

Interfacial engineering of ultra-thin ferroelectric film

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Interfacial engineering of ultra-thin ferroelectric film

Guangqing Liu

A thesis in fulfilment of the requirements for the degree of Doctor
of Philosophy



School of Materials Science and Engineering

Faculty of Science

The University of New South Wales

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Abstract 350 words maximum:			
This dissertation presents systemic studies on the ferroelectric properties of ultra-thin films under different interfacial conditions. In the first part, we focused on the engineering of the polarization rotation in ultra-thin bilayered (tetragonal $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$/rhombohedral $\text{PbZr}_{0.55}\text{Ti}_{0.45}\text{O}_3$) epitaxial (001) PZT film. Robust and reversible in-plane and out-of-plane polarization can be observed at nano scale. The top PZT-T layer is decoupled from the clamping effect of substrate due to an inserted PZT-R layer. Moreover, the PZT-R layer reduces the symmetry of PZT-T layer by inducing an in-plane tensile strain. These facilitate large-scale reversible polarization rotation and enhanced dielectric and electromechanical responses. Next, the effect of an intentional a large depolarization field on PZT ($\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$) is investigated. An intentional depolarization field is achieved by introducing SrTiO_3 (STO) in two 3 nm thick PZT ultra-thin film on (001)-oriented STO substrate. By varying the STO spacer thickness (3 to 10 unit cells), the d-spacing and as-grown domain state of PZT layers are significantly affected. A 6 nm thick single PZT film was also deposited as reference. This 'reference' sample shows elongated PZT c lattice parameter (0.416 nm) with mostly monodomain polarization with downward orientation. It also shows significant imprint in the switching loops under external bias. By contrast, STO spacer changes the domain state from monodomain to stripe-like 180° polydomain in virgin state which reduces the imprint by 80%. In addition, the time duration of external electric field to cause domain switching is decreased dramatically compared to the 'reference' sample. In the third part, the 2 nm bottom electrode is replaced by 20 nm metal-like LSMO in PZT films. The PFM results indicate that the 180° polydomain configuration changes from stripe-like to bubble-like. The nano bubble domains are induced by the net effect of polarization field and external screening conditions in the ultra-thin ferroelectric film. Further, the bubble-like domains turn into strip-like domains by simply repeated scanning. In summary, this thesis shows that it is possible to engineer novel domains in ultra-thin ferroelectric films and hence functional performances via interfacial engineering of mechanical and electrical boundary conditions.			
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Abstract

Lead zirconate titanate ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, PZT) has attracted immense attentions over the past few decades. In recent years, researches have shown that the properties of PZT are dramatically improved in the epitaxial films at the nano scale. In particular, the functional properties of PZT such as polarization switching and imprint can be greatly modulated by the interfacial conditions. In this dissertation, we investigated interfacial effects on the ultra-thin PZT films (thickness < 10 nm) which were prepared via laser pulsed deposition (PLD). The structural and ferroelectric properties characterizations were carried out via transmission electronic microscopes (TEM), X-ray diffraction (XRD) and piezo-response force microscopes (PFM). In order to present systemic studies on engineered ferroelectric properties, the PZT thin films with different interfacial modifications were studied. The key objectives of this dissertation can be divided into three parts.

In the first part of this thesis, we focused on the engineering of polarization rotation in ultra-thin bilayered epitaxial (001) PZT film (tetragonal $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (PZT-T)/ rhombohedral $\text{PbZr}_{0.55}\text{Ti}_{0.45}\text{O}_3$ PZT-R). Robust and reversible in-plane and out-of-plane polarization can be observed at nano scale. The top PZT-T layer is decoupled from the clamping effect of substrate due to the inserted 20 nm thick PZT-R layer. Moreover, the PZT-R layer reduces the symmetry of PZT-T layer by introducing an in-plane tensile strain. These facilitate large-scale reversible polarization rotation and great dielectric and electromechanical responses of PZT bilayer. This study has published in *Advanced Material Interface* ^[1].

The effect of an intentional a large depolarization field on PZT ($\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$) is investigated in the second part of this thesis. The depolarization field is achieved by

introducing SrTiO₃ (STO) in two 3 nm thick PZT ultra-thin film epitaxially grown on (001)-oriented STO substrate. By varying the inserted STO spacer between 3 to 10 unit cells between two 3 nm thick PZT films, the *d*-spacing and as-grown domain state are significantly affected. A 6 nm thick single PZT film was also deposited as reference. This ‘reference’ sample shows elongated PZT *c* lattice parameter (0.416 nm) and major monodomain with polarization downward and certain imprint in the switching loops under external bias. By contrast, STO spacer changes the domain state from monodomain to 180° polydomain in virgin state from the PFM results and hence reducing the imprint by 80%. In addition, the time duration of external electric field to cause domain switching is decreased by two orders of magnitude regarding the ‘reference’ sample. This work has published in *Advanced Material Electronic* ^[2].

In the third part, we provide further investigation on ultra-thin PZT films with inserted STO spacer. Specifically, the 2 nm bottom electrode (LSMO) is replaced by 15 nm LSMO which is metal-like in all epitaxial PZT films. The PFM results indicate that the 180° polydomain transfers from stripe-like to bubble-like configuration. According to PFM and TEM, the nano bubble domains are induced by the net effect of polarization field and appreciated screening in ultra-thin ferroelectric film. Moreover, the bubble-like domains turn into strip-like domains during relaxation by the scanning process.

In summary, this thesis shows that it is possible to engineer novel domains in ultra-thin ferroelectric films and hence functional performances via interfacial engineering of mechanical and electrical boundary conditions.

Thesis Outline

The objective of this dissertation is a systemic investigation of ferroelectric properties of the ultra-thin ferroelectric ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$) films. The thesis outline is as follows: In the chapter one, the research background as well as the experimental details are introduced comprehensively. Following a brief discussion on ferroelectricity, the next part of chapter one explores unique properties for ferroelectric films in nanoscale. Subsequently, the principles of thin film deposition processes and the characterization methods to fulfil these projects are discussed.

Chapter two reviews the engineering of polarization rotation in bilayered epitaxial ferroelectric film. In this study, 20 nm thick $\text{PbZr}_{0.55}\text{Ti}_{0.45}\text{O}_3$ (PZT-R) was employed to be a buffer layer between top $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT-T) and bottom $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ electrodes on (001)-oriented SrTiO_3 (STO) substrate. The introduced PZT-R layer reduced the symmetry of thin PZT-T top layer and caused reversible in- to out-of-plane polarization rotation in the film. This demonstrates that the clamping effect is prohibited and large-scale polarization switching as well as great effective d_{33} is achieved. -

Chapter three demonstrates the positive effects of depolarization field on ferroelectric heterostructure via the purposeful insertion of STO paraelectric spacer. By tuning the thickness of STO spacer from 1 unit cell (u.c.) to 10 u.c, the total electrical behaviour is drastically modified. Specifically, the polarization imprint reduces by approximately 80% for the design of PZT/3u.c. STO/PZT on 2 nm thick LSMO bottom electrode. The speed for external-induced domain switching increases 2 orders of magnitude in comparison to single PZT layer film sample. Additionally, the homogeneous polarization domain of reference sample (single PZT layer film) is broken into 180° polydomain in the as-grown state by inserting STO spacer (i.e. 3 u.c. STO sample). The inserted STO layer also suppresses the c-lattice of PZT layer efficiently.

Chapter four continues this investigation on the effects of depolarization field in ultra-thin films. The PZT/STO/PZT heterostructures were deposited on 15 nm thick LSMO bottom electrode which shows metal-like conductivity (carriers density is $\sim 10^{20}/\text{cm}^{-3}$). The monodomain for a single PZT layer is broken into 180° polydomain (as presented in the chapter four), and the proportion of antiparallel polar domains increases with STO spacer thickness. In addition, the 180° polydomain forms bubble-like pattern rather than stripe-like pattern at the top PZT layer. The radius of the bubble domains is approximately 10 nm some of the smallest in the ferroelectric films. More importantly, it is noticed that tiny bubble domains are in metastable state. Under the scanning of piezo response scanning microscope (PFM), the bubble domain eventually promotes into strip 180° stripe domain configuration.

Chapter five gives the conclusion of this thesis and presents the future work for ultra-thin ferroelectric films.

Chapter 1 Literature Review

1.1 Ferroelectricity

1.1.1 Introduction

Ferroelectricity is a property by which certain materials have spontaneous polarization and this polarization can be reversed by external electric field ^[3]. In some materials, the polarization is almost a linear function when they are polarized by external electric field, and this property is defined as dielectric polarization. When the polarization demonstrates nonlinear enhancement with external electric field, such a material is called paraelectric. Unlike the paraelectric and dielectric materials, polarization-applied electric field dependence produces hysteresis loops (typical ferroelectric hysteresis loop is shown in Fig. 1.1) in ferroelectric materials. From the prospective of crystal structure, there are 10 classes of crystal structures among 32 crystal families show polar axis where spontaneous polarization exists. Within these crystal classes, ferroelectricity is present when two or more spontaneous polar states can be stabilized in the absence of external electric field and the polar states can be switched from one polar orientation to another within the existence of sufficient external electric field^[4]. Additionally, the ferroelectricity only shows up below a certain temperature called Curie temperature, T_c . Ferroelectric materials experience thermal phase transition from non-ferroelectric phase, i.e. paraelectric phase, to ferroelectric phase when temperature decreases below T_c . The paraelectric phase always has a higher structural symmetry than its ferroelectric phase.

