin-film growth, detailed structural characterization, ferroelectric switching studies, and phase-field simulations, I have systematically investigated the interlayer interactions between in-plane polarized ferroelectric layers in bilayer $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ heterostructures. The combination of strain, chemistry, thickness, and device geometry provides a fine level of control of the domain patterns and their arrangement. In turn, these structures have been analyzed in the bilayer configuration for their interlayer coupling-induced exchange-bias-like phenomenon, an idea adapted from the exchange interactions in magnetism. This electric analog of exchange bias in the ferroelectric system can be additionally tuned via an electric field, providing added control of the system, which is then used to realize multistate functionality. Further control via strontium content and thickness selection has shown springy switching nature and coercivity reduction in the bilayer system, respectively, which is analogous to exchange spring in magnetism. Thus, this bilayer system provides a rich playground for tuning interlayer coupling across the system.

CHAPTER 5

Highly Responsive Polar Vortices in All-Ferroelectric Heterostructures

The discovery of polar vortices and skyrmions in ferroelectric-dielectric superlattices [such as $(\text{PbTiO}_3)_n/(\text{SrTiO}_3)_n$] has ushered in an era of novel dipolar topologies and corresponding emergent phenomena once thought impossible. The key to creating such emergent features has generally been considered to be related to counterpoising strongly polar and non-polar materials thus creating the appropriate boundary conditions for these complex structures to form. This requirement, however, limits the utility these materials can have by rendering (effectively) half of the structure unresponsive to applied stimuli. In this chapter, I demonstrate using advanced thin-film deposition and an array of characterization and simulation approaches, the possibility of polar vortex formation in all-ferroelectric trilayers, multilayers, and superlattices built from the fundamental building block of $(\text{PbTiO}_3)_n/(\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3)_n$ wherein in-plane ferroelectric polarization in the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ provides the appropriate boundary conditions. In turn, the superlattices exhibit substantially enhanced piezoelectric and ferroelectric responses in the out-of-plane direction that arises from the ability of the polarization in both layers to rotate to the out-of-plane direction under field. In the in-plane direction, the layers are found to be strongly coupled during switching and when heterostructured with ferroelectric-dielectric building blocks, it is possible to produce multistate switching and polarization stability. This research further expands the realm of systems able to support emergent dipolar texture formation and does so with entirely ferroelectric materials thus greatly improving their response to applied fields.

5.1 Introduction

Emergent topological polar textures, including vortices [53], dipolar waves [187], skyrmions [83], merons [84], and others, have generated considerable interest [188]. Thus far, ferroelectric-dielectric superlattices including those based on $(\text{PbTiO}_3)_n/(\text{SrTiO}_3)_n$ have served as the model system for this work [53] wherein the delicate balance of electric, elastic, and gradient energies can be tailored to manipulate the order parameter [53,83,84,187]. The resulting emergent polar textures also exhibit novel phenomena including coexistence of phases [89], chirality [189], negative capacitance [190,191], and emergent driven phases [192] and modes [193]. The intimate interactions and competition between the strongly polar ferroelectric and non-polar dielectric are thought to be essential for the formation of these features. The fact that half of such superlattices are essentially unresponsive to, for example, electric fields (except in a simple linear-dielectric fashion) means that these structures cannot be readily manipulated and have limited to small effects only in certain directions [194]. At the same time, however, similar polar textures have also been found in ferroelectric-metal superlattices based on $(\text{PbTiO}_3)_n/(\text{SrRuO}_3)_n$ [195,196], but again these materials have limited response to applied fields due to the presence of the periodic metallic layers. This begs the question as to how these novel polar textures can be better controlled using applied fields?

One pathway may be to explore ferroelectric-ferroelectric heterostructures wherein both layers are robustly polar and responsive to applied fields. In fact, researchers have already explored multilayer ferroelectric heterostructures with the goal of manipulating their properties and exploiting the potential for coupling across interfaces. For example, in bilayers based on the $\text{PbZr}_y\text{Ti}_{1-y}\text{O}_3$ system, heterostructures consisting of tetragonal ($y = 0.3$) and rhombohedral ($y = 0.7$) layers showed enhanced piezoelectric response due to increased ferroelastic-domain activity [175] and deterministic reorientation of ferroelastic domain walls [176]. In $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ bilayers, interlayer coupling-induced exchange-bias-like phenomenon has been observed [197]. It remains to be seen, however, if emergent polar structures can be produced in these all-ferroelectric superlattices and, if they can, how this impacts their overall response to applied stimuli?

In this chapter, polar vortices are realized in all-ferroelectric trilayers, multilayers, and superlattices constructed from $(\text{PbTiO}_3)_n/(\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3)_n$ ($x = 0.2, 0.3, 0.4, 0.5$, and 0.6 ; $n = 16$) building blocks, where the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ layers exhibit robust, in-plane polarization, but still provide the boundary conditions to support vortex formation in the PbTiO_3 . Scanning transmission electron microscopy (STEM)-based imaging and ptychography are used to directly image the emergent-vortex structures. In turn, both the out-of- and in-plane response to applied fields is probed. In the out-of-plane direction, all-ferroelectric superlattices exhibit electromechanical and polarization responses that increase systematically with x ultimately being as much as 7.5- and 2.4-times higher, respectively, than similar ferroelectric-dielectric superlattices. Phase-field and molecular-dynamics (MD) simulations reveal that these effects arise from the ability of the polarization in both layers to rotate freely from their ground states (vortex or in-plane polarized) to the out-of-plane direction. In the in-plane direction, exotic coupling and switching behavior is observed. The net-in-plane-polarization components of the vortices in the PbTiO_3 [194] (which is related to the vertical shifting of the vortices in the layer) and the in-plane domains in the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ layers [197] exhibit strong elastic and dipolar coupling. Phase-field and MD simulations again reveal the nature of this coupling and how it responds under field with impacts being found on the overall vortex periodicity, coercivity, and subsequent collective-switching pathways. In multilayers with controlled thicknesses of SrTiO_3 inserted between ferroelectric-ferroelectric and ferroelectric-dielectric building blocks, it is possible to control the strength of that coupling and to

realize exotic effects including multistate polarization switching and stability taking advantage of the different polarization reversal mechanisms in each type of structure.

5.2 Structural Analysis

5.2.1 Reciprocal Space Mapping Studies

For this work, the fundamental building block is $(\text{PbTiO}_3)_n/(\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3)_n$ ($x = 0, 0.2, 0.3, 0.4, 0.5$, and 0.6 ; $n = 16$) and all structures discussed herein were grown on DyScO_3 (110) substrates using RHEED-assisted PLD. Here, a naming convention wherein the chemistry (x) and (as needed) the number of repeats (p) are denoted together with a qualifying description. For example, trilayers of the form $(\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3)_{16}/(\text{PbTiO}_3)_{16}/(\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3)_{16}$ are referred to as $x = 0.3$ trilayers (Fig. 5.1a), multilayers of the form $(\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3)_{16}/(\text{PbTiO}_3)_{16}/(\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3)_{16}/(\text{SrTiO}_3)_{16}/(\text{PbTiO}_3)_{16}/(\text{SrTiO}_3)_{16}$ are referred as $x = 0.3/0$ multilayers, and superlattices of the form $[(\text{PbTiO}_3)_{16}/(\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3)_{16}]_5$ are referred to as $x = 0.3$, $p = 5$ superlattices. These heterostructures were grown in collaboration with Dr. Peter Meisenheimer and Prof. Ramamoorthy Ramesh at the University of California, Berkeley. The evolution of the structures with varying chemistry was probed with X-ray diffraction reciprocal space maps (RSMs) about the 002_{pc} -diffraction condition of the DyScO_3 substrate and along the in-plane direction (H , $[100]_{\text{pc}}$) for a number of trilayers (where pc refers to pseudocubic indices). As a reference, studies of $x = 0$ trilayers reveal satellite peaks corresponding to vortices of period 11.4 nm (Fig. 5.1b). Upon transitioning to $x = 0.3$ (Fig. 5.1c) and $x = 0.5$ trilayers (Fig. 5.1d), studies also reveal satellite

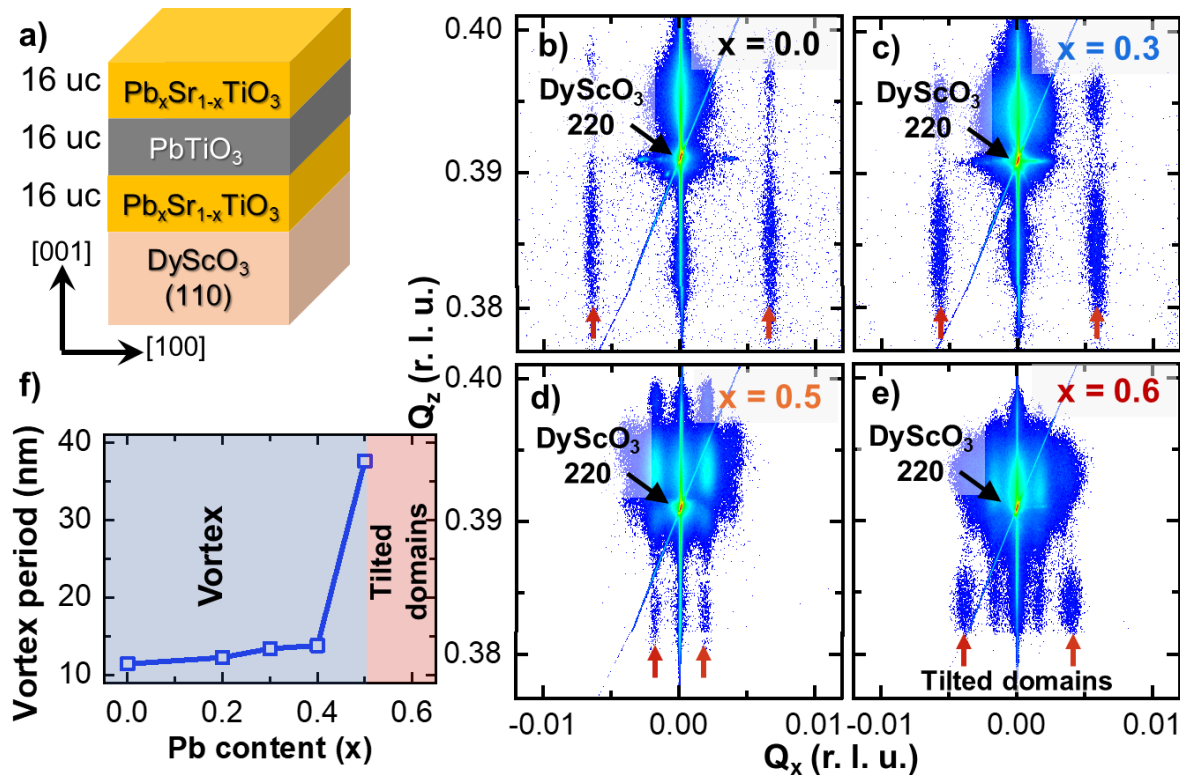


Fig. 5.1 a) Schematic illustration of the trilayers. 2D reciprocal space mapping (RSM) about the 220_{O} -diffraction condition of DyScO_3 (110) and along 332_{O} -direction with a pair of red arrows representing vortex periodicity for trilayers b) $x = 0$, c) $x = 0.3$, d) $x = 0.5$ and e) and tilted domains for $x = 0.6$. f) Vortex periodicity measured as a function of the lead content (x) for the trilayer system.

peaks corresponding to vortices but with periodicities of 13.4 nm and 37.5 nm, respectively. Upon further increasing the lead content, as in $x = 0.6$ trilayers (Fig. 5.1e), however, the structure transforms into periodic c/a domains. The evolution of vortex periodicity with chemistry is summarized (Fig. 5.1f). All told, such studies point towards the formation of vortices in all-ferroelectric heterostructures.

5.2.2 Transmission Electron Microscopy

To confirm that the observed satellite peaks arise from vortex formation, the polarization was analyzed at the atomic scale using STEM-based multislice electron ptychography [198,199] for a representative $x = 0.3$ trilayer (Fig. 5.2a). Such studies were completed by Harikrishnan K.P., Dr. Yu-Tsun Shao, and Prof. David A. Muller at Cornell University. The resulting atomic displacement map (Fig. 5.2b) is created based on the distances between the centroid of the oxygen anions to the centroid of the A-site (lead, strontium) cations for each pseudo-cubic unit cell and it reveals the presence of vortex-like texture in the PbTiO_3 and in-plane polarization in the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$. The enlarged 2×2 pseudocubic unit cell in the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layer (Fig. 5.2c) shows displacement of oxygen atoms in relation to the cations (highlighted by the small white arrows), showing the presence of in-plane polarization. In the PbTiO_3 layer (Fig. 5.2d-g), a large magnitude of the displacement (~ 40 pm) is observed which changes in direction as one transits about the vortex core. In turn, a net in-plane polarization in the PbTiO_3 layer (here, pointing from right to left) is aligned with the polarization in the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layer (Fig. 5.2c). Other displacement maps (Fig.

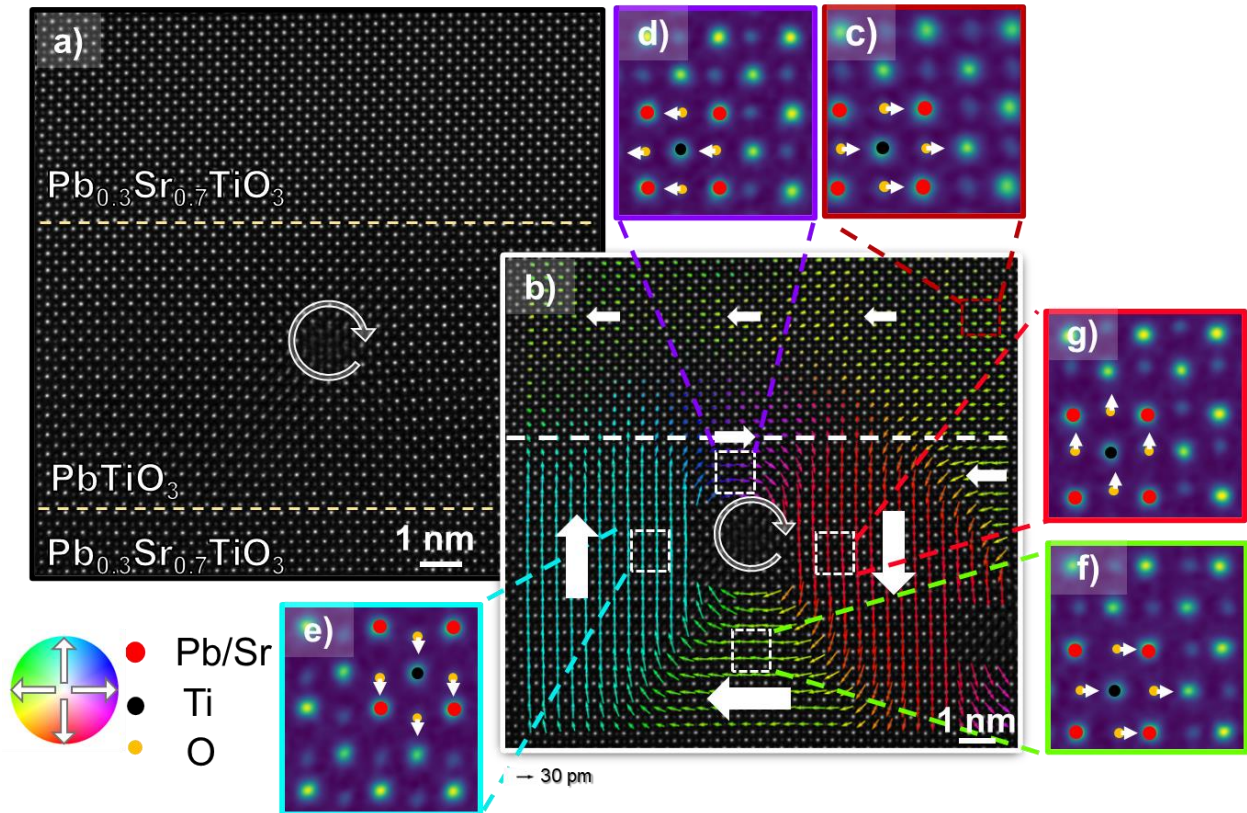


Fig. 5.2 a) Ptychographic reconstruction of the $x = 0.3$ trilayers with the white rotating arrow showing the lattice distortion corresponding to the vortex core. b) Ptychographic reconstructed image shows the displacement of the centroid of the A-site cations with respect to the centroid of the oxygen atoms mapped out for each pseudo-cubic unit cell. Zoom-in regions showing pseudo-cubic unit cells with different atoms having specific colour codes for the c) $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ region, d) vortex top side, e) vortex left side, f) vortex bottom side, and g) vortex right side.

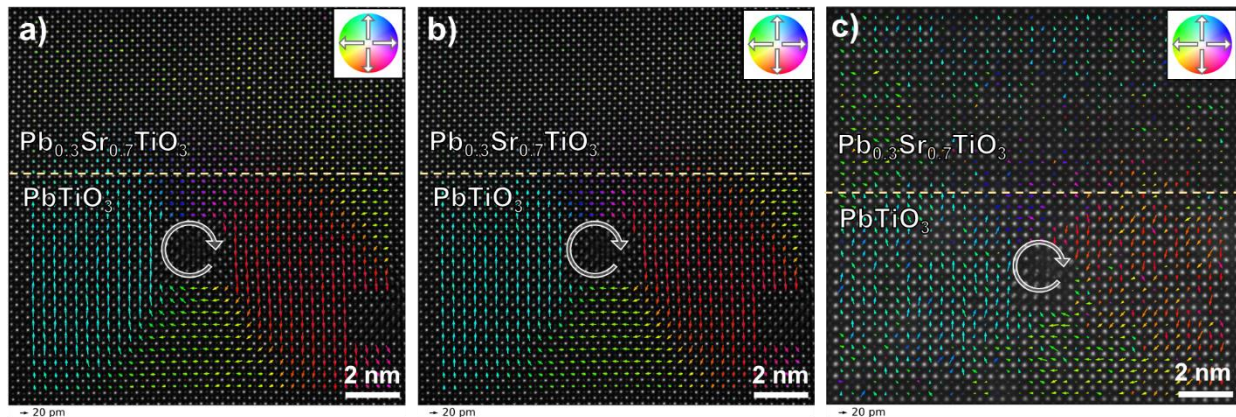


Fig. 5.3 a) Ptychographic image showing the displacement of the centroid of the B-site cations with respect to the centroid of the oxygen atoms mapped out for each pseudo-cubic unit cell. b) Ptychographic image showing the displacement of the centroid of the A-site cations with respect to the centroid of the B-site cations for each pseudo-cubic unit cell. c) HAADF reconstructed image showing the displacement of the centroid of the A-site cations with respect to the centroid of the B-site cations mapped out for each pseudo-cubic unit cell.

5.3a and b) and maps obtained with annular dark field (ADF) imaging are also provided (Fig. 5.3c). All told, the STEM-based image confirms the formation of a novel emergent polarization texture in all-ferroelectric heterostructures.