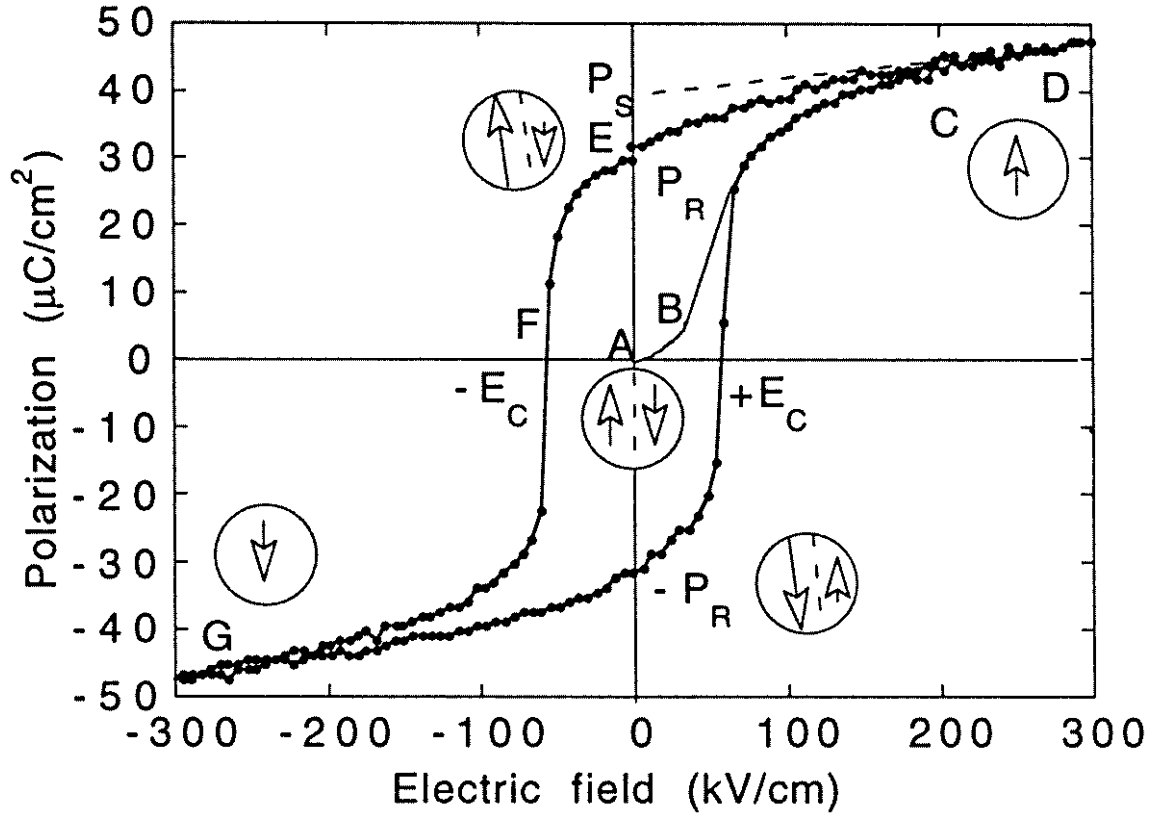


Fig. 1.1. 1 Typical ferroelectric hysteresis loop^[5] E_C is coercive electric field, P_S is the spontaneous polarization and P_R is permanent polarization

1.1.2 Ferroelectric domains and domain walls

Ferroelectric domains are the regions with identical spontaneous polar state in ferroelectrics. In general, the spontaneous polarization cannot be entirely uniform even in the defect-free ferroelectric single crystal because it is energetically costly. Ferroelectric domains form to minimize the overall free energy. This can be realised by 180° domain formation (electric energy minimization) and 90° domain formation (electric and elastic energy minimization) in tetragonal ferroelectrics. The boundary which separates domains is called domain-wall. In this case, boundary between two antiparallel domains is defined as 180° domain walls as described in Fig. 1.2 (a). The

boundary between two regions where the polarization rotates 90° is defined as 90° domain wall as shown in Fig 1.2 (b).

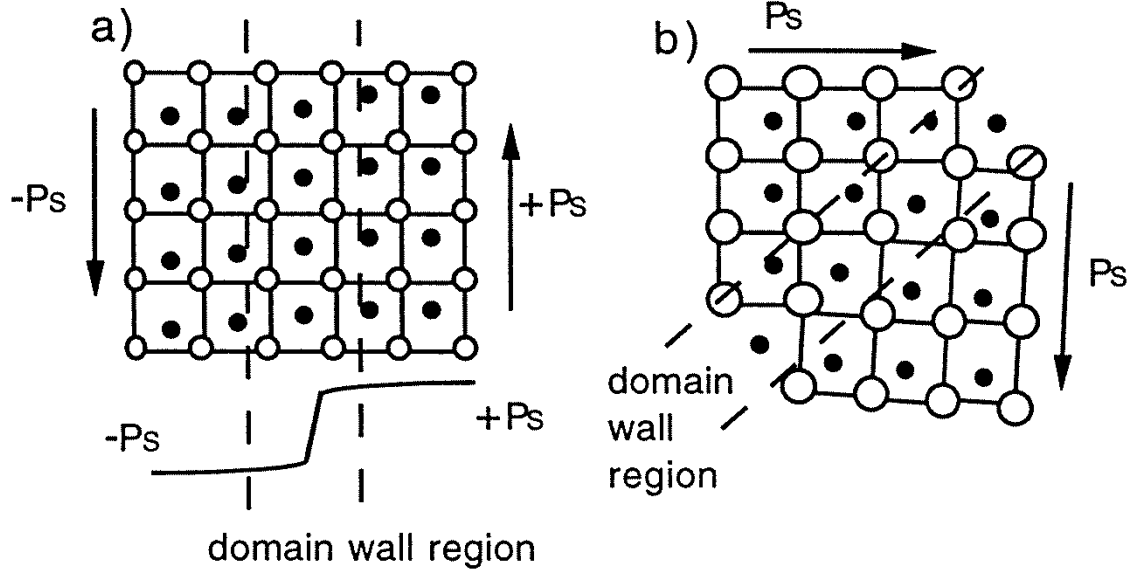


Fig. 1.1. 2 Schematic of 180° domain wall (a) and 90° domain wall (b) in ferroelectrics ^[5]

1.1.3 Depolarization field and strain coupling effects in ferroelectrics

At ferroelectric surface, surface charges are formed due to the discontinuity of polarization. Those charges associated with polarization discontinuity produce electric field to the sample externally and internally. The internal field is defined as depolarization field because of its opposite direction to the spontaneous polarization. Through introduction of 180° domains, electrostatic energy generated from depolarization field is minimized in ferroelectric materials. To be specific, the depolarization field can be decreased by splitting domains with opposite polar orientations in ferroelectrics to reduce the magnitude of polarization at ferroelectric surface. Another dramatic feature of ferroelectric materials is the coupling effect to strain. ^[6] For example, when a cubic crystal transfers to uniform ferroelectric tetragonal,

the coupling effect can be described in this case is μP^2 ^[7] where μ is tetragonal strain field and P depolarization. Depending on the symmetry, the relationship can be varied as linear μP or $\mu^2 P$. However, the strain-polarization is far more complicated in real cases as the presence of domain walls brings other types of energy involved. Especially for the 90° domain walls (indicated by Fig. 1.2 (b)), the 90° domains disturb the strain-field and bring non-uniform strain in the ferroelectric. Thus, domain-wall displacement has significant external effect on the piezo-electric. ^[8], dielectric ^[9] and elastic properties ^[10] in ferroelectric materials as extrinsic contribution.

1.1.4 Ferroelectric metal oxides thin films features and applications

The ferroelectric properties can be either improved or custom-engineered in thin films. Hence, making these ferroelectric materials thin film is attractive from applications' perspective and hence has attracted tremendous great attention for the past few decades. The typical applications include ferroelectric memory device and ferroelectric field effect transistors:

(1) Ferroelectric memories device: Unlike dielectric materials, polarization states are stable in ferroelectrics and also are switchable by sufficient external field. Ferroelectrics can be designed as storable devices by recording information with purposely switching the polarizations under external electric field. Ferroelectric access memories (FRAMs) were regarded as an alternative for Silicon based dynamic random access memories (DRAMs) ^[11] because their high dielectric constants. The challenge is to produce ferroelectric film in the extremely thin region to meet the coercive voltage requirement (<5V) of the semiconductor roadmap ^[12]. With advanced film deposition techniques such as pulsed laser deposition (PLD) in this thesis, ultra-thin film ferroelectrics are achievable but the reliability issues and theoretical understanding are

still not fully resolved. The main ferroelectric material for this thesis, Lead zirconate titanate (PZT), has been the most promising candidate for ferroelectric memories devices ^[13].

(2) Ferroelectric field-effect transistors (FE-FET): In a FE-FET, the insulating layer of a standard transistor is replaced by ferroelectric layer. Through the switching polarization direction of the inserted ferroelectric layer, the conductivity can be modulated in the FE-FET. The main drawback of a ferroelectric FET is long-term data retention failure ^[14]. So far, FE-FET retention has been improved by using thicker ferroelectric films and making better contact with Si ^[15]. An alternate approach, properties of correlated oxide systems are adjusted through the modulation by a ferroelectric field ^[16].

Since most of ferroelectric films display unusual behaviours when the thickness is decreased to nanoscales ^[6], investigations based on thin-film ferroelectrics is not only attraction from a device perspective but is also a rich and fertile playground to understand for low dimensional behaviour in strongly coupled materials.

- In ultrathin ferroelectric film, the scaling effect ($E_c = d^{-2/3}$) fails to predict the relationship of coercive field and film thickness in nano-scale as the depolarization field is limited by incomplete screening in electrodes ^[17].
- The polarization switching (hysteresis behaviour) is quite different from thin film to bulk in identical ferroelectric material ^[18]. The remanent polarization of film is lower than the counterpart in material in general.
- Another feature is the tilted hysteresis loops in ferroelectric films. This feature can be explained that a dielectric layer is formed on top of thin films. The dielectric layer (passive layer) is divided into two parts generally. One is

generated during the deposition of top electrodes and the other is originated during repeated cycling (e.g. fatigue testing) ^[19]. The passive layer (dielectric layer) can be detected between the top electrode and ferroelectric layer.

- Apart from the above, the remanent polarization and switching behaviours heavily depended on the processes of sample fabrication. Hence the lower thickness can play a crucial role to improve performance of ferroelectric films depending on the techniques of thin film synthesis.

1.2 $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) introduction

Among all ferroelectric materials, the PZT family is most popular class due to their outstanding ferroelectric, electromechanical and dielectric properties. In this thesis, thin films of the PZT family are extensively studied. PZT has a typical perovskite ABO_3 crystal structure as shown in Fig 2.1. In this structure, the A-sites are occupied by large cations (Pb in this case) and B-site is occupied by the other cations (Zr/Ti). O atoms are at the face centre forming octahedral structure. Today, many perovskite single crystal substrates are available for strain engineering of PZT such as LaAlO_3 ^[20], YAlO_3 ^[21], LaSrAlO_4 ^[22], and NdAlO_3 ^[23]. In this thesis, we focus on SrTiO_3 substrate as they are known to impose a compressive strain on PZT ferroelectric films and have <3% mismatch with PZT to promote high quality epitaxial growth.

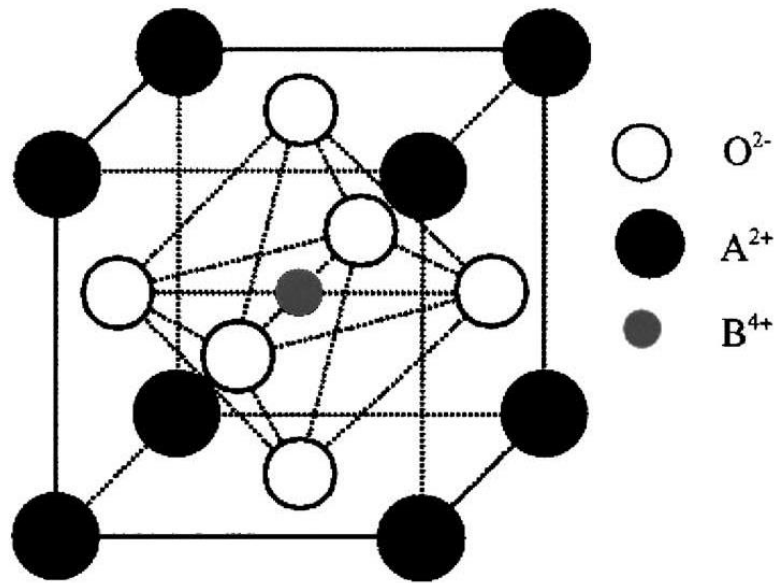


Fig. 1.2. 1 ABO_3 cubic Perovskite structure ^[24]

As shown in Fig. 2.2, the PZT structure changes from tetragonal structure ($x < 0.52$) to rhombohedral structure ($x > 0.52$) as a function of Zr proportion below Curie temperature in ferroelectric state ^[25, 26]. The body-centre ion (Ti^{4+} or Zr^{4+}) of unit cell can be polarised by external electric field in $[111]$ (rhombohedral structure) or $[100]$ (tetragonal structure) direction. In addition, a morphotropic phase boundary (MPB) is found in phase transition diagram. The electromechanical and dielectric properties of PZT are greatly improved at the MPB. The reasons for these are varied and the origin is still under some debates.

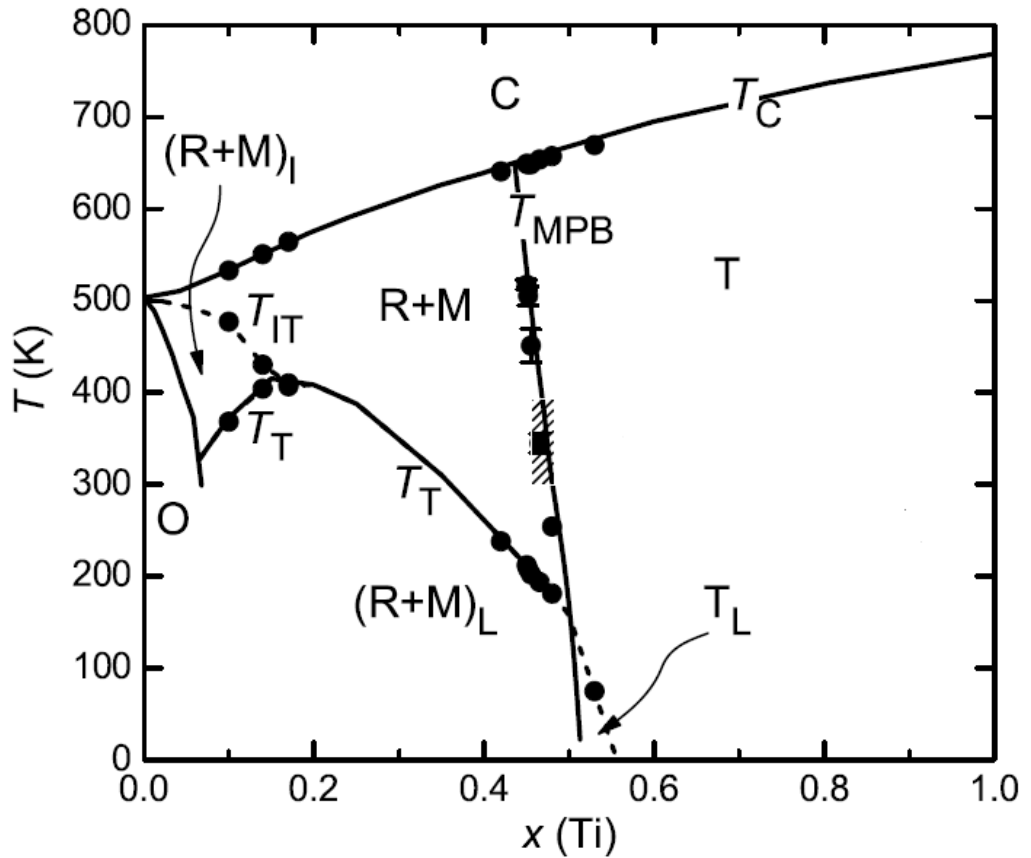


Fig. 1.2. 2 Phase diagram of PZT: C is the paraelectric cubic phase $Pm\bar{3}m$ above Curie temperature, O is the antiferroelectric orthorhombic $Pbam$. All other phases belong to ferroelectric phases: T region is tetragonal $P4mm$, T_L is tilted tetragonal $I4cm$, R+M presents the mixed titled rhombohedral $R3m$ and monoclinic Cm , (R+M)_L is mixed titled rhombohedral $R3c$ and monoclinic Cm , (R+M)_I is mixed rhombohedral and monoclinic with tilted intermediate ^[25].

1.3. Experimental introduction

1.3.1 Ferroelectric thin films synthesis- pulsed laser deposition (PLD)

1.3.1.1 Pulsed laser deposition introduction

Among all techniques in deposition community, PLD has become one of the most popular methods due to its capability for producing the high quality and uniform films and heterostructures with a relatively high efficiency. Target materials are ablated into substrates with stoichiometry composition and desirable uniformity under optimized conditions. Another advantage of PLD is that it is easily to grow

heterostructure. During the deposition, heterostructures or superlattices with careful designs are achievable under program of rotating targets within interval of pulse laser multiple targets can be loaded on a rotating holder to grow samples with different materials.