5.2.3 Molecular-dynamics Simulations Analysis

To better understand how the vortices form and their evolution with chemistry and periodicity, MD simulations were carried out for $x = 0-0.7$ superlattices (Fig. 5.4) in collaboration with Jiayan Yang and Prof. Shi Liu at Westlake University. For example, in $x = 0.3$ superlattices (Fig. 5.4d),

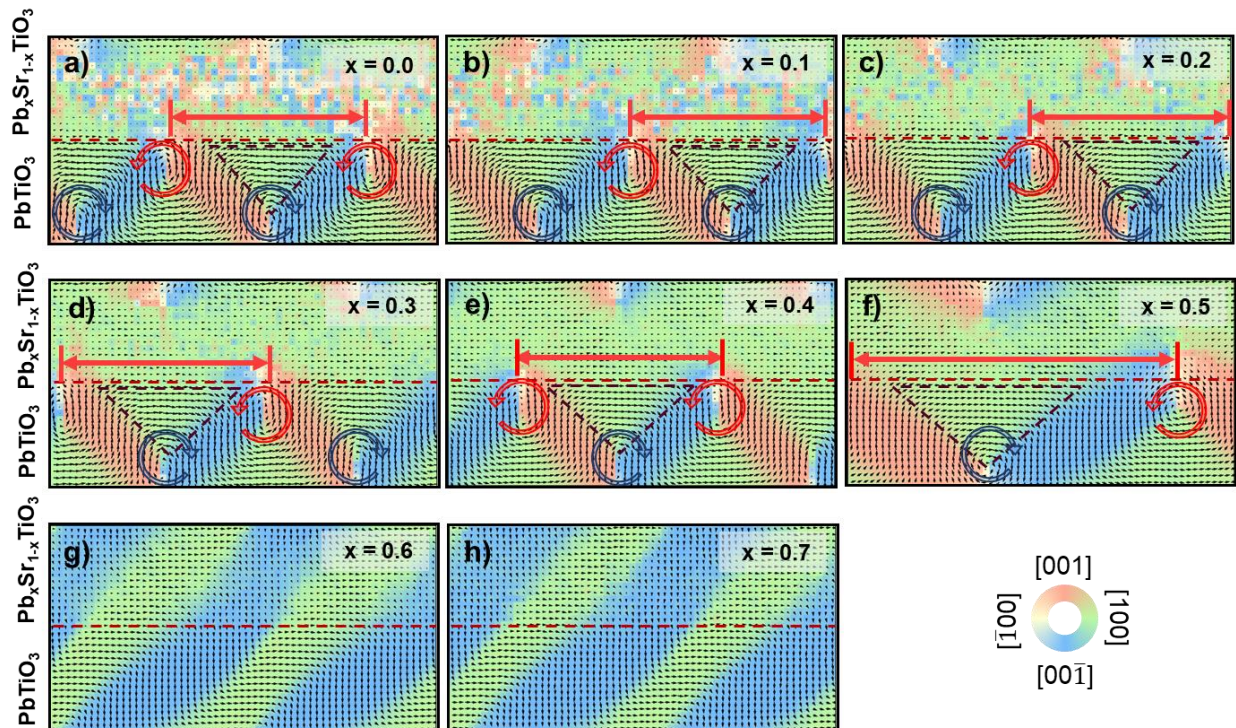


Fig. 5.4 Molecular dynamics (MD) simulations displaying structural evolution as a function of lead content (x) with a) $x = 0.0$, b) $x = 0.1$, c) $x = 0.2$, d) $x = 0.3$, e) $x = 0.4$, f) $x = 0.5$, g) $x = 0.6$, and h) $x = 0.7$.

the equilibrium state includes vortices in the PbTiO_3 and in-plane polarized ferroelectric domains in the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$; consistent with the X-ray and STEM findings. Similar vortices are observed for $x = 0-0.5$ superlattices (Fig. 5.4a-f) before the structure transitions into periodic c/a domains throughout both layers for $x = 0.6-0.7$ superlattices (Fig. 5.4g and h). The staggered vortex configuration (Fig. 5.5a) along with alternating clockwise (rotating blue arrows) and counterclockwise (rotating red arrows) leads to a net in-plane polarization [194] along the $[100]_{\text{pc}}$. As the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ adopts a more pronounced in-plane orientation with increasing lead content (x), the in-plane substructure of the PbTiO_3 layer (dashed brown triangles, Fig. 5.5a and b) enlarges to maintain polarization continuity across the interface. The strain boundary condition being applied to the PbTiO_3 by the DyScO_3 substrates favors c/a domain formation (*i.e.*, a mixture of in- and out-of-plane polarized regions) which ultimately manifests as vortices in these confined heterostructures. The presence of the out-of-plane polarized regions further compel regions within $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ near the interface to undergo local polarization rotation (black, dotted half circle, Fig. 5.5a), leading to additional gradient energy. Therefore, this rearrangement of polarization is induced via short-range interactions at the interfaces and favors larger period vortex structures with increasing lead content (x) before transitioning the structure into periodic c/a domains (Fig. 5.4g and h).

5.3 Out-of-plane Response of All-ferroelectric Superlattices

5.3.1 Out-of-plane Ferroelectric Switching Loops

Having established that novel, emergent vortex order can be produced in all-ferroelectric heterostructures, the question of whether these heterostructures are correspondingly more responsive to applied fields remains. To explore this question, out-of-plane capacitor structures were produced to probe the out-of-plane polarization-electric field evolution (Fig. 5.6a). Classic $x = 0$, $p = 5$ superlattices exhibit linear-dielectric-like response and serve as the reference state (black data, Fig. 5.6a), while $x = 0.3$ and 0.5 , $p = 5$ superlattices exhibit increased saturation polarization (P_s) and response that is antiferroelectric-like in nature (as substantiated by switching-current loops which show four peaks in one complete loop, two on each side; Fig. 5.6b). This antiferroelectric-like response is assigned to the out-of-plane switching of the originally in-plane polarized $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ layers along with the switching of the vortices. Further increasing the lead content, as in $x = 0.6$, $p = 5$ superlattices, reveals ferroelectric-like switching (again substantiated

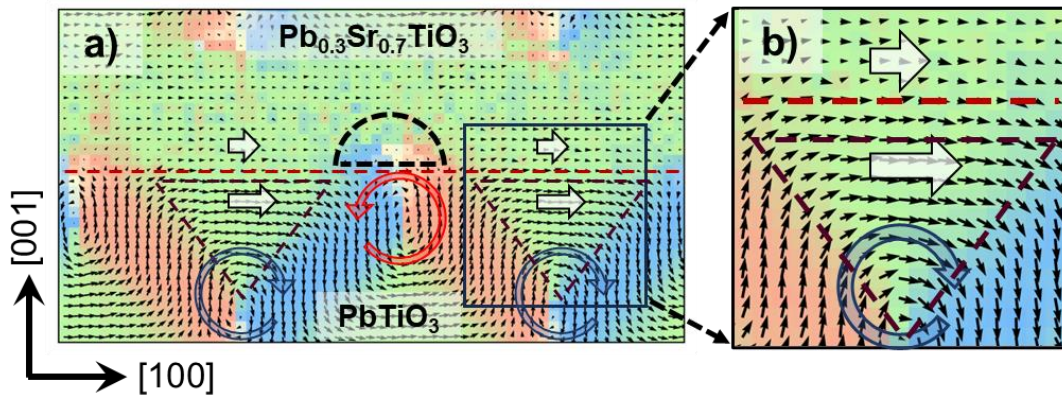


Fig. 5.5 Molecular-dynamics (MD) simulations revealing a) vortex formation in the PbTiO_3 layer and in-plane domains in the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layer for $x = 0.3$ trilayers along with b) a zoom-in of the region at the interface region showing alignment of in-plane components in the same direction.

by switching-current loops which show two peaks in one complete loop, one on each side; Fig. 5.6b) which matches well with the anticipated c/a -domain structure.

5.3.2 Phase-field Simulations of Out-of-plane Switching

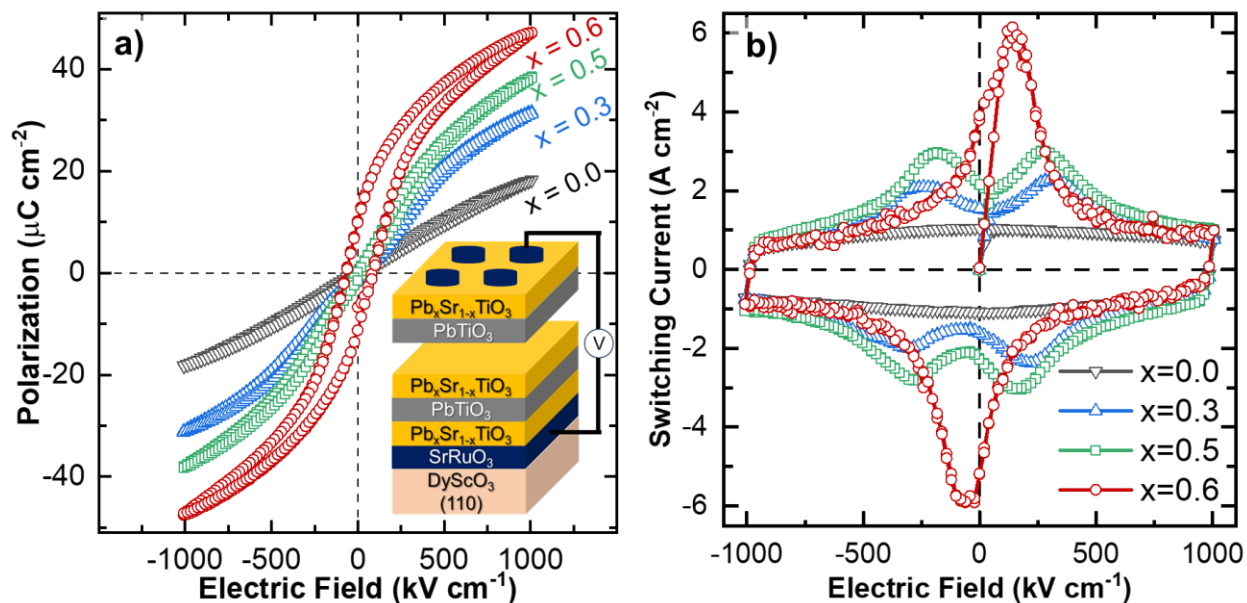


Fig. 5.6 a) Out-of-plane polarization-electric field hysteresis loops measured at 10 kHz for $x = 0, 0.3, 0.5$, and 0.6 , $p = 5$ superlattices. b) Out-of-plane switching current-electric field hysteresis loops measured at 10 kHz for the superlattices with $x = 0.0, 0.3, 0.5$, and 0.6 , $p = 5$ superlattices.

The polarization-electric field evolution can be further analyzed using phase-field simulations which were carried out in collaboration with Aiden M. Ross, Dr. Jacob A. Zorn, and Prof. Long-

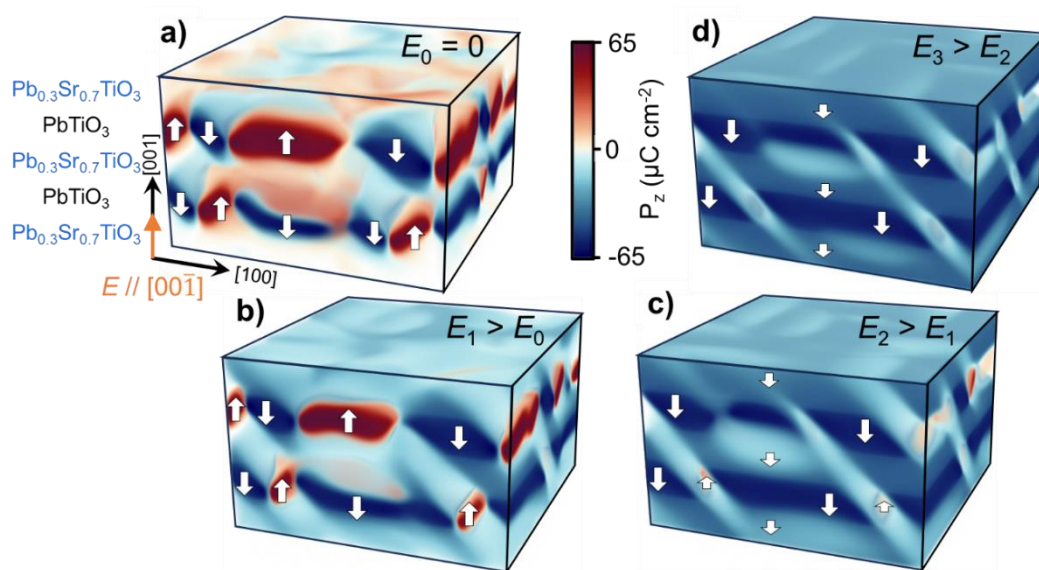


Fig. 5.7 Various switching steps are as extracted from phase-field simulations at different electric field starting with the a) initial state at E_0 , b) intermediate stage at $E_1 > E_0$, c) next intermediate stage at $E_2 > E_1$, and d) final state at E_3 .

Qing Chen at the Pennsylvania State University. Here, the simulations explore a $x = 0.3$ superlattice wherein the applied field increases 50 kV cm^{-1} every 100-time steps until it reaches 1000 kV cm^{-1} , then decreases at the same rate to -1000 kV cm^{-1} , before stopping at 0 kV cm^{-1} to form a complete switching cycle. Starting with electric field $E_0 = 0 \text{ kV cm}^{-1}$ (Fig. 5.7a), vortices are observed in the PbTiO_3 layers by analyzing the P_z component. With $E_1 = 300 \text{ kV cm}^{-1}$ applied along the $[00\bar{1}]$ (after 600-time steps), the fraction of the downward polarized area in the PbTiO_3 layers increases at the same time as there is initiation of downward polarization in the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layers (Fig. 5.7b). Upon further increasing the field to $E_2 = 650 \text{ kV cm}^{-1}$ (after 1200-time steps), the PbTiO_3 layers are nearly fully downward polarized, producing mostly c/a domain structures (Fig. 5.7c). At this same field, the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layers also undergo polarization rotation from the in-plane to the out-of-plane direction to produce a largely c -domain structure with minority areas of a domains which extend from the newly formed a domains in the PbTiO_3 layers. Finally, at $E_3 = 1000 \text{ kV cm}^{-1}$ (after 2000-time steps), the structure has nearly completely transformed into a c -domain structure with small minority a domains (Fig. 5.7d). Upon gradually removing the applied field, a reversible back-switching process takes place wherein the system follows the reverse transition path of that just described; thus explaining the antiferroelectric-like switching behavior.

5.3.3 Electromechanical Response

This polarization rotation from the in-plane to the out-of-plane direction under electric field is unlike what is typically seen in elastically constrained films and more analogous to that observed in bulk versions of near-morphotropic phase boundary [200] or relaxor ferroelectrics [201]. In turn, this warrants investigation of the electromechanical response of this highly responsive system which was accomplished using laser Doppler vibrometry [202]. Beginning with $x = 0$, $p = 5$ superlattices, as a reference, small electromechanical responses (0.1% strain at 1000 kV cm^{-1}) are found, but as x is increased, so does the electromechanical response ($>1\%$ strain at 1000 kV cm^{-1} is possible; Fig. 5.8).

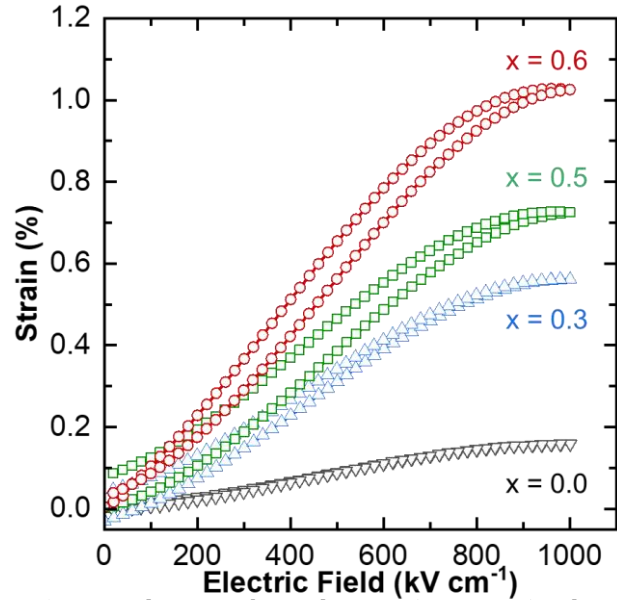


Fig. 5.8 Electromechanical strain (in percent) -electric field loops measured at 10 kHz for $x = 0, 0.3, 0.5$, and 0.6 , $p = 5$ superlattices.

5.3.4 Molecular-dynamics Simulations of Out-of-plane Switching

To understand this evolution, MD simulations were used to explore the polarization of the system at the unit-cell level. Using $x = 0.3$ superlattices (Fig. 5.9) as a model system wherein the ground-state exhibits vortices in PbTiO_3 and in-plane domains in the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layers (Fig. 5.9a), the starting state is such that the majority of the area across the interface has matching in-plane polarization (Fig. 5.9b). Upon increasing the field to $E_1 = 1000 \text{ kV cm}^{-1}$ applied along the $[001]$, regions within the vortices having polarization lying along the $[001]$ expand and the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layer undergoes polarization rotation; essentially converting to c domains (Fig. 5.9c). The out-of-plane polarized $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ facilitates polarization alignment in the PbTiO_3 by mitigating the

depolarization effect at the interface (Fig. 5.9d). This explains the augmented response of the $x =$

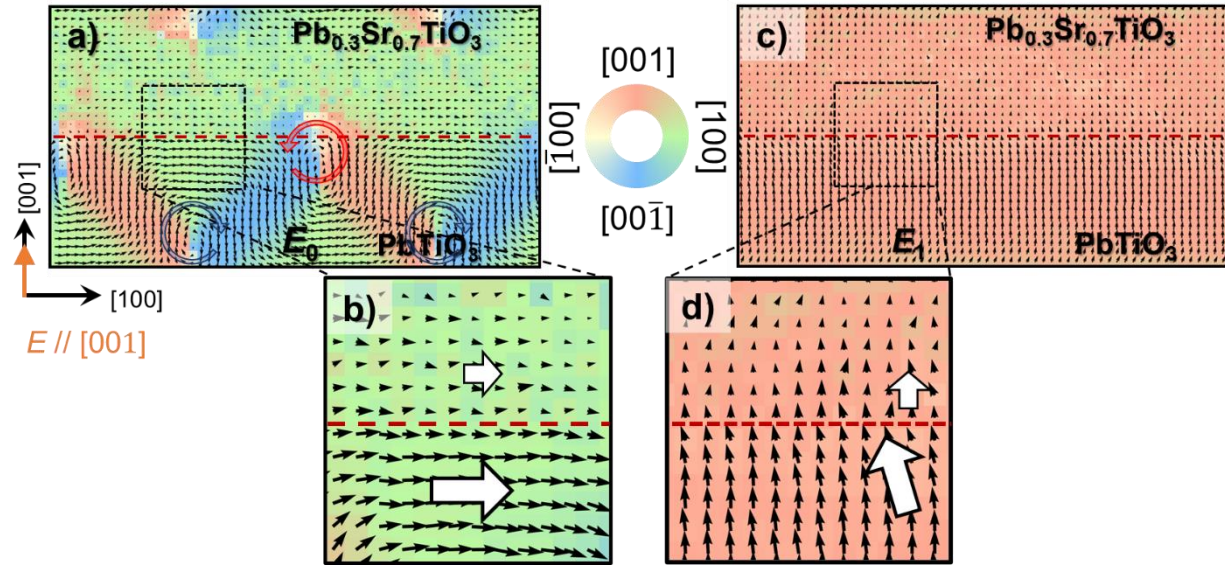


Fig. 5.9 Corresponding MD simulations displaying out-of-plane switching of the $x = 0.3$ superlattices starting with the a) initial state at E_0 with a b) zoom-in area around the interface and the c) final state at E_1 with a d) zoom-in area around the interface at fully switched state.