During the deposition process, a high energy pulsed laser is fired into the target surface to excite the superficial materials. The activated atoms or molecules are combined as thin film on the substrate in the form of plasma plumes. The deposition can be conducted either in ultrahigh vacuum or in specific gas atmosphere. This is the reason that PLD usually is employed to deposit oxides film with oxygen in the deposition chamber ^[27]. Fig. 3.1 shows the common PLD configuration during deposition processes. The laser beam with desired energy and frequency goes through the focussing lens and chamber window firstly to concentrate on the target in a smaller area through a focusing lens to reach high energy density. When the laser beam reach and activate the surficial atoms of target, these excited particles are evaporated to the substrate as plasma plume.

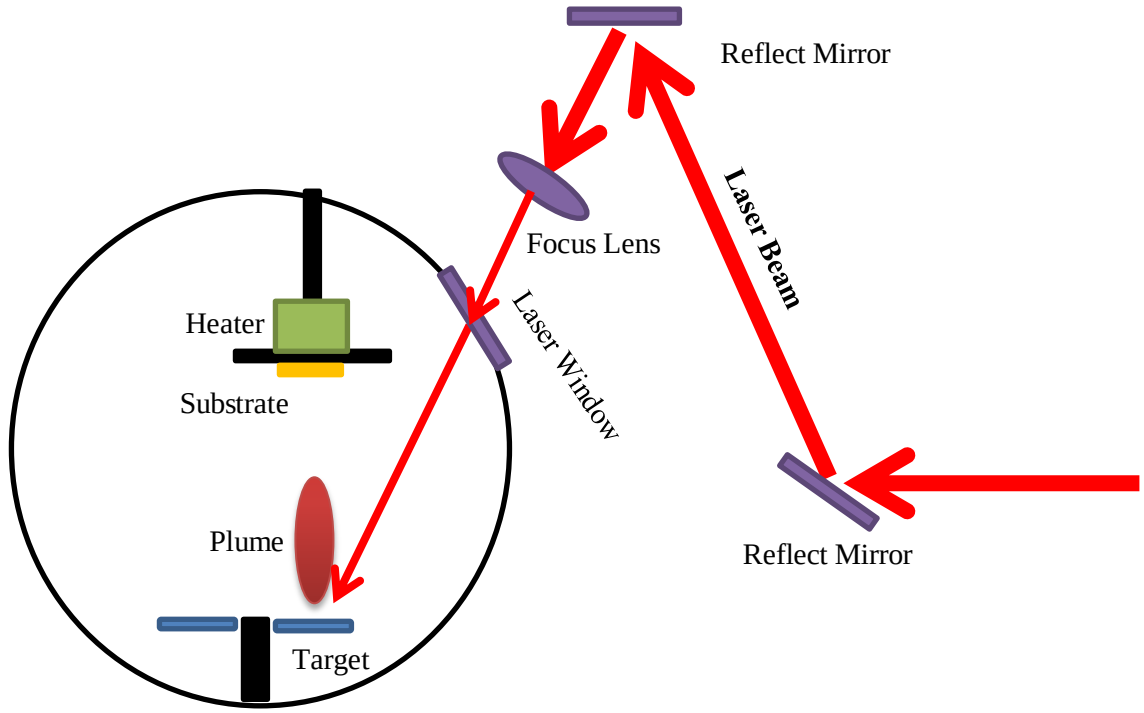


Fig. 1.3. 1 Diagram of Neocera PLD system for samples synthesis in this project

1.3.1.2 PLD for PZT growth:

Knowledge of PZT ferroelectric film growth focuses on Pb loss minimization, pyrochlore phase elimination, surface particles reduction and large-area uniformity. Firstly, laser ablation brings significant changes on surface of targets. The ablation leads to topographical changes which in turn changes the deposition. Thus eventually the deposition rate is altered. The measured deposition rate as a function of the ablation time for PZT targets as shown in Fig 3.2^[28]. As we can see, the growth rate of PZT is not linear, can be expressed as

$$R_{(t)} = (R_0 - R_{\infty})\exp(-t/\tau) + R_{\infty} \quad (1)$$

from Eq. (1) where R_0 is the rate at starting, R_∞ is the rate at infinite time, and τ is the delay time constant. R_0 and R valve relate to laser power density, repetition rate, properties of target (themal conductivity, absorption and melting point) and processing conditions (gas pressure and target-substrate distance).

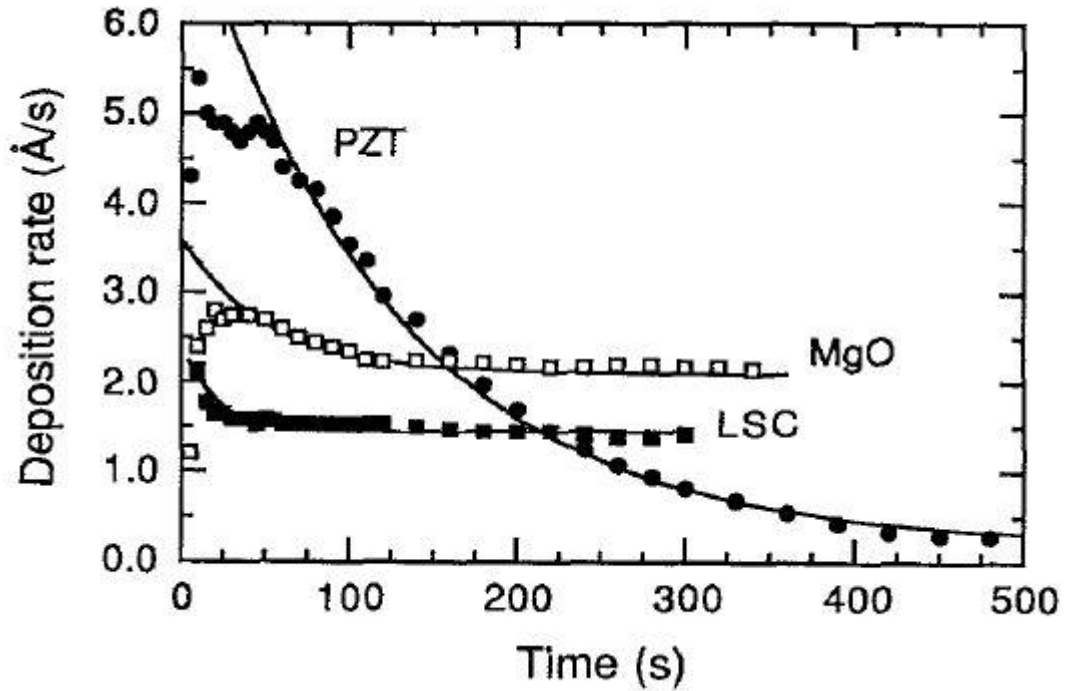


Fig. 1.3. 2 Deposition rate as function of time for PZT, MgO and LSCO targets. The fitting is carried out by equation

(1) Energy dependence of ablation rate for PZT growth:

The laser beam energy is a key factor in optimizing thin films. Laser beam energy can define the initial amount of material to be ablated from targets. There are two general regimes about deposition rates as function of laser energy. One is evaporation regime using lower energy and the other is ablation regime with high energy. In evaporation regime, the relationship of deposition rate and laser energy is nonlinear but appears to be linear in ablation regime^[29]. However, for PZT growth, the deposition rates are almost proportional to input energy. This evidently explains that PZT evaporation rate is comparable with ablation rate so the threshold is covered

between two regimes. Film quality is highly connected with rate regimes as the ablated species distribution can be very diverse from different regimes.

(2) Pressure effects on angular distribution of ablated materials:

Aside the laser energy, the composition stoichiometry and thickness uniformity of deposited film is strongly determined by ablated flux distribution. Background gas plays an important role in shaping angular spread. The ablated flux is clearly visible as plume during PZT deposition. The PZT plume is narrow when the oxygen pressure increases with and the colour changing from white-blue (vacuum) to yellow-orange with white-blue at centre of plume. It is note that the colour transformation of PZT is due to reactions between ablated species and oxygen. In spite of this, the angular distribution of ablated PZT is significantly affected by the working pressure. As studies shown ^[28], the increased oxygen pressure makes ablated distribution more focused. The ablated distribution becomes boarding when oxygen gas is too high because gas scattering effect under high gas pressure. In conclusion, the laser plume narrowing is actually determined by both the working gas pressure and the laser energy. Within in low laser energy regime during ablation, the increased pressure reduces the deposition rate due to scattering effect. In high energy regime, the deposition rate increases initially according to plume focusing effect from high gas pressure. But the deposition rate starts decreasing because too much working gas (for example, the ablation rate of PZT decreases when gas pressure is above 300 mTorr). For non-react working gas, no focusing effect can be observed but scattering effect is still active to decrease deposition rate.

(3) Other factors also influence deposition rates and films qualities:

- Deposition rate changes with time duration. This is because targets' surfaces qualities' variation in the deposition. For instance, during long time growth, the ablation distribution changes dramatically from a fresh polished surface.
- The distance between target and substrate is also important. The ablated plume divides into two parts: front plume has highest flux density and the centre of plume has less working gas according to colour indication. More importantly, the two regions of plume have their own effects on the ablated species energy, the chemical state and ratio of oxygen/ablated species. In border plume region, gas scattering effect greatly decreases the energy of ablated species. However, the reactions of oxygen and ablated species are enhanced at this region during deposition. In the plume focusing region, the ablated species are less affected because ablated materials travel through less oxygen area,

1.3.1.3 Synthesis of electrode films

The electrode-ferroelectric interface is very crucial to the realization of commercial ferroelectric devices^[30]. For example, fatigue can be overcome by replacing the metal bottom electrodes to lanthanum strontium manganite (LSMO)^[31] or strontium ruthenate (SRO)^[32]. The conventional bottom electrodes Pt, normally noble metals, cause large grain boundaries to ferroelectric films even in a nanoscale due to lattice and thermal mismatch. This enhances the degradation of device performances because of charge segregation and decay between ferroelectric layer and electrodes. By applying perovskite bottom electrodes with analogous lattice parameters or pseudo lattice constants (pseudo cubic lattice parameter of is LSMO 3.876Å and the SRO is 3.93Å) to PZT, epitaxy of ferroelectric layer on electrodes is successfully fabricated which results in superior reliability.

1.3.2 Nanoscale imaging of domain dynamics in ferroelectric thin film

1.3.2.1 Piezo response force microscope

Characterizations of piezo response and domain structure are carried out using piezoresponse force microscope techniques^[33]. These approaches provide advanced and fast ways to visualise domain structure and related functions at the nanoscale without damage and easy specimen preparation. As an extension of AFM in contact mode, Piezoresponse Force Microscope (PFM) processing is based on detection of local piezoelectric vibration of the ferroelectric sample by applied reference AC signal. Due to piezoelectric response, the AC bias which feed on sample surface would result sample local displacement to cantilever. Subsequently the vibrated deflection is recorded in response to AC signal on photodiode and picked up by internal amplifier. There are two possibilities of piezo response can be detected from tip-sample interactions. One is vertical deflection which records out-of-plane piezo response component while the other is torsional deflection records in-plane component.

PFM experimental setup is shown in Fig. 3.3, which includes two external lock-in amplifiers are used to tracks in-plane and out-of-plane piezo responses and a conductive tip holder. Due to AC voltage need to apply through tip, conductive tip (Cr/Pt coated silicon tips used in this study, Multi75-G, Budgetsensor) is employed as conductive electrode to determine ferroelectric information of sample.

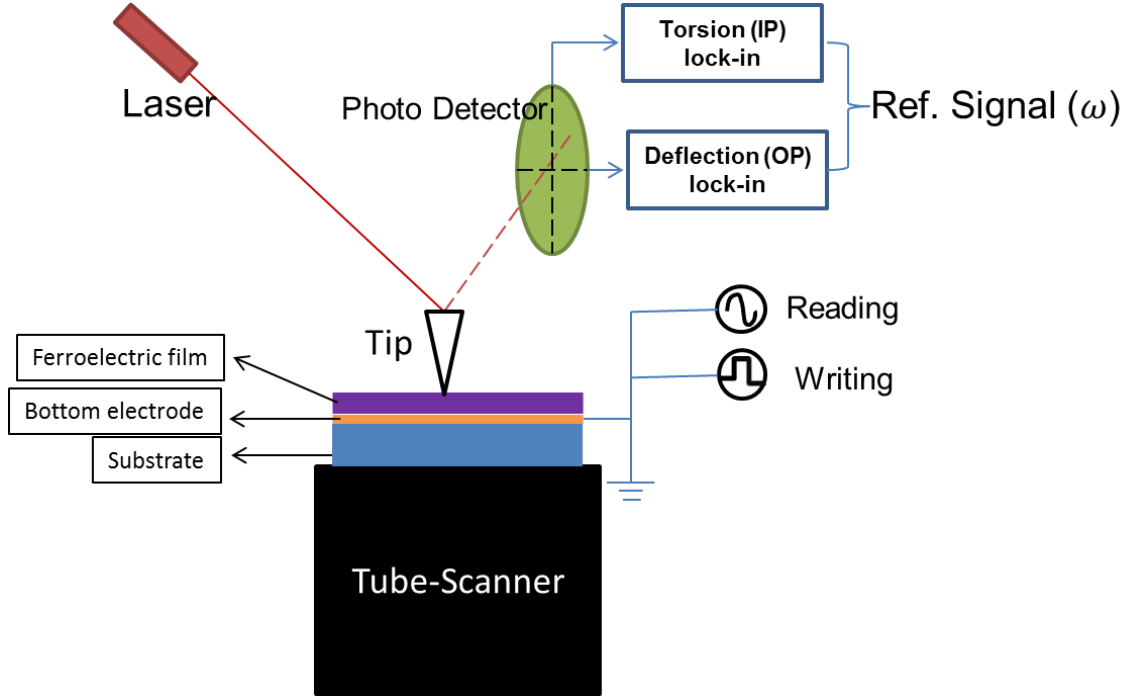


Fig. 1.3. 3 schematic PFM setup for imaging ferroelectric domains

1.3.2.2 Vertical PFM

As Fig. 3.4 (a) indicates, AC voltage places on sample

$$V_{ac} = \sin(\omega t) \quad (2)$$

Surface displacement information of sample depending on external bias are collected from out-of- plane deflection. The relationship between deformation and electric field in vertical direction is defined as

$$z = d_{33}V_{ac} + d_{33}V_{ac}\sin(\omega t + \varphi) \quad (3)$$

where z is small tip movement induced by external electric field and d_{33} is piezoelectric rand-3 tensor component which links to vertical movement ^[34]. The phase φ gives information for different polarization regions in ferroelectric films, i.e. $\varphi = 0^\circ$ means positive voltage causes out-of-plane enlargement when applying to region with downward polarization. On the contrast, in downward polarization areas, the movement

is opposite and $\varphi = 180^\circ$ in eq. (3). Thus, during the PFM scan, three outcomes are obtained including surface topography, PFM amplitude images derived from deflection vibrations of piezo effect and PFM phase images which indicate areas with antiparallel polarization.

Dual AC Resonance Tracking (DART) Mode: To produce measurable feedbacks to single lock-in amplifier, the driving voltage could be as high as several volts in certain materials. However, the ferroelectric polarizations could be reversed or broken down under such high external voltages, especially for ultra-thin films (PZT) in this study, and the detected PFM outcomes are not trust worthy. In addition, many studies have shown that PFM feedback signals are enhanced when tips drive at resonance^[35] so it is promising for nanoscale ferroelectric characterization. However, resonance driving frequency on cantilever also brings significant crosstalk to phase and amplitude measurements^[36, 37]. Thus, we employ DART-PFM in this thesis as it yields accurate PFM measuring at or near resonance without crosstalk issue. As shown in Fig. 3.4 (a), DART mode requires two referenced signal from two separated lock-in amplifier. Conductive cantilevers are continuously driven by two sets of oscillation voltage at resonance frequency during imaging. The sum of deflection is then collected and sent back to two lock-in amplifier with respect to each resource signal. Throughout the scanning, DART mode differs two sets of driving frequency (f_1 is below resonance and f_2 is above) but the difference (Δf) is retained constantly. As shown in Fig. 3.4 (b), the arising amplitudes (A_1 and A_2) are equivalent to each other. Accordingly, PFM crosstalk or other artificial signals are recognised when unequal amplitudes ($A_1 \neq A_2$) appear and eliminated eventually by input frequency adjustment^[38]. All of vertical images in the thesis were achieved using DART mode in Asylum PFM.