0.3 and 0.5 superlattices as compared to that of the $x = 0$ superlattices (Fig. 5.10), where the SrTiO_3 layer is largely unresponsive (*i.e.*, can only be marginally polarized) and thus suppresses the

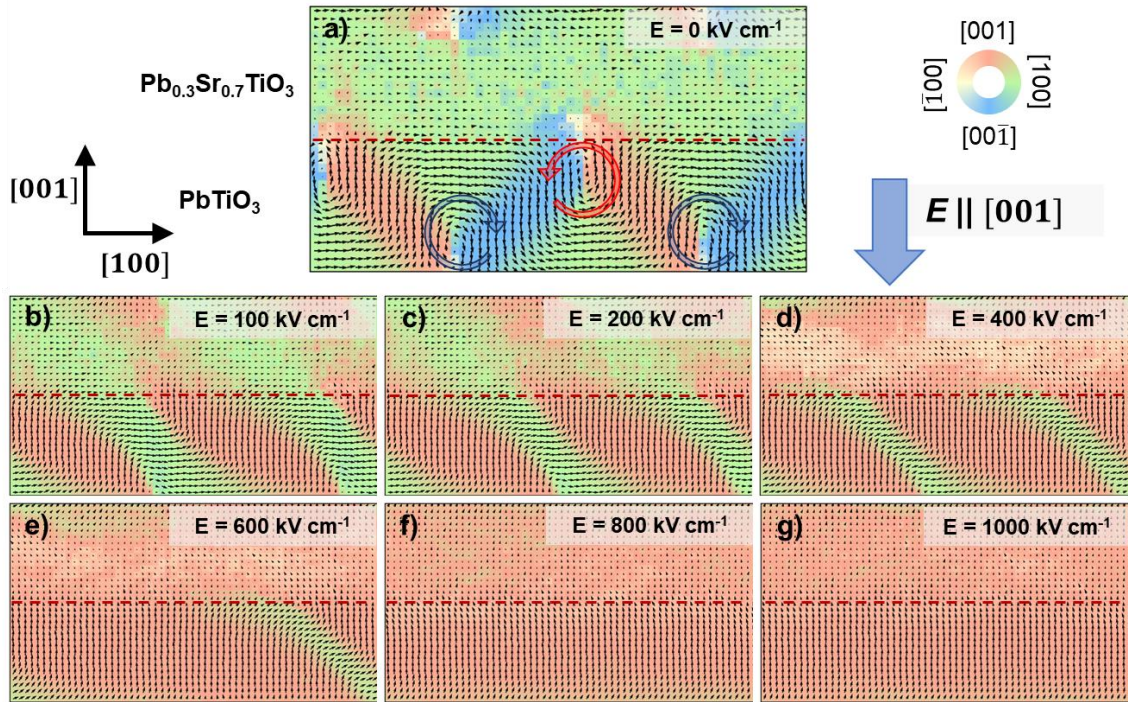


Fig. 5.10 Molecular dynamic (MD) simulations displaying domain structure evolution on application of out-of-plane E on $x = 0.0$ superlattices at values of a) 0 kV cm^{-1} , b) 100 kV cm^{-1} , c) 200 kV cm^{-1} , d) 400 kV cm^{-1} , e) 600 kV cm^{-1} , f) 800 kV cm^{-1} , and g) 1000 kV cm^{-1} .

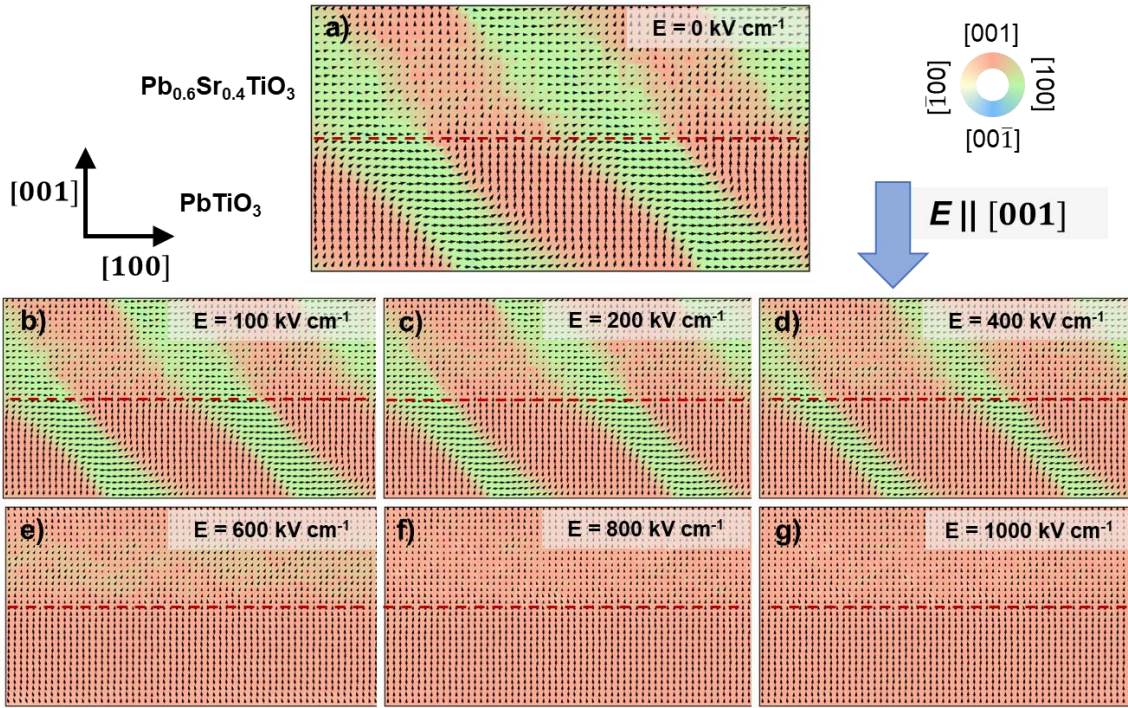


Fig. 5.11 Molecular dynamic (MD) simulations displaying domain structure evolution on application of out-of-plane E on $x = 0.6$ superlattices at values of a) 0 kV cm^{-1} , b) 100 kV cm^{-1} , c) 200 kV cm^{-1} , d) 400 kV cm^{-1} , e) 600 kV cm^{-1} , f) 800 kV cm^{-1} , and g) 1000 kV cm^{-1} .

overall electromechanical response. For $x = 0.6$ superlattices (Fig. 5.11), the MD simulations suggest that the system has a fully c/a -domain structure in the ground state, but unlike single-layer films in the same domain structures, these superlattices undergo extensive polarization rotation and overcome the elastic energy costs by lower the depolarization fields on the PbTiO_3 layer in the fully poled state. In summary, these switching studies, supported by simulations, explain the intricate mechanism behind the out-of-plane vortex switching and resultant enhanced piezoelectric response in all-ferroelectric heterostructures.

5.4 In-plane Response of All-ferroelectric Heterostructures

5.4.1 In-plane Polarization-electric Field Hysteresis Loops for Trilayers

Having established that there is considerably increased susceptibility in the out-of-plane direction, the presence of in-plane polarized domains in the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ layers also begs the question as to the extent of in-plane responsivity. To investigate the in-plane switching behavior, interdigitated electrodes (IDE) were fabricated such that electric fields can be applied along the $[100]_{\text{pc}}$ (Fig. 5.12). For $x = 0$ trilayers (Fig. 5.13a), the observed polarization-electric field hysteresis loops are similar to that of other in-plane-polarized ferroelectrics [197]. Similar hysteresis loops were also observed for $x = 0.3$ trilayers (Fig. 5.13b), but with an increased value of switched polarization and coercivity.

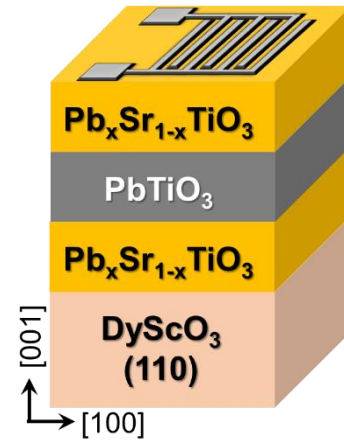


Fig. 5.12 Schematic of interdigitated electrodes (IDE) on the trilayer structures.

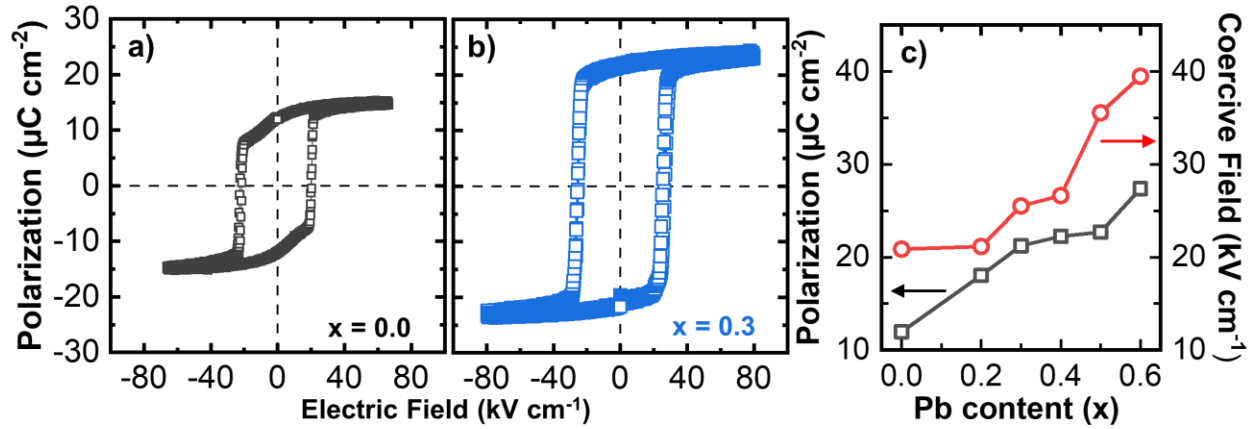


Fig. 5.13 In-plane polarization-electric field hysteresis loops measured at 1 kHz for the a) $x = 0$ and b) $x = 0.3$ trilayers. c) Remanent polarization and coercivity field of the trilayers as a function of lead content (x) in the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ layer.

In this case, both the vortices in the PbTiO_3 layer and the in-plane oriented domains in the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layers contribute to the switched polarization (thus giving a larger overall value). In the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ system [197], the coercivity also increases with x and this, coupled with the polarization and lattice coupling across the interface between the in-plane component of the vortices, contributes to the observed increased coercivity of the trilayers. Overall, the chemistry x provides a deterministic tuning parameter for the switched polarization and coercive field (Fig. 5.13c) for the trilayers.

5.4.2 Phase-field Simulations for In-plane Switching of Trilayers

To understand how the complex polarization architecture (*i.e.*, a mixture of vortices and in-plane polarized domains) in the all-ferroelectric trilayers switch, phase-field simulations were conducted for $x = 0.3$ trilayers starting from the initial reference state (Fig. 5.14a), under applied fields through an intermediate state (Fig. 5.14b), and finally reaching the switched state (Fig. 5.14c). 3D illustrations depicting the P_x component (Fig. 5.14a-c, i) of the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ and the P_z components (Fig. 5.14a-c, ii) of the PbTiO_3 are provided. In the zero-field, initial state, the net in-plane component of the vortices and the polarization of the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layers are all aligned along the $[100]_{\text{pc}}$ (Fig. 5.14a). The $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layers consists of a_{1+} and a_{2+} domains (Fig. 5.14a, i). The P_x and P_y components for the PbTiO_3 layer align in an attempt to match with the stripe domains in the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layers (Fig. 5.14a, i), resulting in a herring-bone-like arrangement of the vortices (Fig. 5.14a, ii). Applying an electric field along the $[\bar{1}00]$ causes the vortex cores to start moving vertically towards the middle of the PbTiO_3 layer and the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layers see the initial formation of $[\bar{1}00]$ -oriented regions at the outer periphery of the vortices which had polarization along the $[\bar{1}00]$ in the initial state (Fig. 5.14b). The $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layers undergo multiple local switching events [197] to produce this intermediate state (Fig. 5.14b, i). Again, the vortices adjust to align with the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ -stripe directions, leading to a transient wavy configuration (Fig. 5.14, ii). Upon further increasing the applied field, both layers complete the switching process by aligning the in-plane component along the $[\bar{1}00]$ (Fig. 5.14c) with the $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layers regaining a local a_{1-} and a_{2+} variant configuration (Fig. 5.14c, i) and the PbTiO_3 layer having vortices with an in-plane component that matches that of each $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ domain stripe (Fig. 5.14c, ii). The investigation of the trilayer-switching

processes sheds light on the highly interconnected, synchronized switching processes occurring between the vortex and $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ layers.

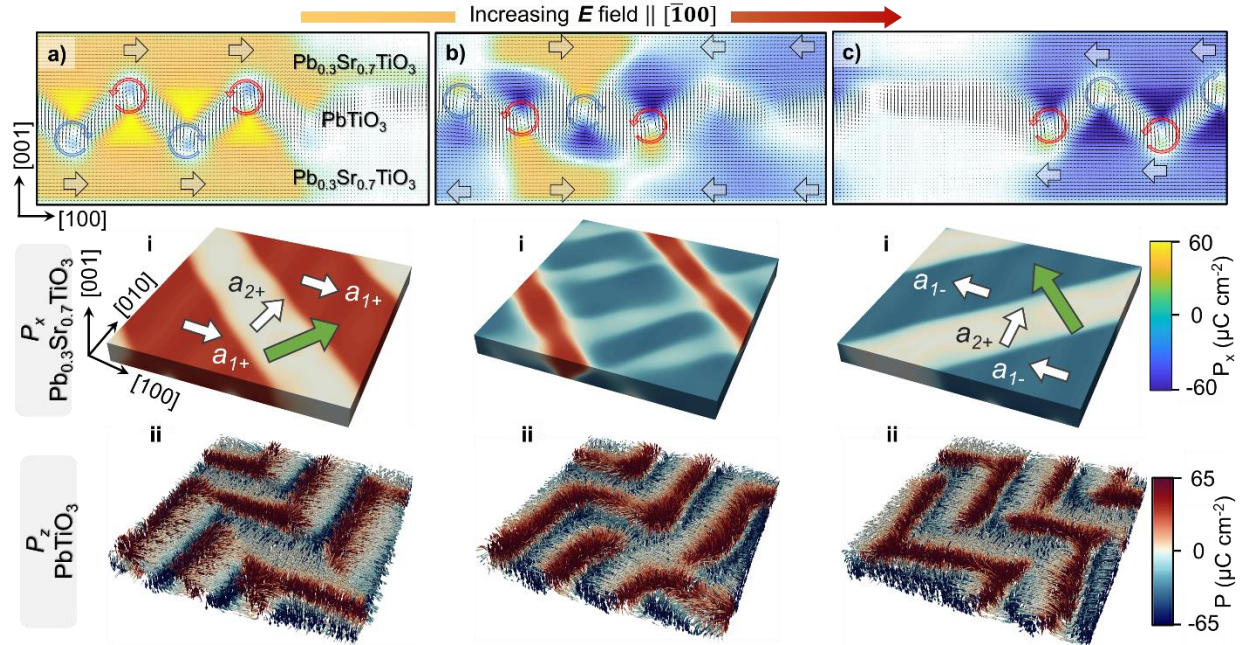


Fig. 5.14 Cross-section views of various switching steps for the $x = 0.3$ trilayers extracted from phase-field simulations including the a) initial state, b) intermediate state, and c) final state after completing switching process. Corresponding 3D views of the mesoscale equilibrium domain structures of the trilayer system showing the a-c, i, P_x component of the top $\text{Pb}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ layer and the a-c, ii, P_z component of the PbTiO_3 layer at each switching step.

5.5 In-plane Multistate Switching of Engineered Multilayers

These robust, but unique in-plane polarization switching mechanisms for the vortices and the in-plane-polarized domains open the door for creative design of functionality by stacking different fundamental units together. These fundamental units (such as $x = 0$ and $x = 0.3$ trilayers) have distinct coercive fields and switched polarization values. To demonstrate this potential, $x = 0.3/0$ multilayers were produced with various thicknesses of the shared SrTiO_3 dielectric layer (Fig. 5.15a). For brevity, focus is given to one variant of this $x = 0.3/0$ multilayer with a SrTiO_3 thickness of 50-unit cells. For this multilayer, two distinct peaks were observed in RSMs (Fig. 5.15b), consistent with a periodicity arising from vortex periodicities of 11.6 nm and 13.1 nm from the $x = 0$ and $x = 0.3$ trilayers in the stack, respectively, and pointing to their effective structural decoupling with this SrTiO_3 thickness. These two distinct periodicities were captured qualitatively with phase-field simulation with a “thick” shared SrTiO_3 layer (Fig. 5.15c). In the thick SrTiO_3 layer (black dotted box, Fig. 5.15c), a significant portion remains unpolarized, emphasizing the decoupling mechanism.

To probe how these stacked-trilayer structures respond under applied field, in-plane polarization hysteresis loops were measured. Here, the main hysteresis loop (black data, Fig. 5.16a) shows two distinct switching events on each side. The first switching takes place at $\pm 21 \text{ kV cm}^{-1}$ and is referred as the “minor loop” (red data, 5.16a) with a switched polarization $\Delta P = 12 \mu\text{C cm}^{-2}$, matching closely with switching characteristics of the $x = 0$ trilayer. A metastable switching event originating from the vertical redistribution of the buckled vortices [194] is also marked. Once

the applied field exceeds $\pm 28 \text{ kV cm}^{-1}$ the remaining material is switched (resulting in complete switching) with a switched polarization $\Delta P = 22 \text{ } \mu\text{C cm}^{-2}$, matching closely with switching characteristics of the $x = 0.3$ trilayer. PUND measurements (inset, 5.16a) reveal a two-step switching process (shown here for positive bias), indicative of the multistate switching characteristics. This multi-step switching process is further illuminated using phase-field

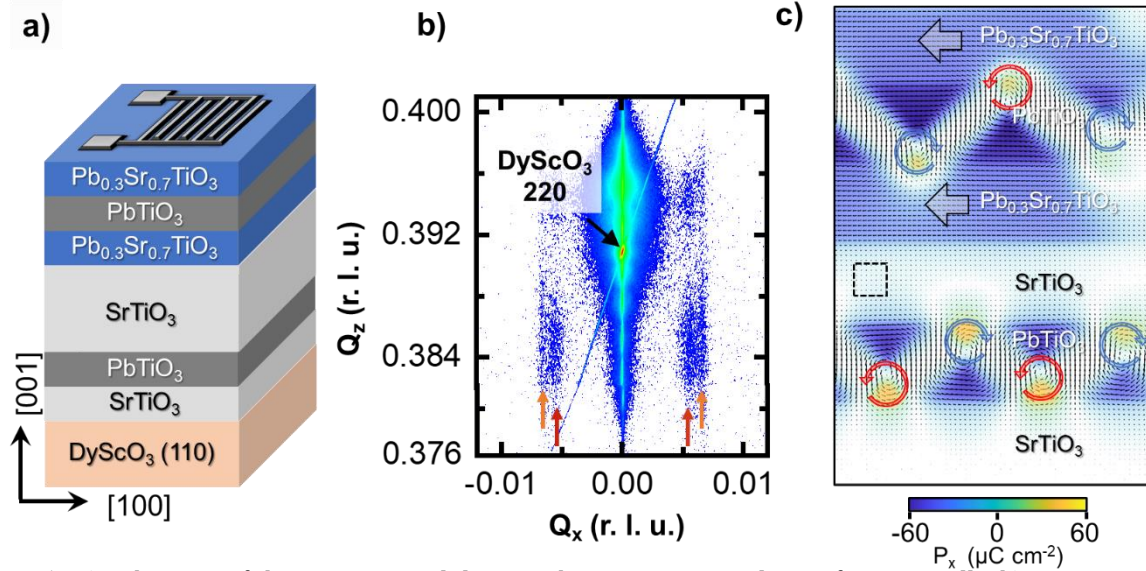


Fig. 5.15 a) Schematic of the $x = 0.3/0$ multilayer with a SrTiO_3 spacer layer of 50-unit cells. b) 2D reciprocal space mapping (RSM) about the 220_{O} -diffraction condition of DyScO_3 (110) and along 332_{O} -direction with a pair of red and orange arrows representing vortex periodicity for the of $x = 0.3/0$ multilayer with SrTiO_3 spacing layer of 50 unit cells. c) Cross-sectional view of the phase-field simulations for the same multilayer structure at its ground state.

simulations. Upon applying E along the $[100]$, the simulations reveal that the first switching event involves only the $x = 0$ trilayer (bottom trilayer, Fig. 5.16b), indicating the structural decoupling

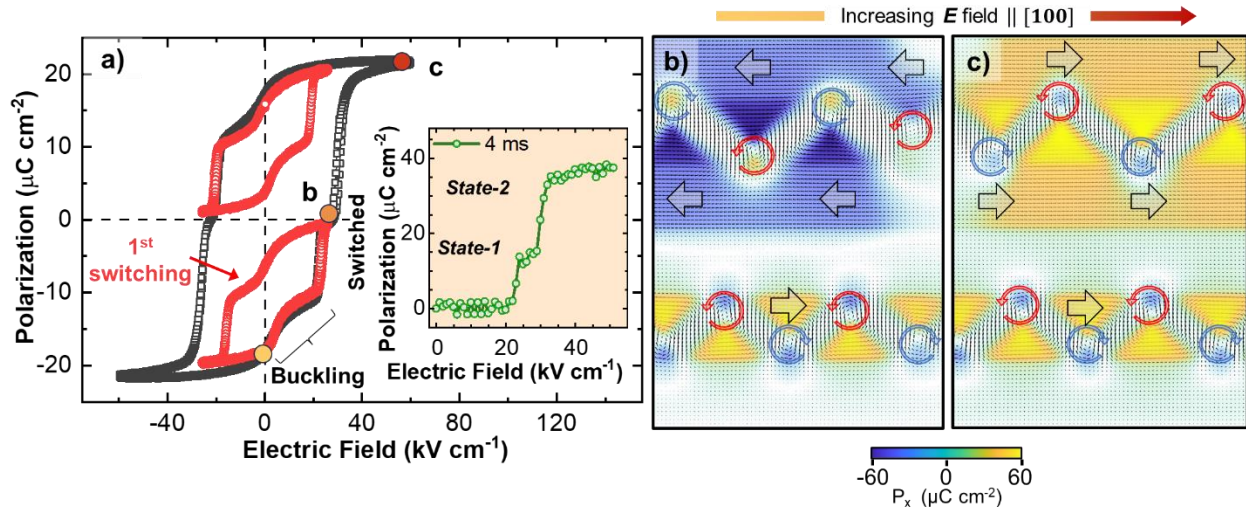


Fig. 5.16 a) In-plane polarization-electric field hysteresis loops measured at 1 kHz for the same multilayer structure wherein the inset shows the positive side of a PUND analysis revealing the multistate character. Cross-sectional phase-field simulations for b) an intermediate switching step and c) the fully switched state.

effects on the overall switching process. Further increasing E , the $x = 0.3$ trilayer switches, leading to the second switching event and the complete switching of the multilayer (Fig. 5.16c).