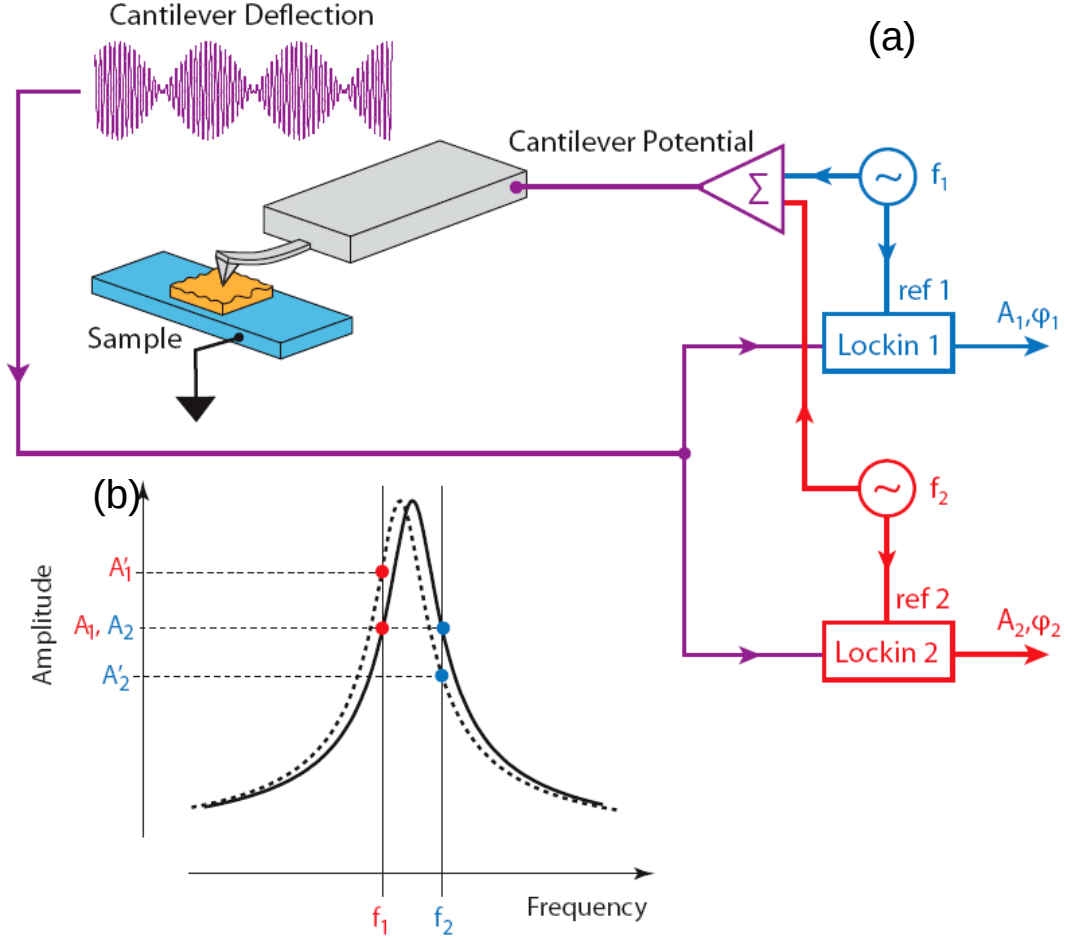


Fig. 1.3. 4 schematic of DART mode PFM setup and (b) In DART mode, the driving frequencies (f_1, f_2) are set near resonance and the piezo amplitudes (A_1, A_2) are monitored to be constant during scanning.

1.3.2.3 Lateral PFM

Lateral PFM refers to the technique which is capable to acquire lateral piezo information from in-plane surface vibrations. Fig 3.5 (b) explains that shear deformation occurs when tip scans across in-plane domains (a domains) ^[39]. The shear deformation is observed through deflection lateral torsion on photodiode. Similar as out-of-plane phase, in-plane PFM phase images are used to determine polar directions as antiparallel polarization is differed during the measurement ^[40]. Combining with vertical PFM, it is possible to draw ferroelectric polarizations in 3-dimensional scales due to the successful description of in-plane and out-of-plane domains^[41] as illustrated in Fig 3.5 (c). Similar as out-of-plane equation, the d_{15} (rand-3 tensor component) is used to describe AC

voltage-induced surface shearing deformation in polarization x (P_x). Accordingly, lateral deflection is defined as

$$\Delta x = \pm d_{15} V_{ac} \sin(\omega t + \varphi) \quad (4)$$

The phase φ contrast also can identify antiparallel domains in x direction. In-plane domains at y direction is achievable by scan same areas after sample 90° rotation.

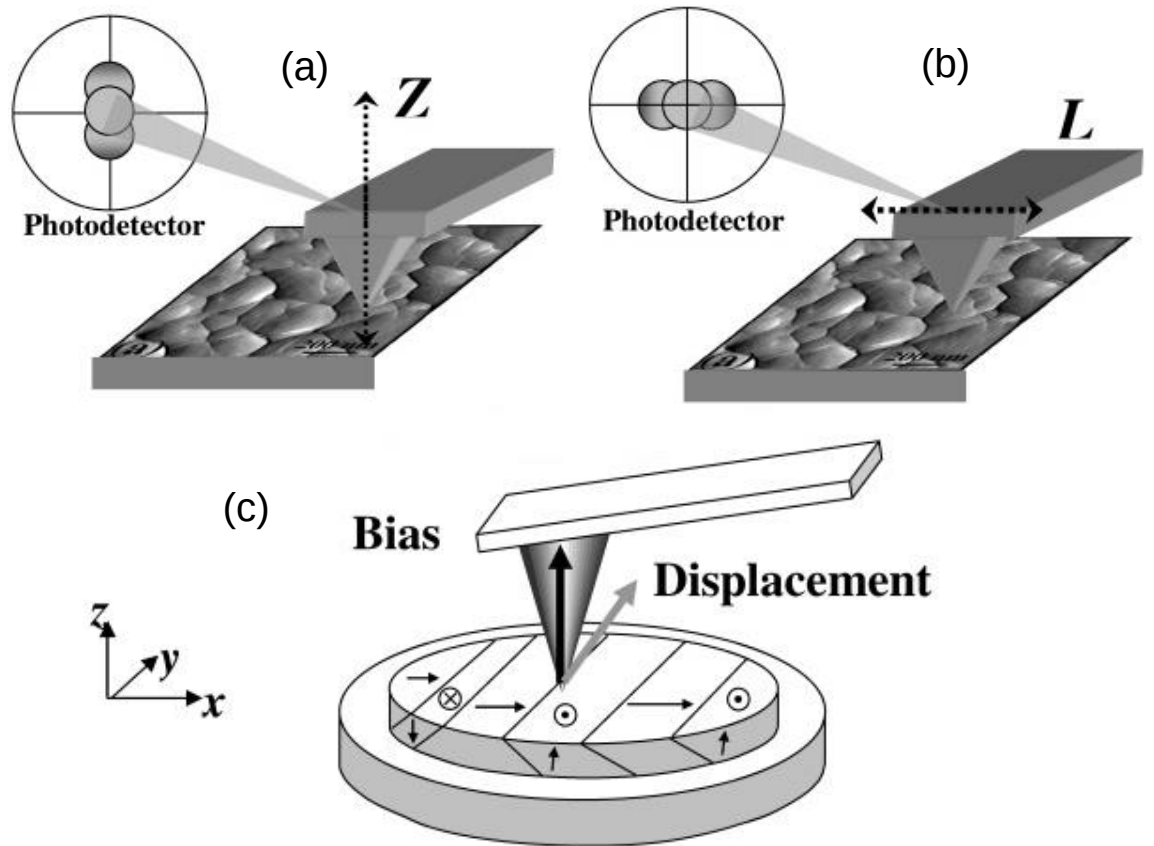


Fig. 1.3. 5 schematic of (a) vertical and (b) lateral vibration during piezo-response force microscope scanning. (c) illustrates 3-dimensional polarization imaging by LPFM and VPFM combination^[42]

1.3.2.4 Lateral PFM flexure or buckling

As explained above, the principle of PFM measurement is determined movement of conductive-AFM probes in response to applied AC voltage. Specifically, vertical

polarization induces out-of-plane electromechanical reaction to cantilever and lateral polarization result in torsional reaction to cantilever which is known as VPFM and LPFM. However, lateral information can be mistaken as vertical deflection in some cases. As shown in Fig 3.6, when in-plane polarization vector or component of in-plane polarization vector aligns with cantilever parallelly, the piezo-response produces longitudinal flexure instead of lateral torsion or vertical movement ^[43].

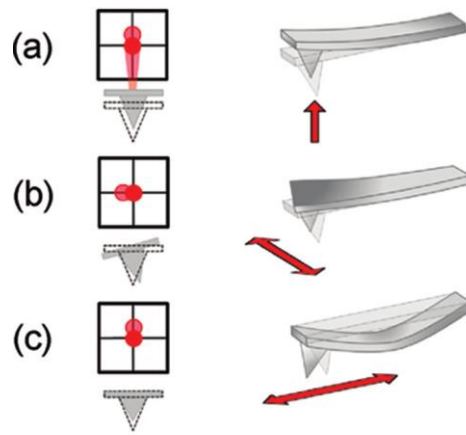


Fig. 1.3. 6 schematic of different cantilever movements includes (a) vertical deflection in response to out-of-plane polarization; (b) lateral deflection in response to in-plane polarization which is perpendicular to cantilever axis; (c) vertical deflection is caused by longitudinal flexure^[44]

1.3.2.5 Spectroscopy modes

Through spectroscopy mode in Asylum PFM, local ferroelectric properties such as local hysteresis loop, imprint and coercive voltage are easily attainable. The ability of ferroelectric detection using a conductive cantilever realizes characterizations in nanoscale, for example on grain boundaries of domain or films' defects. However, the accuracy for cantilever on desirable locations is hard to achieve due to drifting of macroscopic. Switching spectroscopy PFM (SS-PFM) is a new approach to validate spectroscopy mapping in real space. Combining with scanned topography and PFM

images in the identical areas, the local ferroelectric performances can be related with positions within ferroelectric materials or nanostructures. A sine wave is used in SS-PFM which consists of square steps with constant time interval and the voltage is re-set to zero between voltage steps. SS-PFM is capable to determine ferroelectric hysteresis loops in a grid map on surface. In addition, input signal is programmable on users' requirement.