The stability of these multistate-switching characteristics was further characterized via retention and fatigue testing for all four states. All four states in these heterostructures were found to be stable and showed minimal change in polarization with time in retention testing over five hours (Fig. 5.17a). Further, it was

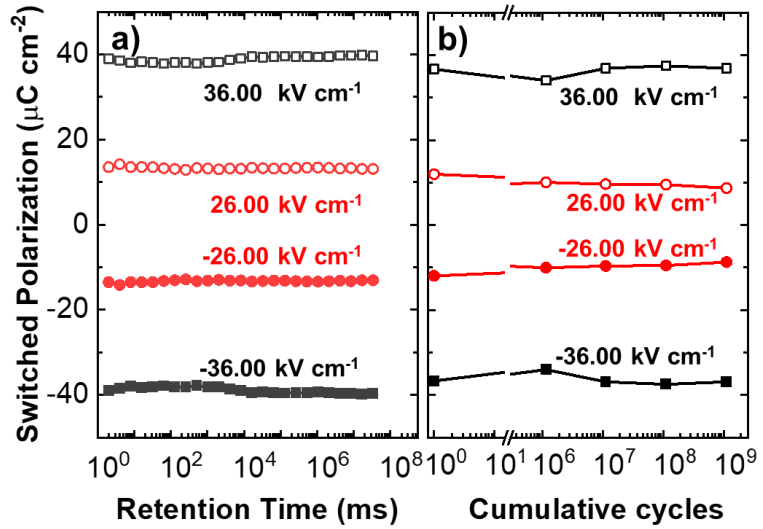


Fig. 5.17 a) The long-term retention of the multiple polarization states and the b) stability of the multiple polarization states after repeated switching cycles.

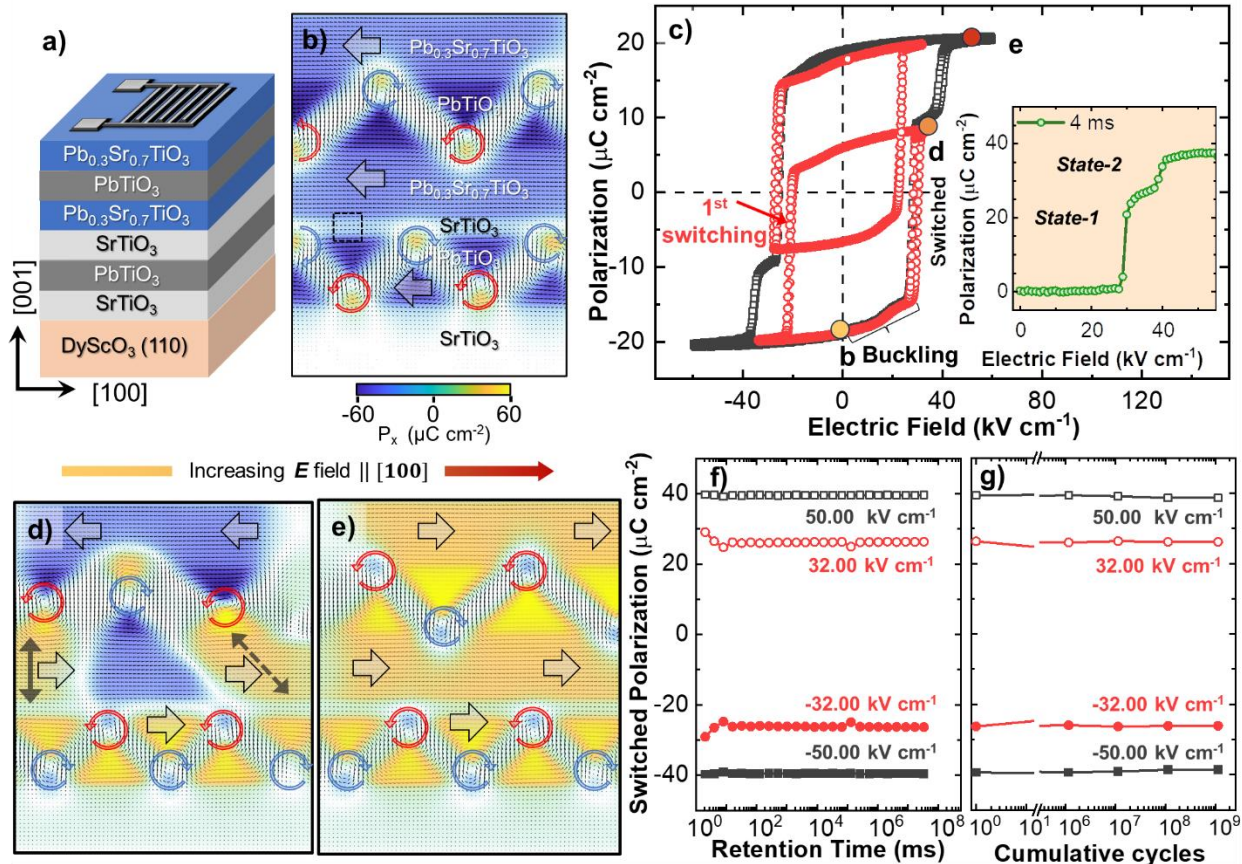


Fig. 5.18 a) Schematic of $x = 0.3/0$ multilayer with SrTiO_3 spacing layer of 16 unit cells. b) Phase-field simulations generated multilayer structure for the ground state. c) In-plane polarization-electric field (P. vs. E.) loops measured at 1 kHz frequency for multilayer structure and inset showing positive side of the PUND analysis showing multistate characteristics. d) Phase-field simulations generated intermediate switching step and e) fully switched state. f) The long-term retention and stability of the multiple polarization states. g) Stability of the multiple polarization states after long fatigue cycles.

found that each state could be repeatedly accessed and was easily distinguishable even after $>10^9$ write cycles (Fig. 5.17b). These results indicate several essential features required for robust multistate operation.

It is also noted that the multistate nature can be tuned by engineering the thickness of the shared SrTiO_3 layer. For example, data for other cases including a “thin” SrTiO_3 layer thickness (Fig. 5.18) are shown to produce similar multistate function while multilayers without a SrTiO_3 -separating layer exhibit a single switching event on each side due to strong interlayer coupling (Fig. 5.19). In essence, the shared SrTiO_3 serves as an adjustable parameter by which one can achieve tunable multistate memory in stacked heterostructures.

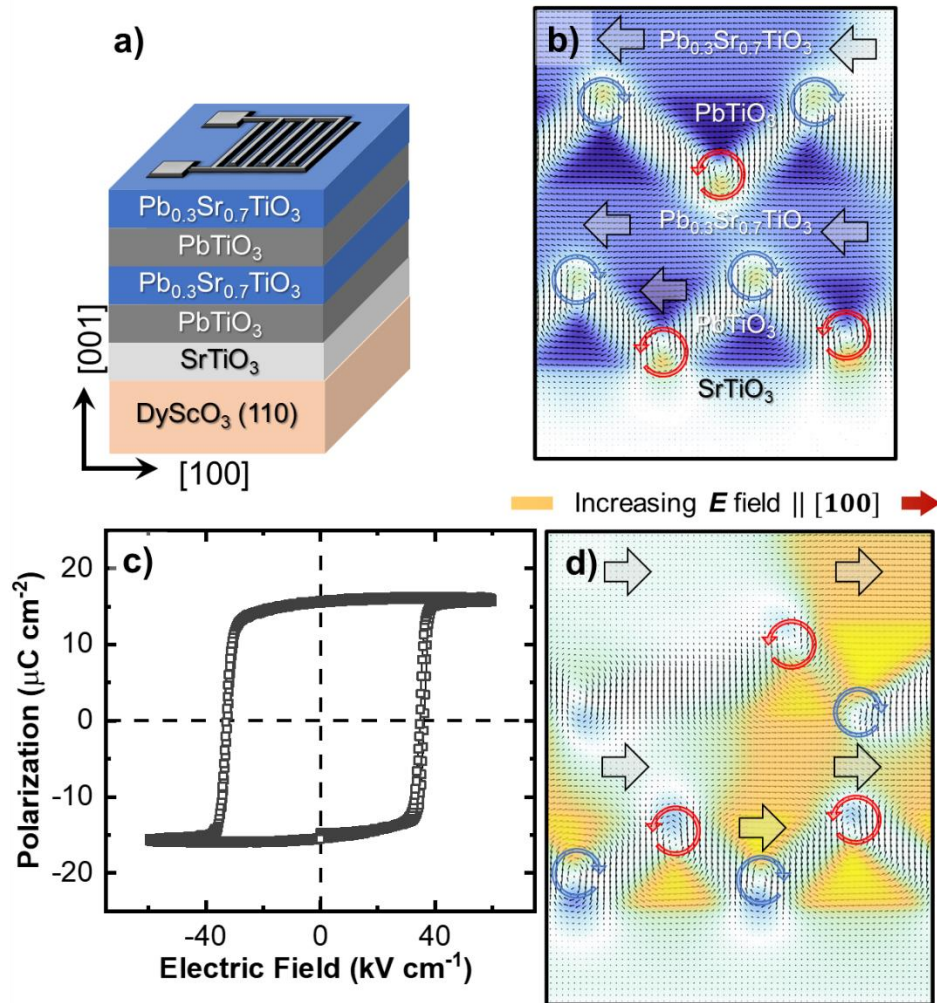


Fig. 5.19 a) Schematic of $x = 0.3/0$ multilayer without SrTiO_3 spacing layer. b) Phase-field simulations generated multilayer structure for the ground state. c) In-plane polarization-electric field hysteresis (P. vs. E.) loops measured at 1 kHz frequency for multilayers. d) Phase-field simulations generated fully switched state of the multilayers.

5.6 Conclusions

This study showcases the formation of vortices within all-ferroelectric heterostructures. Unlike their cousins in ferroelectric-dielectric heterostructures, these emergent vortices demonstrate superior response to applied stimuli, including large out-of-plane piezoelectric strains and

ferroelectric polarization due to the ability to freely and reversibly rotate polarization in all layers. In the in-plane direction, robust polar and lattice coupling across the layers leads to synchronized and complete in-plane switching which can then be tuned to allow for multistate switching by stacking different trilayer structures with controlled SrTiO_3 spacer layer thicknesses, elucidated the role of intra-layer coupling and its implications on structural periodicity and multistate switching behavior. All told, this work provides access to highly responsive emergent dipolar textures and access to new functionality.

CHAPTER 6

Enabling Ultralow-Voltage Function in BaTiO₃-based Ferroelectric Field-effect Transistors

Despite enhanced computing efficiency, the rapidly growing energy consumption of the computing sector prompts a need for critical reevaluation of computational methodologies. Ferroelectric field-effect transistors (FEFETs) combine ferroelectric materials with a semiconductor in a transistor structure. As a result, it can combine logic and memory functionalities at the single-device level, bringing some of the most pressing hardware-level demands for emerging computing paradigms. Ultimately the goal is to achieve highly energy-efficient computing via the use of FEFETs operating at voltages < 200 mV; something that remains a challenge and an opportunity. FEFETs offer promising features such as non-destructive read-out processes and integrated memory/logic functions, potentially alleviating memory-logic interconnect limitations. Several challenges hinder their realization, however, including the need for ferroelectric films that are switchable at low voltages (< 200 mV) and the optimization of metal-ferroelectric-semiconductor interfaces. Recent advancements in epitaxial BaTiO₃ thin films, exhibiting ferroelectric properties akin to single crystals with coercive voltages < 100 mV, offer a promising avenue. Therefore, leveraging BaTiO₃ as a model system, I explore complex-oxide electrode optimization for ferroelectric capacitors, laying the groundwork for low coercive field FEFET development. Metal-ferroelectric-metal heterostructures, chiefly built from SrRuO₃/BaTiO₃/SrRuO₃, are investigated to enable reduced coercive field and robust polarization, and to explore ultrathin SrRuO₃ for its channel-resistance modulation achieved via field effects. These endeavors pave the way for future applications, fostering the development of novel channel materials.

6.1 Introduction

Despite ever-improving computing efficiency, information technology represents the fastest-growing energy consuming sector. Researchers are now rethinking how computation is performed and developing next-generation, beyond-CMOS microelectronics. One exciting opportunity for basic research is to enable highly energy-efficient computing by creating the know-how about and testing the feasibility of FEFETs [203,204] that operate at < 200 mV. The non-destructive read-out process and combined memory/logic functions of FEFETs could enable “logic-in-memory” operation, overcoming the memory-logic interconnect bottleneck thus potentially bringing down energy costs and offering time-saving advantages [54]. The resurgence of FEFET research comes at an opportune moment [205,206]. Computing is undergoing a profound transformation driven by data-centric applications [207]. The traditional foundations of the semiconductor industry – such as dimensional scaling and the von Neumann architecture, which separates memory blocks and logic cores – are proving inadequate for supporting the emerging ecosystem [208]. To efficiently handle vast quantities of data with high throughput and energy efficiency, future compute hardware must address the bottleneck posed by memory-logic interconnects. This necessitates adopting new architectures, such as near-memory [208] or in-memory designs [209], that blur the distinctions between memory and logic. These innovations are essential to sustain performance improvements at a rate that exceeds historical scaling trends.

There are multiple challenges to enabling such devices. First, despite years of work on ferroelectric films, obtaining films that can be switched (reliably) at < 200 mV remains a challenge and an opportunity for study that requires exploring switching dynamics in the ultrathin limit. Size effects have been studied in ferroelectrics [62] and the prevailing feature is a suppression of the order parameter as the thickness is reduced; a concern for the realization of devices that would likely need to be < 10 nm in all dimensions. Addressing this requires attention to interfaces in the capacitor building block as they influence the stability of the polar state (*e.g.*, arising from incomplete screening of polarization [210–212]), charge transport through the ferroelectric or leakage (*e.g.*, interfacial potential barriers between the ferroelectric and electrode impact how carriers move from a metal contact into an adjacent semiconductor [212]), and the role of point defects (*e.g.*, in pinning or effecting polarization reversal [213]) – factors that all become more important in films just 10-50 unit cells thick. Second, despite being investigated since the 1950s [214], FEFETs remain elusive since the carrier density in the semiconductor should not (ideally) be greater than the polarization charge induced by the ferroelectric. For example, a ferroelectric with $P_s = 10, 30,$ or $60 \mu\text{C}/\text{cm}^2$ has (ideally) a surface-charge density of $6.2 \times 10^{13}, 1.9 \times 10^{14},$ or $3.7 \times 10^{14} \text{ cm}^{-2}$, respectively. Also, the interface between the ferroelectric and semiconductor is not always perfect (producing trap states) [215]. Some have explored all-oxide FEFETs [216,217], but much of that work using perovskite ferroelectrics focuses on thick films such as 400-nm-thick $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ with large coercive voltages (V_c) of ~ 3 V [216] to create large “memory windows” (*i.e.*, a difference in the threshold voltages between on- and off-state).

Thus, by better understanding oxide metal-ferroelectric interfaces, there is an opportunity to enable the material function required to produce viable FEFETs and to lower their operation voltage while maintaining a viable memory window. Recently, high-quality, epitaxial BaTiO_3 thin films grown via pulsed-laser deposition have demonstrated ferroelectric properties that approach those of BaTiO_3 single crystals, where the thickness-scaling studies produced films 100 nm in thickness that already exhibited $V_c < 200$ mV [218]. The films also exhibited fast switching (as short as ~ 2 ns for 25-nm-thick films with 5- μm -diameter capacitors), and lateral scaling studies revealed a route to sub-nanosecond switching in devices as large as $10 \mu\text{m}^2$. Also, the

depolarization fields have shown impact on the polar state stability in thicker films but fortunately suppressed the coercive field, thus driving a deviation from Janovec–Kay–Dunn scaling and enabling a constant coercive field for films <150 nm in thickness.

Much of the prior work on BaTiO₃ has focused on SrRuO₃ electrodes because SrRuO₃ is readily grown, used as an electrode for many ferroelectrics, and has reasonably low resistivity and high n-type carrier density [219]. Other candidate oxide electrodes for such FEFET studies include YBa₂Cu₃O₇ [220,221], LaNiO₃ [222,223], La_{1-x}Sr_xCoO₃ [224], La_{1-x}Sr_xMnO₃ [225], La-doped BaSnO₃ [226,227], and BaPb_{1-x}Bi_xO₃ [228,229]. For example, LaNiO₃ has a resistivity and carrier concentration comparable to that of the standard SrRuO₃, but with p-type carriers rather than n-type [222,223]. La_{1-x}Sr_xMnO₃ and La_{1-x}Sr_xCoO₃ are p-type conductors which can be alloyed to different carrier concentrations and have large differences in resistivity [228,229]. While the candidate electrodes offer a wide range of properties, some have large lattice mismatches with BaTiO₃ and could result in (partial) relaxation of the BaTiO₃ during growth and potential deleterious effects on switching. This puts some practical limitations on the selection of the electrode materials. In a real electrode/ferroelectric/electrode device with imperfectly screening electrodes, the existence of a depolarization field is likely to be felt even with relatively thick films which would affect the stability of the polarization state [230], affecting remanent polarization and in turn non-volatile nature of the ferroelectric material. Electrodes with large carrier concentrations screen the polarization more optimally (reducing depolarization), but also require larger polarization to drive changes in transport. Considering all these factors, optimal combinations of the ferroelectric material, its thickness, and the right corresponding electrode material and its thickness are key.

Therefore, using BaTiO₃ as the model system, in this chapter, I explore and identify optimized complex-oxide electrodes to be used in the production of ferroelectric capacitors that will serve as the foundation for FEFETs. In this work, I studied 5, 6, and 7 unit cell SrRuO₃/100 nm BaTiO₃/10 nm SrRuO₃ metal-ferroelectric-metal heterostructures, where the ultrathin top SrRuO₃ functioned as both the top electrode and channel for the FEFETs. If the ferroelectric material is not a perfect insulator, which can be the case in ultra-thin ferroelectrics, the leakage current may overwhelm the polarization switching current in a *P-E* hysteresis loop [231]. The amplified effects of non-idealities such as leakage current arising from thermionic or quantum-mechanical tunneling and volatile dielectric response impede the observation of real polarization in ultra-thin materials [232]. Therefore, in this study, the thickness of the ferroelectric BaTiO₃ has been maintained at 100-nm as a model system. The constant coercive field observed for films <150 nm in thickness in BaTiO₃ thin films offers a promising approach to decrease the operational voltage of similar devices by simply reducing the thickness. Such heterostructures enabled reduced *V_c* and robust polarization in ferroelectric films along with ultrathin SrRuO₃ to establish field effects studies via channel-resistance modulation. For these channels the metallic character is (generally) preserved down to 4-5 unit cells, although there is often a gradual increase in resistivity down to critical thickness. The channel-resistance modulation as a function of gate voltage in these FEFET devices is then measured for various SrRuO₃ thicknesses to examine the impact of a thickness-induced metal-to-insulator transition. These devices were then further explored at low temperatures to analyze the potential for improved (or idealized) nonvolatile ferroelectric field effect due to the stability of switched polarization upon lowering the temperature. Along with that, enhanced channel-resistance modulation was also observed which was attributed to improved charge screening at low temperatures. Such temperature-dependent studies also provide insight into the best potential performance one might expect for the system. The charge screening provided

by the conductive channel is essential for minimizing the depolarization field, reducing domain formation, and maintaining ferroelectricity. Such studies help to establish the factors under which SrRuO_3 can function both as an electrode and a channel material. Also, the integration of such BaTiO_3 -based heterostructures on SrTiO_3 -buffered Si (001) substrates has shown comparable properties which demonstrate a first step towards integrating these materials with silicon. Lastly, new channel materials such as La-substituted BaSnO_3 [226,227] that have high mobility can enable stronger effects. Overall, this research lays the groundwork for enhancing the utility of such novel channel materials that can serve dual roles as both electrode and channel materials, and suggests strategies such as lowering the temperature to further improving the properties of FEFETs.

6.2 Structural Analysis of Heterostructure

The primary characteristic of a ferroelectric is the presence of a spontaneous polarization that can be reoriented by an external electric field. The existence of such spontaneous polarization results in the formation of positive and negative bound polarization charge at the corresponding polarized surfaces. In order to realize large values of channel-resistance modulation in FEFETs, the number of carriers in the channel should not be too large with respect to the amount of available charge induced by the ferroelectric [217]. In that regard, ultrathin SrRuO_3 offers a suitable platform to investigate whether significant channel-resistance modulation can be achieved. Here, SrRuO_3 not only functions as a channel material but also as a top electrode to change the polarization state of the ferroelectric. To explore the potential of such heterostructures containing ultrathin SrRuO_3 [of the form 5 or 6 unit cells SrRuO_3 /100 nm BaTiO_3 /10 nm SrRuO_3], I synthesized heterostructures via pulsed-laser deposition following an established procedure [230]. All three constituent layers were grown *in situ*, wherein the top and bottom SrRuO_3 are grown during the same growth as the BaTiO_3 to achieve pristine interfaces in the heterostructures. This method was found to be essential to produce the combination of properties such as low coercive field/voltage, robust polarization desired [230]. I then compare its structural characterization and electrical properties with that of a symmetric trilayer sample composed of prototypical “thick” SrRuO_3 electrode thickness (*i.e.*, 10

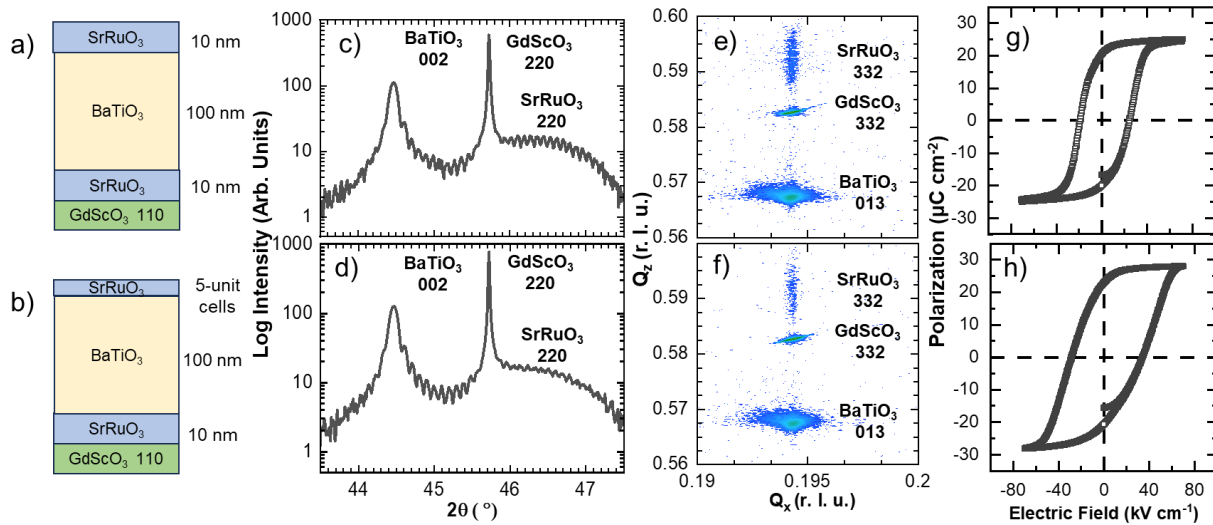


Fig. 6.1 Fig. 6. Schematic of trilayer heterostructure with a) 10 nm SrRuO_3 /100 nm BaTiO_3 /10 nm SrRuO_3 and b) 5-unit cells SrRuO_3 /100 nm BaTiO_3 /10 nm SrRuO_3 . Corresponding x-ray diffraction line scan for c) 10 nm top SrRuO_3 case and d) 5-unit cells top SrRuO_3 case. Asymmetric reciprocal space mapping for e) 10 nm top SrRuO_3 case and f) 5-unit cells top SrRuO_3 case. Polarization vs. electric field hysteresis loop for g) 10 nm top SrRuO_3 case and h) 5-unit cells top SrRuO_3 case.

nm SrRuO₃/100 nm BaTiO₃/10 nm SrRuO₃). Schematics of these two structures, one with a symmetric trilayer sample (Fig. 6.1a) and one with ultrathin top SrRuO₃ of 5-unit cells (Fig. 6.1b), are shown. Following the growth, detailed structural studies were completed via X-ray diffraction to probe the evolution of the crystal structure of both heterostructures. High-quality films were obtained for both heterostructures as supported by the presence of Laue fringes (Fig. 6.1c and d) associated with the 002-diffraction condition of the 100-nm-thick BaTiO₃ layer [233]. Both heterostructures have a similar structure, except for the top SrRuO₃ layer. Each has a 100-nm-thick layer of BaTiO₃ and a 10-nm-thick bottom layer of SrRuO₃, resulting in similar X-ray diffraction line scan. Further structural details about the heterostructure can be obtained by exploring various features in RSM studies. Here, to confirm the epitaxial nature of the heterostructures, asymmetric RSM studies about the GdScO₃ 332₀-diffraction condition were completed for both heterostructure types. Studies (Fig. 6.1e and f) reveal film peaks corresponding to the 103-diffraction condition of the BaTiO₃ and the 332-diffraction condition of the SrRuO₃ that have the same Q_x as the GdScO₃ 332₀-diffraction peak, indicating that the entire heterostructure grows coherently strained to the underlying GdScO₃ substrates. As anticipated, the intensity of the 332-

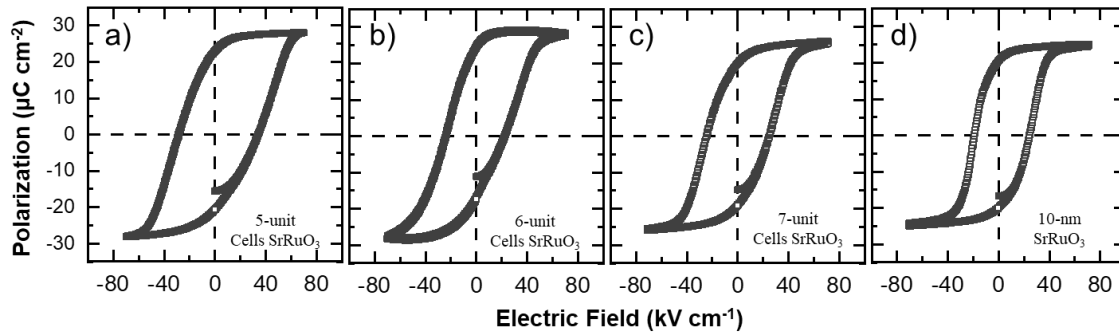


Fig. 6.2 Polarization vs. electric field hysteresis loop for a) 5-unit cells top SrRuO₃ case, b) 6-unit cells top SrRuO₃ case, c) 7-unit cells top SrRuO₃ case and d) 10 nm top SrRuO₃ case.

diffraction condition of the SrRuO₃ can be seen to be reduced for the ultrathin top SrRuO₃ case (Fig. 6.1f) as compared to the symmetric trilayers (Fig. 6.1e). Next, polarization-electric field hysteresis loops (reported at 1 kHz) were measured for the heterostructures. The heterostructures were fabricated into capacitor structures, as discussed in Chapter 2. Compared to the symmetric trilayer heterostructures (Fig. 6.1g) with a coercive field of ~20 kV/cm, the heterostructures with the ultrathin top SrRuO₃ showed (in general) a slightly higher coercive field of ~25 kV/cm (Fig. 6.1h) along with a more slanted loop. This could be related to the less metallic and higher resistance for the top ultrathin SrRuO₃ electrodes [234] which results in a need to apply a higher voltage to get a similar voltage drop across the ferroelectric and thus drive switching. Along with 5-unit cell case (Fig. 6.2a), similar hysteresis loops were also captured for heterostructures with 6- and 7-unit cell SrRuO₃ top electrodes (Fig. 6.2b and c) where analogous slightly enhanced coercive field was observed compared to the 10-nm top SrRuO₃ electrodes case (Fig. 6.2d). Other properties, such as saturation and remanent polarization, have shown comparable performance across all samples (Fig. 6.2a-d). Hysteresis loop measurement for 4-unit cells SrRuO₃ was not possible due to the excessively high resistive nature of the top ultrathin SrRuO₃ layer, matching well with previously reported resistivity data [234].

Resistivity vs. temperature data was captured using a four-probe method (Fig. 6.3) for 5- and 6-unit cells SrRuO₃. Here, the 5-unit-cell SrRuO₃ (Fig. 6.3a) resistance remains almost

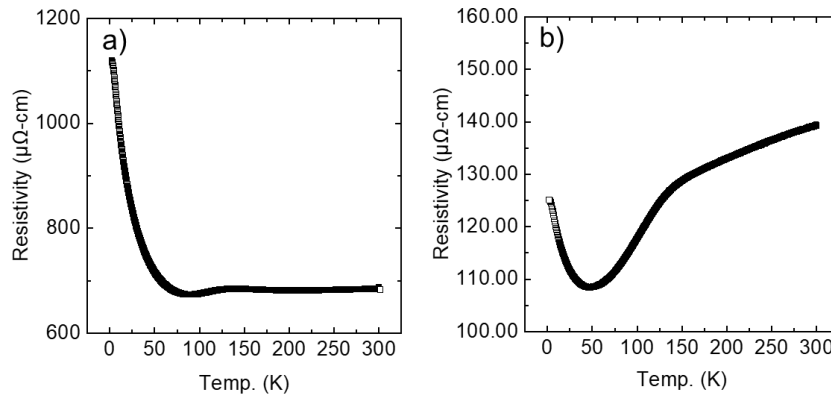


Fig. 6.3 Resistivity vs. temperature data of a) 5-unit-cell SrRuO_3 and b) 6-unit-cell SrRuO_3 .

constant as temperature decreases down to ~ 50 K, indicating its close proximity to the insulating nature, again consistent with the previously reported data [234,235]. An upturn in the resistivity data indicates a temperature-induced metal-insulator transition which occurs because due to the weak localization effect [235]. In these ultrathin SrRuO_3 films, weak localization caused by microstructural disorder may play a critical role in the resistivity increment at low temperatures. Electrons may encounter a series of random scatterings in electronic systems with disordered impurities. The interference of electron wave functions may cause weak localization around these impurities and consequently increases the resistivity [234]. In ultrathin SrRuO_3 films, the transport characteristics can be interpreted by the competition of localization and delocalization of electron states near Fermi level [236], which can be tuned by the degree of disorder. With increasing temperature, localization is suppressed, and the strengthened delocalization leads to a decrease in resistance. As the temperature further increases, delocalization is saturated, and electrons are scattered by electrons. This results in the presence of minima in resistance-temperature curves.

Similarly, resistivity vs. temperature data (Fig. 6.3b) was captured using a four-probe method for 6-unit cell SrRuO_3 . Here, the resistance continuously decreases as the temperature decreases down to ~ 50 K, indicating the metallic nature of the 6-unit-cell SrRuO_3 , consistent with previously reported data [234,235]. Below this point, there is an up-turn in the resistivity due to the weak localization effect. There is a kink in the sheet resistance-temperature dependence around 130K. This transition in transport characteristics is associated with the paramagnetic to ferromagnetic transition in SrRuO_3 [234]. This observation points towards largely metallic nature for all SrRuO_3 films thicker than 6 unit cells and setting up stage for potential sample selection for measurements of FEFET properties at ultrathin regime of SrRuO_3 channel.

6.3 FEFET Device Fabrication

The FEFET device structures in the form of Hall bars (Fig. 6.4) were fabricated on the top surface of the heterostructure so that the device could be measured in standard source, drain, and ground configuration. FEFET device fabrication was divided into three steps based on the three mask layers involved in the process. Again, these devices are based on a Hall-bar geometry with six terminals. Starting with trilayer samples of the form $\sim 5\text{-}7$ unit cell $\text{SrRuO}_3/100$ nm $\text{BaTiO}_3/10$ nm $\text{SrRuO}_3/\text{GdScO}_3(110)$. Step 1 consists of the fabrication of platinum alignment marks (Fig. 6.5a), which are essential for the next two steps of the alignment process. Then, photoresist was spin-coated, exposed, and developed (Fig. 6.5b and c), like the previously discussed capacitor-

fabrication process. After patterning, a layer of ~ 5 nm of titanium (which is used as an adhesion layer) and a layer of ~ 80 nm of platinum was deposited (Fig. 6.5d) at room temperature via DC magnetron sputtering with base pressure of $\sim 10^{-8}$ Torr. Titanium and platinum were sputtered at 20 W and 15 W, respectively, in argon pressures of 3.3 mTorr and 7.0 mTorr resulting in growth rates of 1.7 nm min^{-1} and 8.7 nm min^{-1} , respectively. Finally, the extra platinum deposited on the photoresist was stripped with acetone (Fig. 6.5e) to achieve platinum alignment marks on the bare samples (Fig. 6.5f and g).

Step 2 involves patterning the Hall bars (Fig. 6.5h). Similar lithographic steps were carried out as previously discussed (Fig. 6.5i and j), but this time by taking reference with respect to the deposited platinum-alignment marks. Then, the sample was ion-milled (Nanoquest, Intlvac Thin Film Corp.) a milling angle of 40° with a beam voltage of 300 V, acceleration voltage of 45 V, and beam current of 5 mA to the top of the BaTiO_3 surface (using a SIMS detector) to isolate the SrRuO_3 Hall bars on the sample's top surface (Fig. 6.5k). After

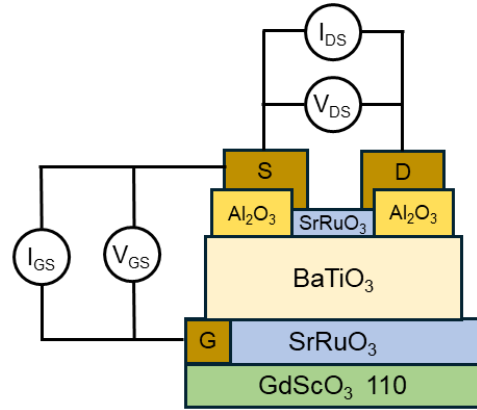


Fig. 6.4 Schematic of trilayer heterostructure with fabricated FEFET structure showing source, drain and gate configuration.

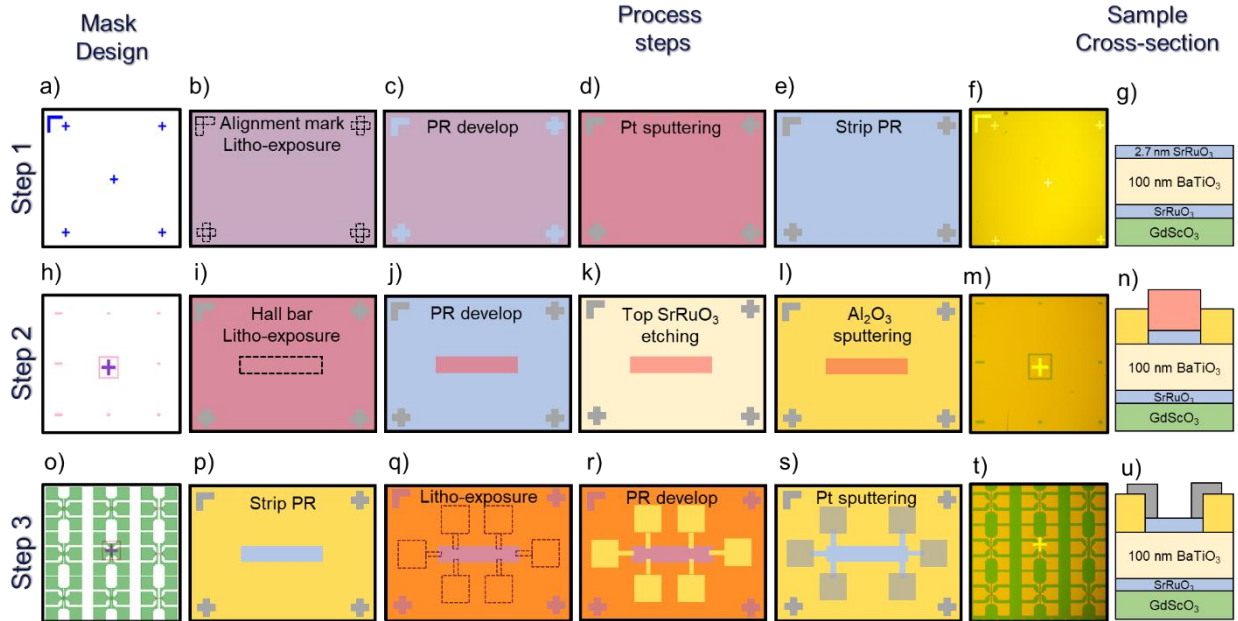


Fig. 6.5 Microfabrication process for Hall-bar devices. a) Mask layer 1 consisting of alignment marks. b) Spin coating of photoresist and photolithography exposure. c) Photoresist development. d) Pt metal sputtering. e) Remaining photoresist stripped using acetone. f) Final image of Pt alignment marks. g) Cross section of the sample after step 1 completion. h) Mask layer 1 consisting of alignment marks. i) Spin coating of photoresist and photolithography exposure of hall bars. j) Photoresist development step. k) Ion milling of external SrRuO_3 beyond defined hall bars. l) Insulating Al_2O_3 layer sputtering. m) Final image after Pt alignment marks and hall bar lithographic step. n) Cross section of the sample after step 2 completion. o) Mask layer 3 consisting of alignment Pt contact pad. p) Removal of photoresist in acetone. q) Spin coating of photoresist and photolithographic exposure. r) Pt contact pads area after development step. s) Final device. Photoresist was removed in acetone after deposition of Pt. t) Optical microscope image of an actual sample after completion of all steps. u) Cross section of the sample after all steps completion.

confirming the removal of the external SrRuO_3 outside the Hall-bar patterns by inspection of surface conductivity with a multimeter, the samples were transferred to an Al_2O_3 sputtering step (Fig. 6.5l). Here, Al_2O_3 functions as an insulating layer between the BaTiO_3 and platinum contact pads. ~ 200 nm of Al_2O_3 is sputtered to obtain suitable isolation thickness between the BaTiO_3 and platinum contact pads (Fig. 6.5l-n). After this step, the photoresist pattern defining the Hall bars was stripped using acetone to expose the top SrRuO_3 for the next step (Fig. 6.5o and p).