Chapter 2 Reversible polarization rotation in epitaxial ferroelectric bilayers

Abstract

Polarization rotation engineering is a promising path to giant dielectric and electromechanical responses in ferroelectric materials and devices. In this work, we demonstrate robust and reversible in- to out-of-plane polarization rotation in ultra-thin (nanoscale) epitaxial (001) tetragonal $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (PZT-T)/rhombohedral $\text{PbZr}_{0.55}\text{Ti}_{0.45}\text{O}_3$ (PZT-R) ferroelectric bilayers. An underlying 20 nm thick PZT-R layer reduces the symmetry in a 5nm-thick PZT-T layer by imposing an in-plane tensile strain while simultaneously decoupling the PZT-T layer from the substrate. This prevents clamping and facilitates large-scale polarization rotation switching ($\sim 60 \mu\text{C}/\text{cm}^2$) and an effective d_{33} response 500% ($\sim 250 \text{ pm}/\text{V}$) larger than the PZT-R layer alone. Furthermore, this enhancement is stable for more than 10^7 electrical switching cycles. These bilayers present a simple and highly controllable means to design and optimize rotational polar systems as an alternate to traditional composition-based approaches. The precise control of the subtle interface-driven interactions between the lattice and the external factors that control polarization opens a new door to enhanced – or completely new – functional properties.

2.1. Introduction

Ferroelectrics are an important class of ferroic materials in which the order parameter - spontaneous polarization - is defined by the distribution of charge within the crystalline structure^[6]. Under an external electric field, polarization couples to a strong, anisotropic electromechanical response. The traditional approach to electromechanical

enhancement is therefore to align the polarization vector parallel to the field direction. However, a newer, and more effective approach, is *polarization rotation engineering*, in which the polarization vector is canted away from its nominal direction such that it rotates under off-axis applied fields ^[45]. Such rotational polar domains can result in giant piezoelectric and dielectric coefficients up to 3000 times larger than the intrinsic lattice expansion^[46].

Canting the polarization vector necessitates a phase transition from the higher-symmetry structure (e.g. tetragonal), where the spontaneous polarization vector is restricted by symmetry to specific crystallographic directions, to a lower-symmetry structure (e.g. monoclinic) where it is confined to only a plane^[47]. This has previously been attempted through chemical modification (classically through a morphotropic phase boundary) ^[48] or complex microstructural configurations^[49]. In bulk single crystals or ceramics this may be induced through large hydrostatic pressure (several GPa) without mechanical failure^[50].

In epitaxial thin films, polarization rotation engineering is achieved by carefully tuning the electrical and mechanical boundary conditions. In the simplest case, symmetry can be lowered through epitaxial strain alone ^[51]: low-symmetry phases with rotational polar domains can be induced in a nominally tetragonal film with out-of-plane spontaneous polarization (i.e. along the *c*-axis) by applying an in-plane tensile strain (Fig. 2.1(a)). Catalan *et al.* ^[52] reported strain-induced rotational monoclinic *ac* and *r* phases (nomenclature first suggested in ^[53] and then expanded in Pertsev ^[51]) in 5nm-thick lead titanate (PbTiO₃) grown coherently on DyScO₃ substrates. However whether an applied electric field would re-cant the polarization or not was not discussed. The most plausible outcome would be that the substrate induced constraint would have

pinned the polarization moment. First-principles theoretical studies also suggest this can be achieved through phase transitions that help polarization screening in order to minimize the electrostatic energy related to a depolarization field^[54] That is, for ultra-thin films the electrical boundary conditions are equally important. Indeed the combination of both electrical- and strain-driven transitions has also been exploited in PbTiO₃-based bi- and trilayer ferroelectric superlattices to induce polarization rotation and enhance electromechanical properties^[55, 56]. Crucially, however, the best-performing superlattices had tetragonality greater than one (based on average lattice parameter), meaning that - although canted - the polarization vector was predominantly out-of-plane. In other words, tuning the interface boundary conditions such that canting of the “as-grown” polarization vector causes it predominantly lie along in-plane direction, and its subsequent reorientation to an out-of-plane direction still remains elusive. Achieving this is significant as such re-orientation would result in some of the highest electromechanical strains, and hence piezoelectric coefficients possible. More recently, Noheda *et al.* ^[57] showed that a monoclinic phase could be induced in tetragonal barium titanate (BaTiO₃) under appropriate mechanical and electrical boundary conditions. In this case, piezoresponse force microscopy (PFM) demonstrated in-plane domain switching and robust piezo-hysteresis loops, albeit without quantitative measurements of the effect of polarization rotation. Whether it is ever possible to achieve reversible rotation of an in-plane canted polarization to out-of-plane under an applied electric field therefore remains an open question.

The key obstacle to realizing the full potential of rotational polar domains is that the substrate-induced clamping is simply too strong – the very substrate that drives the polarization rotation also inhibits switching. This necessitates not only an innovative

means of inducing the tensile strain-driven polarization rotation, but also a simultaneous consequence of eliminating mechanical constraints to the polarization switching.

We show reversible polarization rotation can be achieved in ultra-thin (nanoscale) epitaxial (001) tetragonal $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (PZT-T)/rhombohedral $\text{PbZr}_{0.55}\text{Ti}_{0.45}\text{O}_3$ (PZT-R) ferroelectric bilayers. We induce a rotational phase in the top T-layer by growing it on an intermediate R-layer with entirely different symmetry from the cubic SrTiO_3 substrate. The driving principle is schematically shown in Fig. 2.1(b). The PZT-R layer reduces the symmetry in the PZT-T layer above by imposing an in-plane tensile strain while, crucially, decoupling it from the underlying substrate. Thus it behaves like an intermediary electroactive channel, as opposed to being just a passive strain template. This prevents clamping from the substrate, facilitating uninhibited (i.e. unpinning) in- to out-of-plane polarization switching ($\sim 60 \mu\text{C}/\text{cm}^2$) and an effective d_{33} response 500% ($\sim 250 \text{ pm/V}$) larger than PZT-R layer alone. Furthermore, this rotation mechanism is stable for more than 10^7 electrical switching cycles. Though inherently simple in concept and execution, this approach breaks a fundamental impasse for thin film ferroelectrics, defining a new and exciting opportunity for integrable nanomaterials with giant electromechanical properties.

As an alternate to traditional (and often laborious) approaches of property enhancement through compositional modification, the demonstrated strain engineering approach is simpler and more precise; it facilitates new materials with giant electromechanical properties by exploiting the subtle interface-driven interactions between the lattice and the external factors that control polarization direction.^[58]

2.2 Results

The bilayer approach was carried out using 5 nm-thick PZT-T and 20 nm-thick PZT-R layers on an underlying 15 nm-thick $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ buffer layer on a (001)-oriented SrTiO_3 substrate (illustrated in Fig. 2.1c), with all layers grown by pulsed laser deposition. The room-temperature bulk lattice parameters of the PZT-T layer are ~ 0.396 nm in-plane (a -axis) and ~ 0.411 nm an out-of-plane (c -axis) at room temperature, compared to $a=b=c \sim 0.410$ nm ($\alpha = 89.3^\circ$) for the PZT-R layer. Thus, neglecting the effects of the substrate and the ferroelectric phase transitions, we can estimate that the PZT-T layer will be subject to a 3.4% in-plane tensile strain within the bilayer - a magnitude more than sufficient to cant the spontaneous polarization vector in the PZT-T layer. Both films were deposited at a growth temperature of 700°C and have similar coefficients of thermal expansion. The thickness, smoothness and interfacial quality (i.e. distinctness) of the layers was confirmed by transmission electron microscopy (TEM) (Fig. 2.1(d)). The arrows in the inset to Fig. 2.1(d) highlight fine domains, which we will discuss later. Fig. 2.1(e) and 1(f) are vertical and lateral piezoresponse force microscopy (PFM) images of the as-grown state. Utmost care was taken to reduce artifacts including photodiode and cantilever induced cross-talk (detailed in the appendix materials), and separating the contributions of the R- and T- layers in the observed contrast was not trivial. However, these challenges do not undermine our key observation: very strong in- and out-of-plane domain contrast. This is crucial, as it implies that polarization vectors must have both in- and out-of-plane components – in other words, they must be canted.