Step 3 involves patterning the platinum contact pads (Fig. 6.5o). Again, lithographic process steps like those used in Step 1 were carried out (Fig. 6.5q and r), but this time again by carefully aligning with the Hall-bar patterns defined during the previous steps and with the help of previously defined platinum-alignment marks. Next, a layer of ~ 5 nm of titanium (which is used as an adhesion layer) and a layer of ~ 80 nm of platinum was deposited (Fig. 6.5s). Again, the extra platinum deposited on the photoresist-defined pattern area was stripped away using the acetone to get the final six terminal Hall-bar devices (Fig. 6.5t and u).

6.4 Testing of FEFET Device

The following sections introduce two testing protocols implemented to measure the channel-resistance modulation as a function of applied gate voltage to the FEFET devices. In the first kind of testing, referred to here as *volatile testing*, a gate voltage is set at a specific value to maintain the ferroelectric material to a certain level of switched polarization magnitude and then the channel resistance is measured. In the second kind of testing, referred to here as *non-volatile testing*, the gate voltage is applied to pole the ferroelectric part of FEFET to achieve a certain switched polarization magnitude, but then the gate voltage is removed just prior to the channel-resistance measurement to see the effect of switching transients caused by ferroelectric backswitching behavior impacting the channel-resistance modulation. Specific details of each procedure are provided in detail in the coming sections.

6.4.1 Volatile Testing

Again, in what I refer to as *volatile testing*, a gate voltage is set to a specific value and maintained during the channel-resistance measurement to maintain the ferroelectric material to a certain level of switched polarization magnitude. For this evaluation, fully fabricated devices comprising ground, source, and drain ports are employed (Fig. 6.6a). The top view of the device is also provided (Fig. 6.6b). Two Keithley 2400 sourcemeters are utilized for this testing procedure (Fig.

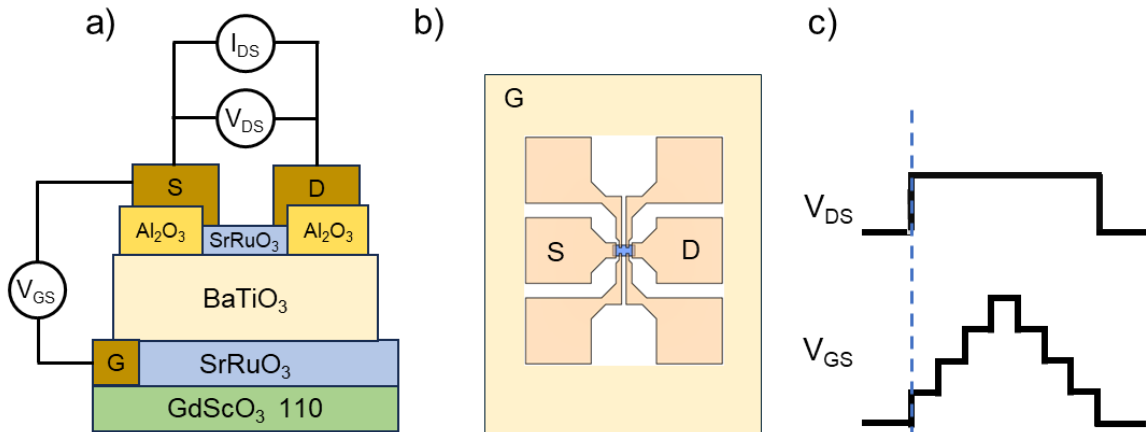


Fig. 6.6 a) Schematic cross section illustrations of the FeFET device under test. b) Schematic of the FeFET device in the hall bar geometry. c) V_{DS} and V_{GS} profile schematic used for testing procedure.

6.6a). The constant low magnitude V_{DS} (drain-to-source voltage) such as 30 mV is applied using one of the Keithley 2400 sourcemeters. The V_{GS} (gate-to-source voltage) is varied between -1 V and 1 V in increments of 0.1 V (Fig. 6.6c) using another Keithley 2400 sourcemeter. The I_{DS} vs. V_{GS} is measured at fixed V_{DS} to get the channel-resistance modulation of FEFET devices.

6.4.2 Non-volatile Testing

In what is called *non-volatile testing*, the gate voltage is applied to pole the ferroelectric material to achieve a certain switched polarization magnitude, but then removed prior to the channel-resistance measurement which commences after a delay period of ~ 100 ms to see the effect of any

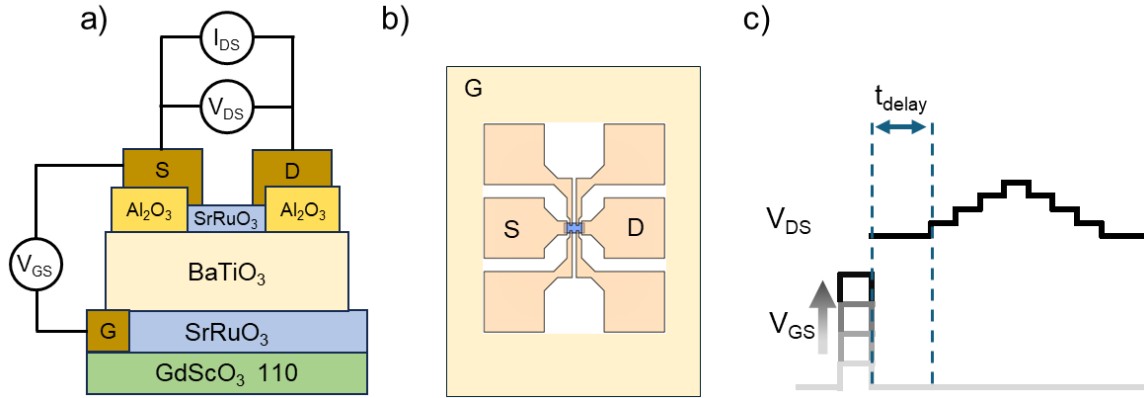


Fig. 6.7 a) Schematic cross section illustrations of the FeFET device under test. b) Schematic of the FeFET device in the hall bar geometry. c) V_{DS} and V_{GS} profile schematic used for non-volatile testing procedure.

switching transients. In other words, this measurement assesses how switching transients caused by ferroelectric backswitching impact the channel resistance of the FEFET devices. Like the volatile case, fully fabricated devices comprising ground, source, and drain ports are employed (Fig. 6.7a). The top view of the device is also provided (Fig. 6.7b). Two Keithley 2400 sourcemeters are utilized for this testing procedure. The V_{GS} (gate-to-source voltage) is varied between -1 V and 1 V in increments of 0.1 V, while the V_{DS} (drain-to-source voltage) ranges from -20 mV to 20 mV in steps of 1 mV (Fig 6.7c). Unlike volatile testing, in non-volatile testing, I_{DS} (drain current) is recorded as a function of V_{DS} after a ~ 100 ms delay upon applying V_{GS} to allow any ferroelectric back-switching to occur. This delay ensures that the channel resistance is measured in accordance with the non-volatile nature of ferroelectric switching. Specifically, V_{GS} is turned off during the I_{DS} vs. V_{DS} measurement period to maintain the ferroelectric material in its equilibrium state following the application of a specific poling voltage of V_{GS} .

6.4.3 Volatile Testing of FEFET Devices

To begin, trilayer heterostructures featuring ultrathin 6-unit cell SrRuO_3 channels [of the form 6 unit cells SrRuO_3 / 100 nm BaTiO_3 / 10 nm SrRuO_3] were analyzed for its channel-resistance modulation as a function of V_{GS} at room temperature with a volatile-testing sequence. Here, the V_{GS} is incrementally varied from -1 V to 1 V in steps of 0.1 V. A resulting hysteresis loop is obtained by measuring the channel resistance as a function of applied V_{GS} (Fig. 6.8a). Typical devices showed channel modulation $[(R_{\max} - R_{\min})/R_{\min} \cdot 100]$ of $\sim 35\%$ at room temperature. As FETs, unsurprisingly because of the high carrier concentration in metal oxide SrRuO_3 [237], these devices show relatively low modulation and high on-state resistance. Still, this ratio is similar to

that of dynamic random-access memory (DRAM), and the channel resistance is not excessively high for such applications [216].

The channel modulation observed (Fig. 6.8a) can be attributed to a field effect. As the SrRuO_3 channel is an n -type material [233], so the majority carriers in the channel are electrons.

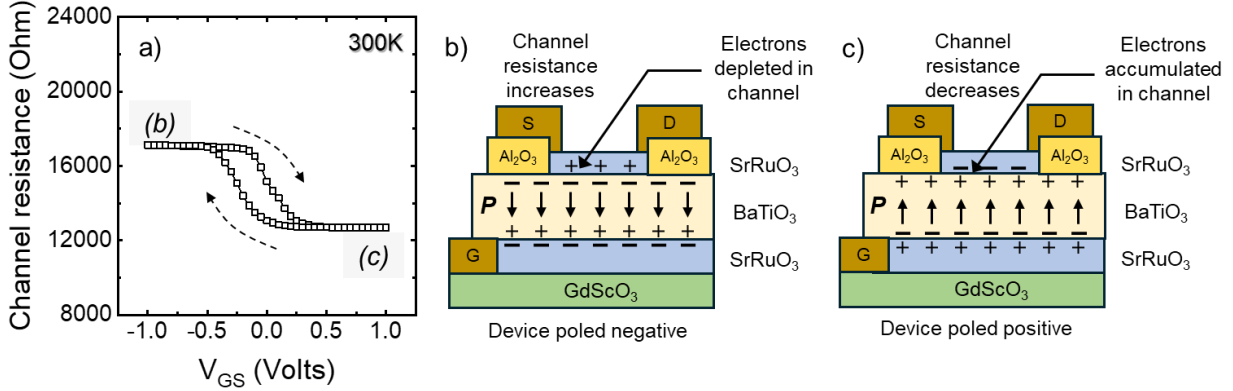


Fig. 6.8 a) Channel resistance hysteresis loop for an all-oxide FEFET. Channel resistance is measured with the gate voltage on. Note that the counterclockwise direction of the loop indicating the ferroelectric switching process. Schematic diagram of a simplified model for the field effect in a n -type FEFET at b) channel depletion and, at c) channel accumulation state.

Applying a negative voltage to the bottom gate device polarizes the ferroelectric such that the electric-dipole moments point downwards (Fig. 6.8b). This rearrangement effectively causes the buildup of a negative charge on the top side of the ferroelectric that will tend to be compensated by positive carriers in the channel, thereby depleting the channel of negative electrons. Therefore, the channel resistance is expected to increase. On the other hand, applying positive gate voltage results in channel accumulation, reducing channel resistance (Fig. 6.8c).

In the process of calculating the channel-resistance change as a function of gate voltage, leakage current across the device (*i.e.*, I_{GS} or the current across the gate-to-source), is also measured to make sure that it has the minimal contribution to the measured I_{DS} (the current across drain-to-source) (Fig. 6.9a). This is confirmed by ensuring that the magnitude of I_{GS} is an order of

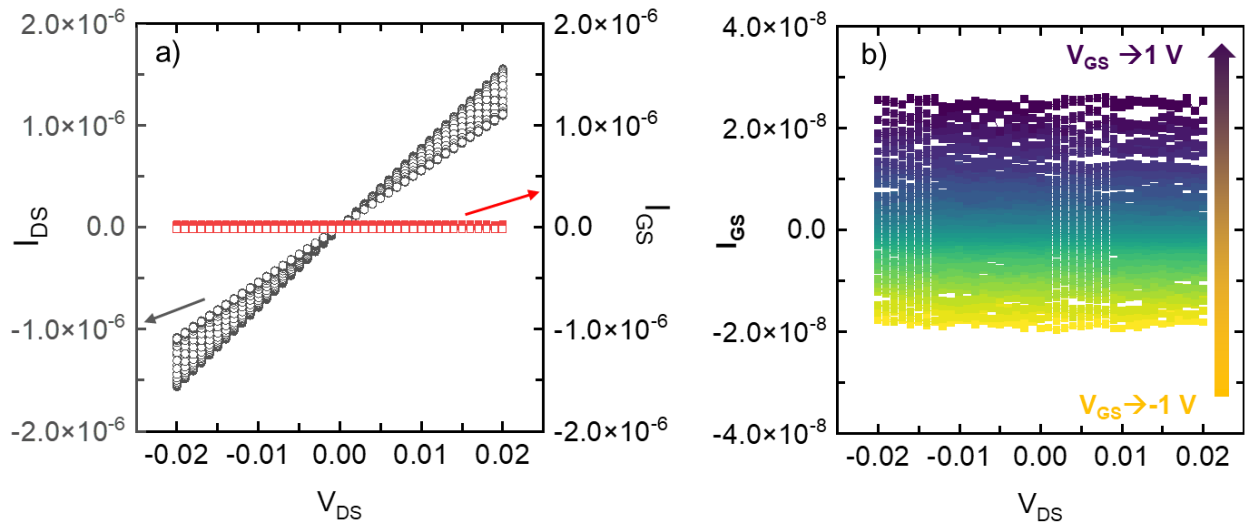


Fig. 6.9 Various current measured during FEFET measurements in the volatile testing case. a) Simultaneous measurement of I_{DS} and I_{GS} as a function of V_{DS} . Zoom in view of I_{GS} as a function of V_{DS} for better visualization.

magnitude smaller than that of I_{DS} during the measurements (Fig. 6.9b). As discussed previously regarding, the 7-unit-cell SrRuO_3 channel which is anticipated to be more metallic than the 6-unit-cell SrRuO_3 (Fig. 6.10) has shown an even lower channel-resistance modulation of 17% due to reduced ability of the ferroelectric to deplete or accumulate the more numerous carriers in the thicker SrRuO_3 with given surface charge provided by BaTiO_3 ferroelectric polarization.

6.4.4 Non-volatile Testing of FEFET Devices

Apart from the volatile testing, where the V_{GS} was kept on during the channel-resistance measurement, a non-volatile type of testing was also carried out, where the V_{GS} was applied but then removed during the channel-resistance measurement after the delay period to see the effect of any switching transients to die down. FEFETs can exhibit both volatile and non-volatile behavior, depending on their design and application [238]. Non-volatile FEFETs can retain their state even when power is removed, making them suitable for non-volatile memory applications. Non-volatile FEFETs can significantly reduce power consumption by eliminating the need for constant refreshing of memory states, which is essential for low-power applications [239]. Volatile FEFETs do not retain their state when power is removed, like conventional transistors used in volatile memory like DRAM. Volatile FEFETs typically operate with lower coercive field requirements compared to non-volatile FEFETs which also generally offer faster switching speeds compared to non-volatile FEFETs, making them suitable for high-performance logic applications where data retention after power loss is not required [238]. In the current devices, ferroelectric backswitching due to the low room-temperature coercive field of BaTiO_3 could cause the remanent polarization value to be smaller than the saturation polarization. Due to this difference in saturation

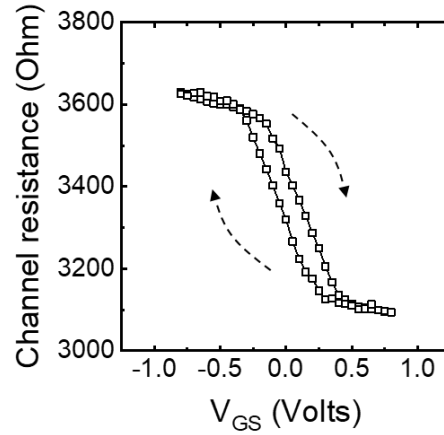


Fig. 6.10 Channel resistance hysteresis loop for an all-oxide FEFET of 7-unit cell SrRuO_3 channel.

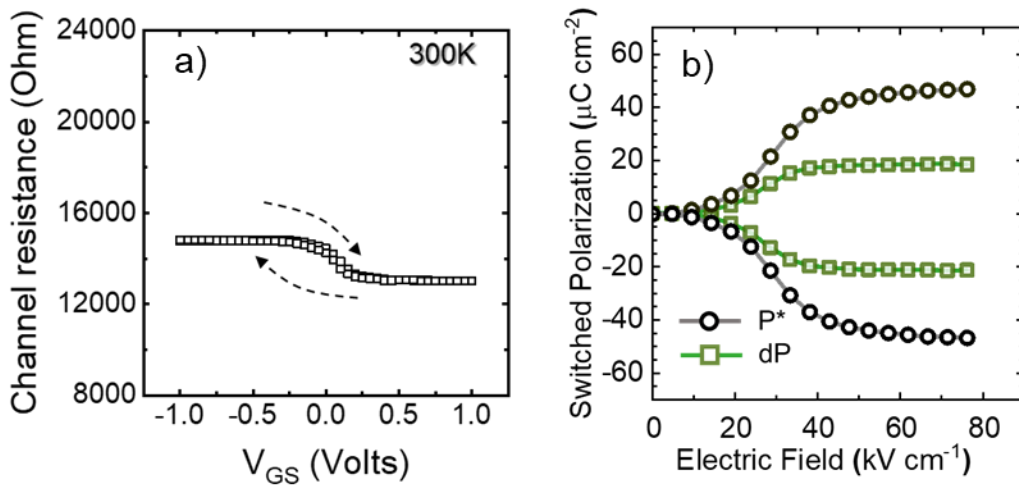


Fig. 6.11 a) Channel resistance is measured with non-volatile testing. b) Pulsed switching measurement showing total switched polarization magnitude and remanence after back-switching.

and remanent polarization value, the non-volatile testing resulted in a smaller channel modulation of ~14% (Fig. 6.11a) than the volatile testing approach (~35%) at 300 K. To confirm this, pulsed-switching studies were carried out (Fig. 6.11b). Here, for example, the pulsed-switching studies showed total switched polarization value (P^*) and reduced remanent polarization value (dP) after the back-switching event. For fully switched ferroelectric state, the switched polarization value is $\sim 40 \mu\text{C}/\text{cm}^2$, but the remanent switched polarization value is $\sim 20 \mu\text{C}/\text{cm}^2$ indicating potential backswitching happening upon removal of applied voltage to the ferroelectric material.

6.5 Temperature Dependent FEFET Testing

6.5.1 6-Unit-Cell Channel Thickness Case

The temperature-dependence of the channel-resistance modulation of the heterostructure was also studied for two reasons: First, such studies help to assess whether the nonvolatile ferroelectric field effect can be improved by reducing backswitching tendency of ferroelectric material; essentially probing the optimal performance of the devices. Second, it helps probe whether the thickness-induced reduction in metallicity in the channel material (which impacts both the number of carriers and the charge screening) can be improved to augment the channel-resistance modulation. To check this, volatile and non-volatile channel-resistance modulation hysteresis loops were captured from room temperature to liquid nitrogen temperature at regular intervals. Here, three different

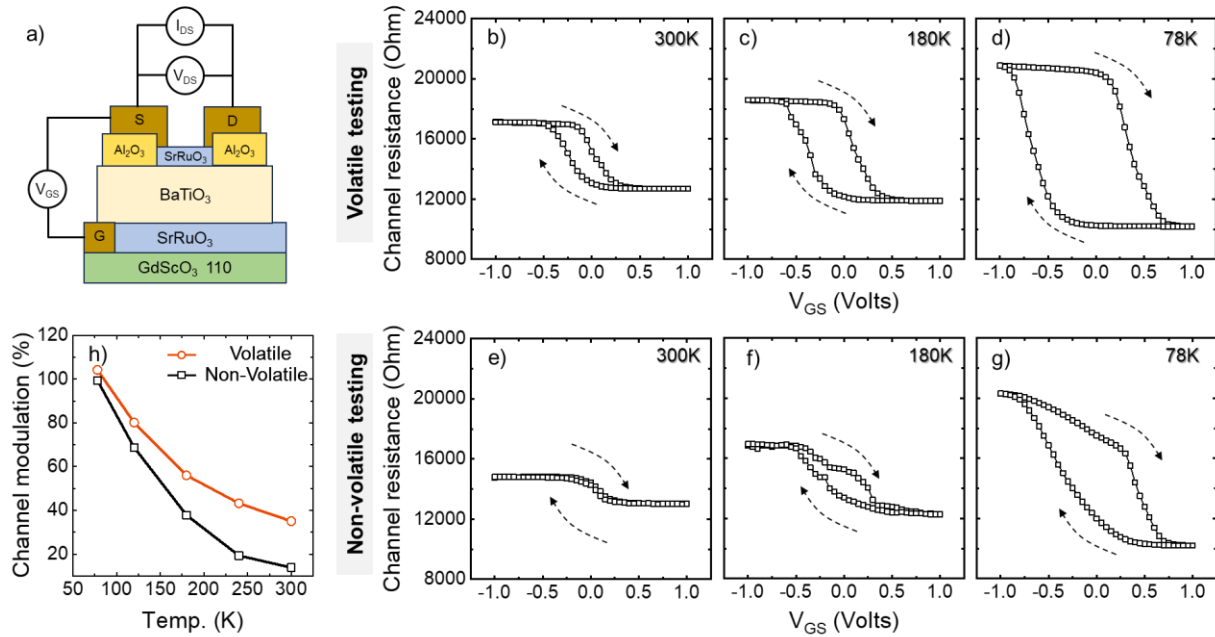


Fig. 6.12 a) Schematic of trilayer heterostructure with fabricated FEFET structure for 6-unit-cell thick SrRuO₃ channel showing source, drain and gate configuration. Channel resistance is measured at various temperatures with volatile testing at b) 300K, c) 180K, d) 78K and, non-volatile testing at e) 300K, f) 180K and, g) 78K. h) Graph indicating channel modulation (%) as a function of system temperature for volatile and non-volatile testing.

temperatures, namely 78, 180, and 300 K datasets are shown for brevity. As the temperature decreases, the channel-resistance modulation hysteresis loops captured by volatile testing sequence show an increased modulation (Fig. 6.12b-d) from 35% at 300K to 105% at 78K. Also, modulation required an application of higher V_{GS} at 78 K (~ 0.5 V) as compared to at 300 K (~ 0.2 V). In terms of kinetics, the switching of domains in ferroelectric materials by an applied electric field is believed to occur by the formation of new domain nuclei with favored orientation of

polarization, which later expand and grow at the expense of the existing domains [240,241]. Under low temperature, the ferroelectric domains are more difficult to be switched because of the low nucleation rate and grow rate, thus higher electric field is needed [240–242]. The polarization switching in ferroelectric materials can also be understood from the Landau-Devonshire Theory perspective [243]. The Gibbs free energy versus electric displacement curve varies with different temperatures. According to the Landau-Devonshire Theory, this free energy has the shape of a double well potential with two free energy minima related to the $+P_s$ and $-P_s$ at temperature below T_0 (T_0 is lower than the Curie Point) for ferroelectrics with first order phase transformation. As the temperature continues to fall, the double well potential of the Gibbs free energy becomes deeper. Therefore, it requires higher electric field to switch the ferroelectric domains at low temperatures as the coercive field increases with decreasing temperature. Additionally, previous studies of ferroelectric films have shown that structural defects such as isolated point defects, complexes, or clusters induced by synthesis pin domain-wall motion during switching [163,244,245]. At low temperatures, the pinning effect becomes more pronounced because the thermal energy is reduced, making it harder for domain walls to overcome the energy barriers created by defects [246], resulting in increased coercivity. Here, a similar kind of the increased coercivity of the BaTiO₃ was observed upon decreasing temperature. This is confirmed by capturing hysteresis loops of capacitors fabricated from heterostructure consisting of 100 nm BaTiO₃ at lower temperatures where similarly increased coercivity was observed (Fig. 6.13). At the same time, the non-volatile channel-resistance modulation hysteresis loops (Fig. 6.12e-g) also showed an enhanced channel modulation from 14% at 300 K to 100% at 78 K and gradually matched the value that of the volatile testing values (Fig. 6.12h). This can be attributed to the better retention of BaTiO₃ polarization upon decreasing the system temperature. Domain wall motion in ferroelectrics can be significantly affected by defect pinning [247], especially at low temperatures. As the thermal energy is reduced, making it demanding for domain walls to overcome the energy barriers created by defects [246], resulting into better retention performance of the switched ferroelectric domains. As temperature decreases, there is also less thermal energy available to disrupt the aligned dipoles that create the spontaneous polarization. This makes it harder for the polarization to randomize or switch directions. Also, the motion of domain walls, which separate regions of different polarization orientation, becomes more restricted at lower temperatures. This makes it harder for domains to switch or reorganize, contributing to overall polarization stability [248]. Hysteresis loops for channel modulation at intermediate temperatures are also included for completeness (Fig. 6.14b-d). Upon closer examination of the channel modulation hysteresis loops in relation to temperature, it becomes evident that the resistance of the “on state,” where the channel remains in the electron accumulation state, reduces with decreasing temperature, suggesting the channel is still in a metallic state. Also, it can be seen that the “off-state” resistance

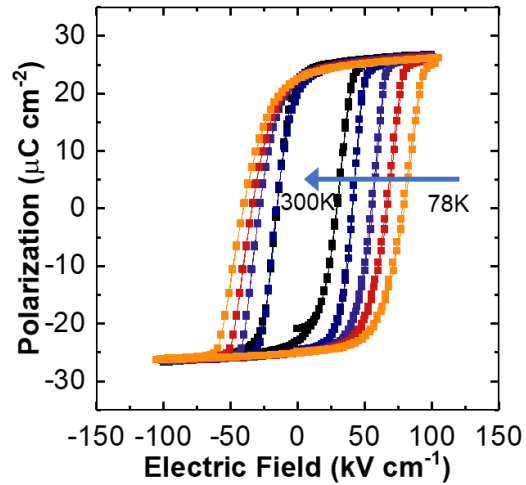


Fig. 6.13 Polarization vs. electric field hysteresis loops for 300K, 240K, 180K, 120K and, 78K for SrRuO₃ (10nm)/BaTiO₃ (100nm)/SrRuO₃ (10nm) heterostructure measured at 1KHz.

when the channel is in depletion increases as temperature decreases, which can be assigned to enhanced charge depletion as temperature decreases [249]. The SrRuO₃/BaTiO₃ interface has been shown to form a unit cell of SrTiO₃ at the interface based on growth conditions [250]. The impact of temperature lowering on the dielectric constant enhancement of the SrTiO₃ has been studied previously [251,252]. The high dielectric constant at low temperatures enhances the material's ability to polarize in response to an electric field, which improves charge screening. As the effective polarization from BaTiO₃ is not changing significantly as temperature decreases (Fig. 6.13), the potential enhancement of screening effects can be assigned to the change of the dielectric constant of the SrTiO₃ dielectric layer.

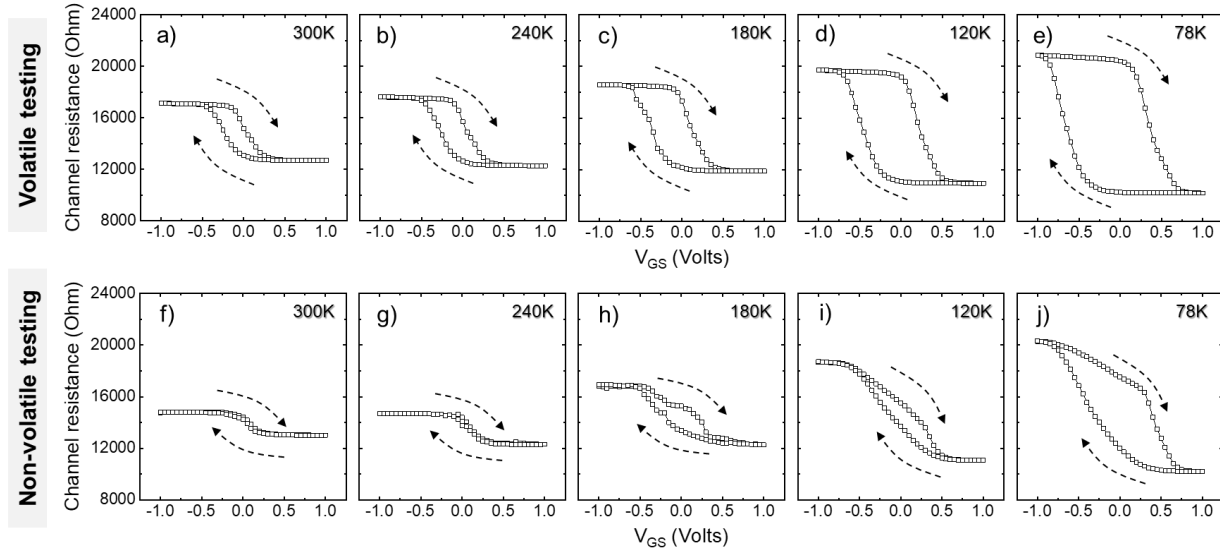


Fig. 6.14 Channel modulation hysteresis loops for FEFET structure made up of 6-unit-cell thick SrRuO₃ channel thickness. Channel resistance is measured at various temperatures with volatile testing at a) 300K, b) 240K, c) 180K, d) 120K, e) 78K and, non-volatile testing at f) 300K, g) 240K, h) 180K, i) 120K, j) 78K.

6.5.2 5-Unit-Cell Channel Thickness Case

It has been previously observed that resistivity and the metal-to-insulator crossover in (ungated) SrRuO₃ thin films strongly depend on the film thickness, with decreasing layers [253]. Also, it has been shown that when the SrRuO₃ film thickness is reduced to 4-5 monolayers, the sample's resistivity can increase by orders of magnitude compared to the thicker ones, and it becomes insulating in the entire accessible temperature range $T < 300\text{K}$ [234]. To investigate the impact of such reduction of SrRuO₃ channel thickness on the channel-resistance modulation, a heterostructure composed of 5-unit-cell SrRuO₃ channel (Fig. 6.15a), i.e., SrRuO₃ (5-unit cells)/100 nm BaTiO₃ /10 nm SrRuO₃ was analyzed for its FEFET characterization. As observed in the 6-unit cell case, volatile (Fig. 6.15b-d) and non-volatile (Fig. 6.15e-g) channel modulation increases with decreasing temperature. Similarly, the non-volatile channel-resistance modulation magnitude matched that of the volatile testing at low temperatures, indicating better retention of BaTiO₃ polarization upon reducing the system temperature (Fig. 6.15h). Compared to the 6-unit-cell channel case, the 5-unit-cell channel thickness case has demonstrated significantly enhanced

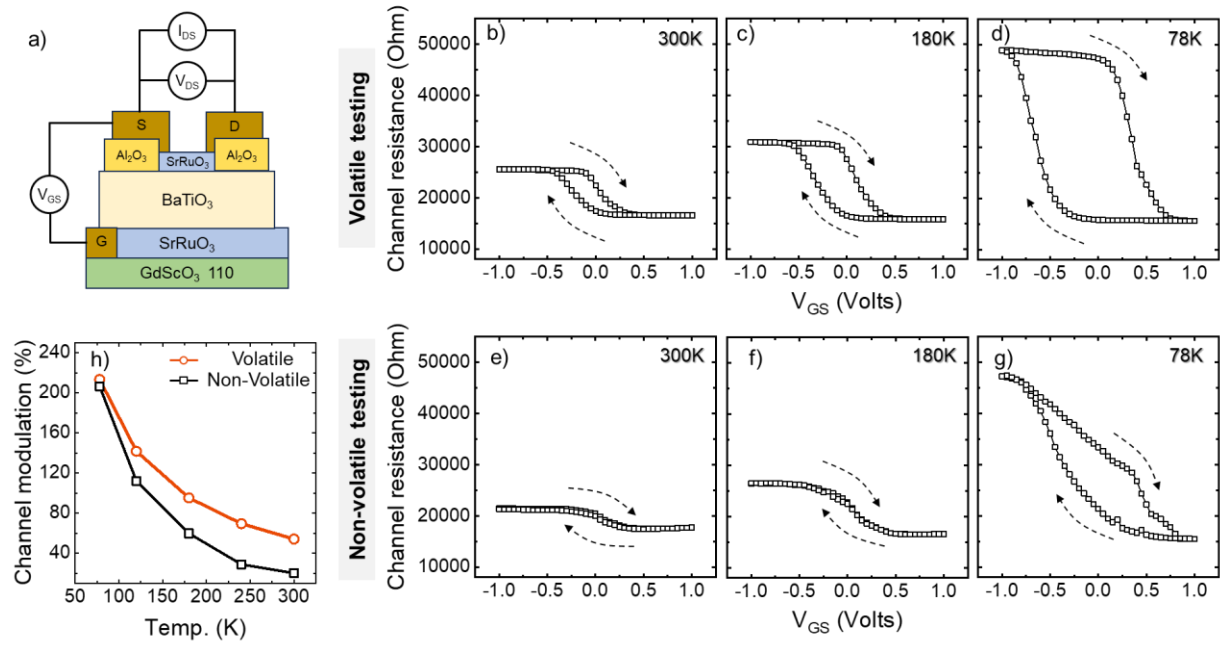


Fig. 6.15 a) Schematic of trilayer heterostructure with fabricated FEFET structure for 5-unit-cell thick SrRuO_3 channel showing source, drain and gate configuration. Channel resistance is measured at various temperatures with volatile testing at b) 300K, c) 180K, d) 78K and, non-volatile testing at e) 300K, f) 180K and, g) 78K. h) Graph indicating channel modulation (%) as a function of system temperature for volatile and non-volatile testing.

performance, nearly doubling the channel modulation magnitude than that of the 6-unit-cell channel across all temperatures and in both volatile and non-volatile scenarios, reaching 220% at 78K (Fig. 6.15h). Also, the overall channel resistance is higher compared to the 6-unit cell case, which can be assigned to thickness-dependent metal-insulator transition [234]. Hysteresis loops for channel modulation at intermediate temperatures are also included for completeness (Fig.

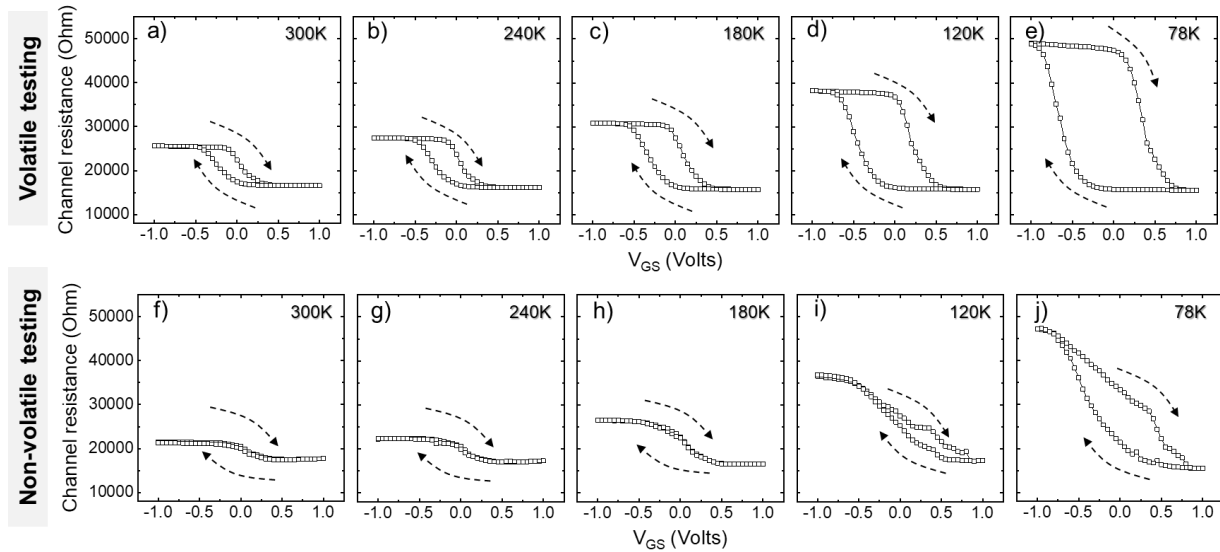


Fig. 6.16 Channel modulation hysteresis loops for FEFET structure made up of 5-unit-cell thick SrRuO_3 channel thickness. Channel resistance is measured at various temperatures with volatile testing at a) 300K, b) 240K, c) 180K, d) 120K, e) 78K and, non-volatile testing at f) 300K, g) 240K, h) 180K, i) 120K, j) 78K.

6.16a-j). In this case, upon closer examination of the channel modulation hysteresis loops with temperature, it becomes evident that the resistance of the “on state” where the electron accumulation occurs remains almost constant with decreasing temperature. This suggests that the channel is less affected by accumulation due to its lesser metallic state and its entry into the thickness-dependent metal-insulator region [235]. Previously reported in LaNiO_3 [254] and $\text{La}_{0.75}\text{Sr}_{0.25}\text{VO}_3$ [255] films, the temperature-driven metal-insulator transition in correlated thin films could be attributed to the weak localization effect. Here also, it can be seen that the “off-state” resistance increases as temperature decreases, which can be assigned to enhanced charge depletion as temperature decreases along with reduced majority carriers due to thickness-dependent metal-insulator transition [249].

6.6 Conclusion

In summary, I have reported the fabrication and characterization of ultrathin thickness SrRuO_3 channel integrated with low coercive field BaTiO_3 ferroelectric material-based FEFET devices to achieve the gate voltage-controlled channel-resistance modulation. Keeping channel thickness in the range of 6- and 5-unit cells has shown that a gradual increase in resistivity down to the critical thickness is an effective way to improve channel-resistance modulation. This observed channel modulation is then further enhanced by reducing the system temperature to liquid nitrogen, which also helped improve the non-volatile properties of ferroelectric material. The present results demonstrate that a significantly improved, non-volatile ferroelectric field effect device can be constructed of perovskite heterostructures with ruthenates as the channel material. The enhanced interface characteristics associated with the ferroelectric-ruthenates interface allow for the fabrication of field effect devices with channel-resistance modulation of at least a factor of 2.

CHAPTER 7

Summary of Findings and Suggestions for Future Work

7.1 Summary of Findings in this Dissertation

In this Dissertation, I developed an understanding of the control and manipulation of ferroelectric polarization to produce new phenomena and to enhance the utility of ferroelectric materials using the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ and BaTiO_3 as model systems. Herein, the ferroelectric polarization under different chemistries and heterostructure geometries, such as single-layer, multilayer, and superlattice films have been studied. After briefly recapping fundamental principles of ferroelectric materials (Chapter 1) and the synthesis and characterization methods utilized in this work (Chapter 2), I transitioned to focus on the core findings of this Dissertation. In Chapter 3, I studied the biaxial strain-induced evolution of coexisting c/a and a_1/a_2 mixed-phase nanodomains in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system. In this work, I developed a thin-film-synthesis route for compositionally controlled $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films and performed detailed structural, domain, and physical-property characterization. It was observed that the system undergoes a gradual transformation (with increasing strontium content) from droplet-like a_1/a_2 domains in a c/a domain matrix, to a connected-labyrinth geometry of c/a domains, to a disconnected labyrinth structure of the same, and, finally, to droplet-like c/a domains in an a_1/a_2 domain matrix. Through collaborations with Dr. Jacob A. Zorn, Dr. Bo Wang, and Prof. Long-Qing Chen from the Pennsylvania State University, who performed phase-field simulations, I studied the similar evolution of the different mixed-phase domain patterns. With that, a strain-temperature-strontium content 3D-phase diagram of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system was established. These structures were then analyzed for their topological nature (both experimentally and theoretically), and approaches adapted from other fields to identify topological transitions across different patterns. The phase-field simulations also provided insights about the mechanism and various energy terms involved in domain coarsening induced formation of parallel c/a and a_1/a_2 domain stripes upon starting with the connected-labyrinth structure and then subjecting the system to extended annealing. I also investigated the ferroelectric and dielectric properties, unveiling that the dielectric constant is significantly boosted, and the maximum extrinsic contribution to the dielectric response is observed when the domains are organized in a connected-labyrinth fashion. This finding aligns with the observation of the highest shared normalized domain perimeter within the same structures. These results imply that deterministic control of specific mixed-phase domain configurations through careful chemistry control, as shown in this case, could effectively control its structural, topological, and dielectric properties.

After exploring the mixed-phase domain structures in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films, I studied the formation of purely in-plane polarized domains in the higher strontium content ($x \geq 0.6$) region of the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system (Chapter 4). The detailed PFM analysis of the as-grown films provided details of local domain and global superdomain formation, and domain-size evolution as a function of strontium chemistry. RSM studies further supported this domain evolution. By performing switching studies using in-plane devices aligned at different angles and leveraging the phase-field modelling developed by Aiden M. Ross, Dr. Jacob A. Zorn, and Prof. Long-Qing Chen from the Pennsylvania State University, I related the observed switching behavior of the various superdomain variants under different electric-field directions. These simulations further provided information on the switching pathways and how each unit cell responds to the applied electric

field. Both coercive field and remanent polarization were decreased with increasing strontium content. Using these distinct composition films as a building block, bilayer configurations were then analyzed for their interlayer coupling-induced exchange-bias-like phenomena, an idea adapted from the exchange interactions in magnetism. This electric/polarization analog of exchange bias in the ferroelectric system can be additionally tuned with thickness control of each layer, which was then used to realize multistate functionality. Further control via strontium chemistry and thickness selection showed the possibility of realizing a springy nature of the switching process and coercivity reduction in the bilayer system; analogous to an exchange spring in magnetism. Hence, this bilayer system provided a rich playground for tuning interlayer coupling across the purely in-plane ferroelectric system.

Building upon this understanding about the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system, I further studied superlattice versions of the $(\text{PbTiO}_3)_n/(\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3)_n$ thin films (Chapter 5) to explore the potential for the formation of ferroelectric polar vortices in fully ferroelectric $\text{PbTiO}_3/\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ trilayers and superlattices. Previously, similar topologies have been shown to form in ferroelectric-dielectric systems such as $\text{PbTiO}_3/\text{SrTiO}_3$, where SrTiO_3 provides the appropriate boundary conditions for these complex structures to form. Such systems are, however, effectively have half of the structure unresponsive to applied stimuli. To tackle this, I investigated the $(\text{PbTiO}_3)_n/(\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3)_n$ system wherein in-plane ferroelectric polarization in the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ also provides the appropriate boundary conditions for vortex formation. Incorporating such an in-plane ferroelectric layer within the superlattices led to a significant enhancement in piezoelectric and ferroelectric responses along the out-of-plane direction. This enhancement stemmed from the ability of polarization within both layers to reorient towards the out-of-plane direction under an applied field. In addition to the improvements observed in the out-of-plane properties, the layers exhibited strong coupling during switching. This configuration demonstrated multistate switching capabilities and polarization stability in the in-plane direction when heterostructured with ferroelectric-dielectric building blocks. This research further expands the realm of systems able to support emergent dipolar texture formation, and it does so with entirely ferroelectric materials, thus significantly improving their responses to applied fields.

Finally, the last part of this Dissertation concentrates on utilizing ferroelectric polarization in the production of ferroelectric capacitors that will serve as the foundation for FEFETs (Chapter 6). Herein, I analyzed perovskite heterostructures of the form SrRuO_3 (5 and 6-unit cells)/ BaTiO_3 (100nm)/ SrRuO_3 (10nm) [metal-ferroelectric-metal heterostructures, wherein the top SrRuO_3 served as the channel]. Such heterostructures enabled reduced coercive field (V_c) and robust polarization in ferroelectric films and the utilization of the ultrathin SrRuO_3 to establish field effects via channel-resistance modulation. By keeping the channel thickness in the range of 5-6 unit cells, close to a thickness-induced metal-insulator transition, provides a pathway for a gradual increase in resistivity down to the critical thickness and an effective way to improve channel resistance modulation. This modulation is measured as a function of temperature, where enhanced channel-resistance modulation was observed upon cooling. Thus, this research demonstrates a foundation for developing novel channel materials for FEFETs and further expands the utility of non-volatile, low coercive field BaTiO_3 ferroelectric thin films with entirely perovskite oxide heterostructure for field effect-based devices, showing pathways to combine logic and memory functionalities at the single-device level.

Overall, the work presented in this Dissertation offers new insights into the relationships between structure and properties in ferroelectric heterostructures. This understanding provides

pathways to uncover novel phenomena in ferroelectric materials, enhance its utility and performance through diverse heterostructures and interface-driven processes.

7.2 Suggestions for Future Work

7.2.1 Compositionally Graded $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ Thin Films

In ferroelectrics such as $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) and $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT), studies on the effect of compositional gradients have shown the formation of novel domain structures such as needle domains [91] and functionalities such as (nearly) temperature-independent dielectric response [93] that are not found in parent single-composition counterparts. In the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system, however, this remains primarily uncharted territory. In the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system, PbTiO_3 and SrTiO_3 are the end members of the system. Strontium alloying in the $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system reduces the c lattice parameter without changing the tetragonal geometry of the unit cell [116], providing better control at the unit cell level compared to the PZT system where increasing zirconium content leads to tetragonal to rhombohedral to orthorhombic unit cell structure [55]. Depending on the position of the end members of the compositionally graded films within the phase diagram, multiple versions for compositional grading can be made such as i) upgraded versions going from PbTiO_3 to $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.6$), ii) downgraded versions going from $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ to PbTiO_3 ($x = 0.6$), iii) upgraded-downgraded versions going from PbTiO_3 to $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ to PbTiO_3 ($x = 0.6$), and iv) downgraded-upgraded versions going from $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ to PbTiO_3 to $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.6$). Each of these variants represents the possibility of a unique domain structure and associated properties. For example, needle-shaped domains (Fig. 7.1a and b), curved or pinched domain walls (Fig. 7.1c), and wholly embedded c domain in a domain matrix (Fig. 7.1d). Such unique control over the domain structure achieved via compositionally grading could provide an exciting platform for domain architecture studies via TEM to analyze the effect of curved domain walls and any charged domain-wall formation, if any. One such sample of a 50-nm-thick compositionally graded thin film made up of upgraded PbTiO_3 to $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.6$) has been analyzed via TEM by Dr. Abinash Kumar and Prof. James M. LeBeau at the Massachusetts Institute of Technology to

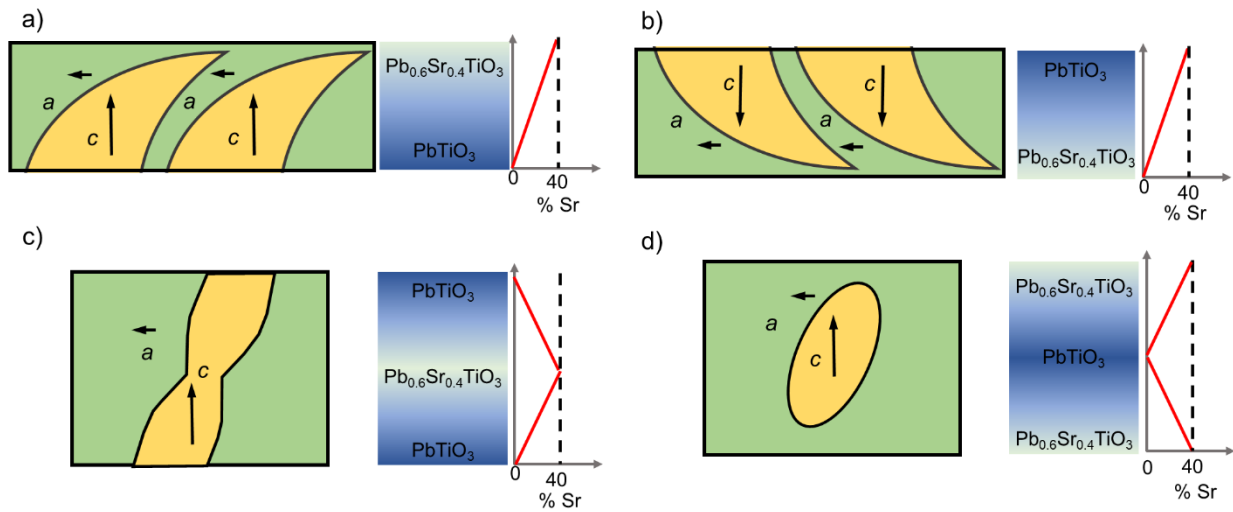


Fig. 7.1 a) upgraded version of PbTiO_3 to $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.6$), b) downgraded version of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ to PbTiO_3 ($x = 0.6$), c) upgraded-downgraded version of PbTiO_3 to $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ to PbTiO_3 ($x = 0.6$), d) downgraded-upgraded- downgraded version of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ to PbTiO_3 to $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.6$).

provide subtle details about the domain architectures (Fig. 7.2a). Here, the formation of periodic needle-like domains in c/a domain architectures can be seen (Fig. 7.2b). The high concentration of the depolarization field shrinks a part of the a domain near the needle tip and terminates the a domain within the compositionally graded thin film. These facilitate the stabilization of needle-like domains with curved domain walls in the compositionally graded thin film.

Results obtained from recent phase-field studies also indicated an essential role flexoelectricity which has been proven to play a role in the voltage offset of the hysteresis loop, which could be used for electrocaloric- and pyroelectric-effect studies [256]. Apart from that, the ferroelectric switching process analyzed via phase-field modeling in the compositionally graded thin film exhibits a vastly different response in comparison to that in homogeneous ferroelectric thin films, including local switching initiation and formation and annihilation of vortex-antivortex pairs during the switching [257]. This can provide an interesting test case for the *in situ* TEM analysis.

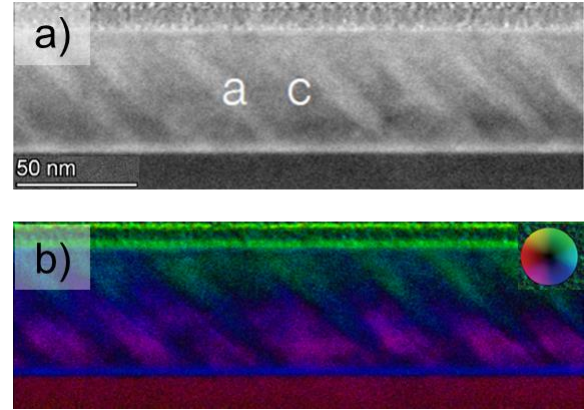


Fig. 7.2 a) HAADF image of the compositionally graded 50 nm upgraded version of PbTiO_3 to $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ 50 nm thin film which shows diffraction contrast corresponding to c and a domains. b) DPC image showing polarization corresponding to c and a domains.

7.2.2 Observation of Polar Skyrmions in $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ / PbTiO_3 Superlattices

In Chapter 5, I have discussed the formation of ferroelectric polar vortices in ferroelectric/ferroelectric superlattices made up of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3/\text{PbTiO}_3$ grown on DyScO_3 substrates. In this case, vortices have been observed in the PbTiO_3 layer, and in-plane domain formation in the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ layer, which provides the required electric boundary conditions for such polar-topology formation. The specific polar topologies observed in these systems, such as vortices, skyrmions, and/or merons, are determined by a combination of the electric boundary conditions and the strain state induced by the substrate. In that regard, $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3/\text{PbTiO}_3$ superlattices grown on SrTiO_3 substrates could provide suitable conditions for forming skyrmions in fully ferroelectric superlattices. In contrast to the vortices, where the formation of in-plane polarized domains in $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ facilitates the necessary insulating boundary conditions for the emergence of polar vortices, the electric-boundary conditions offered by $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ in the case of skyrmions are less favorable due to potentially surface charge development between $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ and PbTiO_3 . Despite these limitations, some early attempts have shown the signatures of skyrmion-like polar topologies formation in this system even with $x = 0.6$. This raises reconsideration of the long-held belief of the strict requirement of the insulating layer for forming such polar topologies. Increased skyrmion size with increasing lead content (x) in the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ layer matches with some internal studies where similar phenomena have been observed with decreasing SrTiO_3 layer thickness, making SrTiO_3 layer more ferroelectric due to the ferroelectric proximity effect [182].

Detailed TEM analysis could show the polarization arrangement around the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3/\text{PbTiO}_3$ interfaces. These skyrmions are potentially expected to show enhanced dielectric behavior and improve tunability by introducing the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ layer compared to the pure SrTiO_3

dielectric layer. Also, the ferroelectric switching nature of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ in the out-of-plane direction makes them (more) highly susceptible to enhanced piezoelectric response compared to skyrmions in $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices. $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ system has T_c close to 100-120° C when $x \leq 0.6$ [49]. This makes $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3/\text{PbTiO}_3$ interesting for studying how skyrmion size changes and how the total dielectric response changes when system temperature is elevated. At higher temperatures, $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ becomes paraelectric, and the overall system is like the $\text{PbTiO}_3/\text{SrTiO}_3$ system. Lab-based XRD installed with an Anton Paar heating stage and temperature-dependent dielectric measurement setups can be used to carry out these experiments.

7.2.3 Novel Polar Textures in $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3/\text{PbTiO}_3$ Superlattices

Emergent topological polar textures, including vortices [53], dipolar waves [187], skyrmions [83], merons [84], and others, have generated considerable interest [188]. Thus far, ferroelectric-dielectric superlattices, mostly based on $(\text{PbTiO}_3)_n/(\text{SrTiO}_3)_n$, have served as the model system for this work [53] wherein the delicate balance of electric, elastic, and gradient energies can be tailored to manipulate the order parameter [53,83,84,187]. The resulting emergent polar textures also exhibit novel phenomena, including the coexistence of phases [89], chirality [189], negative capacitance [190,191], and emergent driven phases [192] and modes [193]. Recent searches for such ferroelectric polar topologies have garnered interest in SrTiO_3 , where antivortex formation

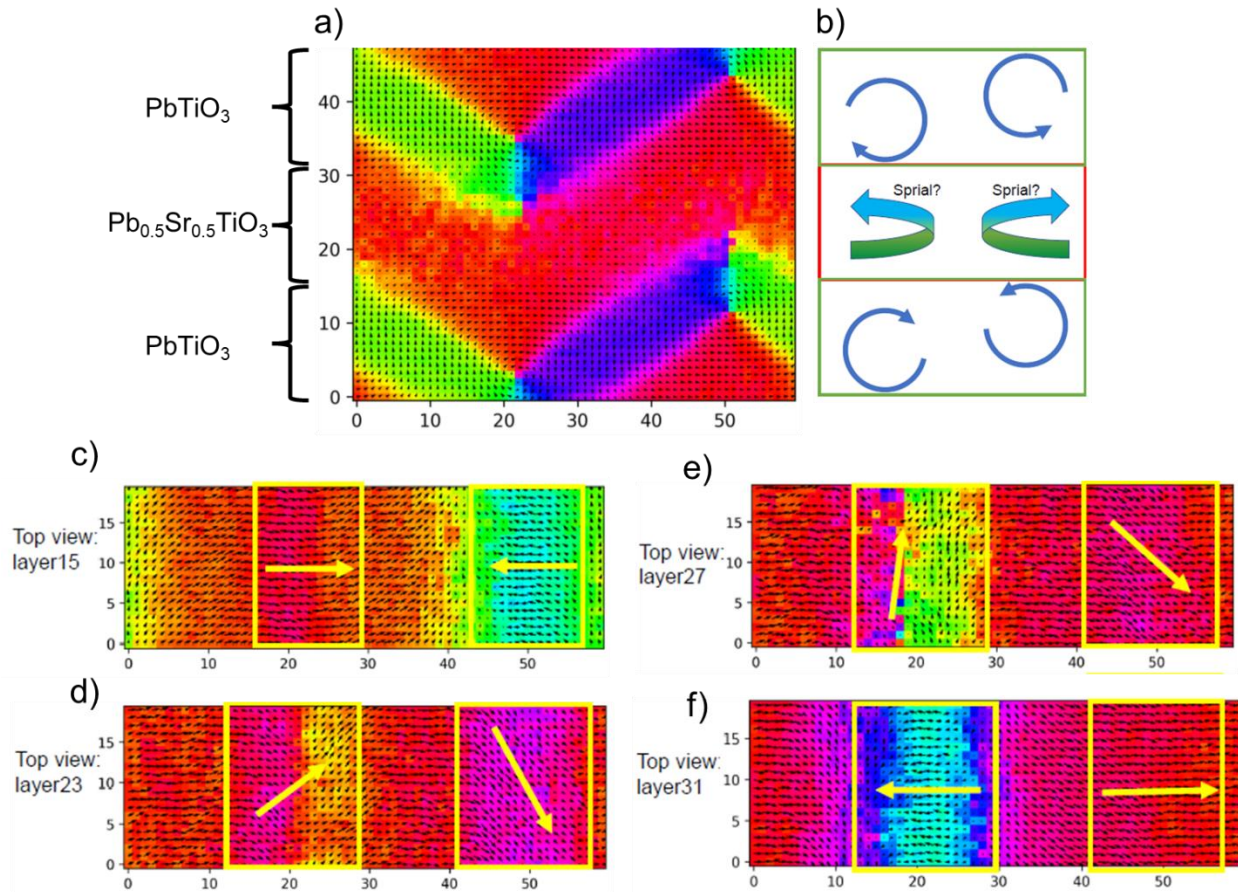


Fig. 7.3 MD simulation generated stacked trilayer of $(\text{Pb}_{0.5}\text{Sr}_{0.5}\text{TiO}_3)_{16}/(\text{PbTiO}_3)_{16}$ heterostructure. Schematic showing mapped ordered vortices in the two PbTiO_3 layer and spiral staircase-like polar topology in the connecting $\text{Pb}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ layer. Top view of $\text{Pb}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ layers with layer number c) 15, d) 23, e) 27, and f) 31.

has been observed through TEM studies [258]. Also, SrTiO_3 and other relevant spacer layers have influenced ordering [259] and phase selection [259]. This prompts the inquiry of whether any intriguing features and properties are associated with the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ layer in $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3/\text{PbTiO}_3$ superlattices. Here, the initial studies done with MD simulations in collaboration with Jiyuan Yang and Prof. Shi Liu from Westlake University for $\text{Pb}_{0.5}\text{Sr}_{0.5}\text{TiO}_3/\text{PbTiO}_3$ superlattices have predicted the formation of so-called spiral staircase-style topological features (Fig. 7.3a and b) within the $\text{Pb}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ layer to maintain the polar continuity with the vortices across the different levels to maintain vortex ordering (Fig. 7.3c). This polar topology could be analyzed via advanced ptychography-based TEM methods. Previously, vortices have shown different modes based on terahertz-field excitation [193]. This novel polar texture could potentially exhibit a distinct excitation mode and a new avenue of phonon engineering in fully ferroelectric superlattices.

Overall, the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ material system offers exciting opportunities to explore a range of unexplored phenomena, domain structures, and diverse topological polar textures through different material chemistries and heterostructure geometries.

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