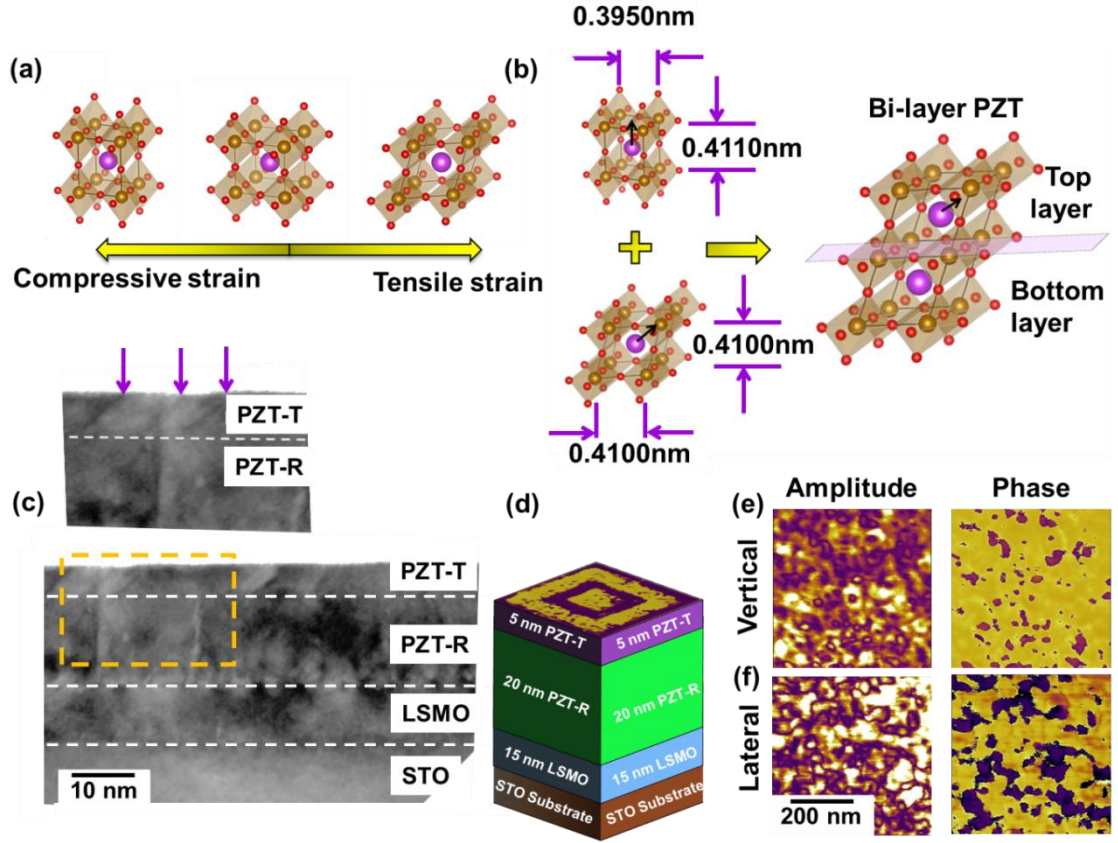


Fig. 2. 1 (a) Schematic of strain tuning of ferroic phase transitions in epitaxial perovskite thin films. (b) Concept of $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (PZT-T)/rhombohedral $\text{PbZr}_{0.55}\text{Ti}_{0.45}\text{O}_3$ (PZT-R) ferroelectric bilayers. A low-symmetry rotational phase is induced in the top PZT-T layer by applying an in-plane tensile strain imposed by the underlying PZT-R layer. (c) Pictorial depiction of the complete oxide heterostructure investigated here (d) TEM cross-section of the sample. The arrows indicate possible domain walls. (e) Vertical Piezoresponse Force Microscope (VPFM) and lateral PFM (LPFM) Fig. 2.1(f) for the as grown bilayer structure. Clear curved domain walls are seen in both, signifying that the polarization vector for the bilayer has both components, and is therefore tilted.

As a first validation of our bilayer approach, we predicted the domain and crystallographic state for the PZT-T layer using phenomenological phase field modeling developed specifically for this bilayer configuration^[59] (See Appendix A1.1. for details). The model predicted a domain structure (see Fig. 2.2(a)) with fine 8-10nm domains in the T-layer and coarse 20-40nm domains in the R-layer. Due to inter-layer and inter-domain misfit strains,^[60] these two microstructural types are intergrown, with an adaptive structure across the interface and small R-type domains extending to the top

surface of the bilayer. The R-type regions have an appreciable vertical polarization component P_z of $\sim 0.4 \text{ C/m}^2$ (Fig. 2.2(b)) in comparison to the predominantly in-plane polarization (*i.e.* P_z of $\sim 0 \text{ C/m}^2$) in the T-layer. This variation in P_z is sufficient to cant the spontaneous polarization vector by an average of 2° across the sampling surface and up to 10° in the R-type regions, shown in Fig. 2.2(c). Such canting demands a transition to monoclinic crystal symmetry, which in turn allows the formation of ultra-fine domains with r_1/r_2 walls. These localized regions of monoclinic nano-domains are shown as an inset to Fig. 2.2(c), and provide a likely explanation for the similar structures highlighted in Fig. 2.1(d).

Simulated ferroelectric switching measurements of the bilayer demonstrates classic polarization-voltage (P-V) hysteresis with a saturation polarization of $\sim 50 \mu\text{C/cm}^2$ and a coercive voltage of $\sim 1 \text{ V}$, shown in Fig. 2.2(d) for a bias range from -4V to +4V. The evolution of the domain structure during the switching process (Appendix A1) shows that the fine in-plane domains vanish at large electric field magnitude in favour of large R-type domains with curved 71° walls. This results in significant electric-field-induced polarization rotation, with a correspondingly large value for the piezoresponse coefficient of $d_{33} \sim 120 \text{ pm/V}$ (calculated by $d_{33} = \frac{du_3}{d\phi}$) - more than double the value typically observed for substrate-constrained single-layer PZT-T films.

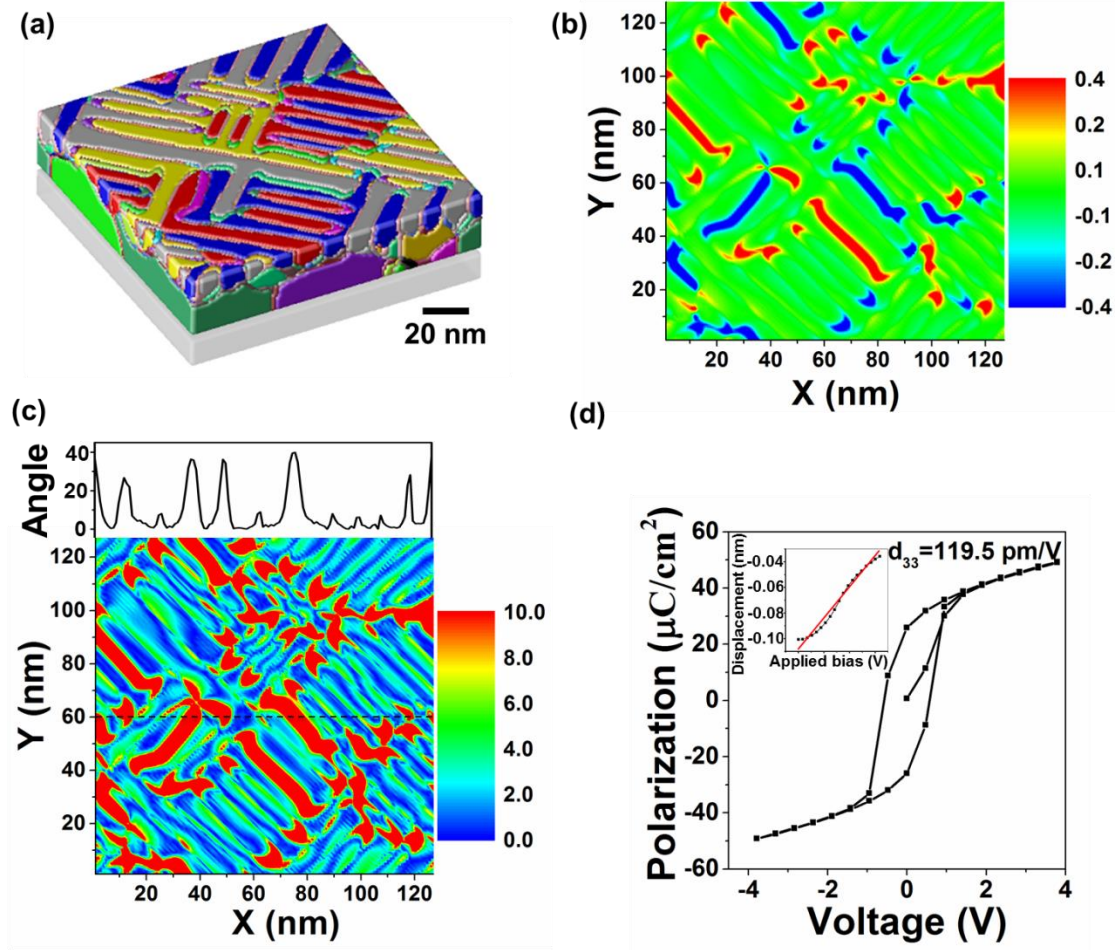


Fig. 2. 2 Phase field simulations (a) Domain structure predicted for the bilayer based on phase-field thermodynamic simulations. (b) Out-of-plane Polarization (P_z) map which shows T-like domains (green) mixed with R-like domains (blue and red.) (c) Map of the canting angle, defined as the angle between the spontaneous polarization and in-plane component vectors, $\sin\theta = \frac{P_z}{P}$. The T-like and R-like domain are actually monoclinic structure with inset showing the canting angle profile across the black line running along the centre. (d) Simulated P-V hysteresis loop of bilayer with calculated d_{33} (~ 119 pm/V) as inset.

Having established the thermodynamic feasibility of the bilayer approach, we now provide evidence that the as-grown bilayers possess the structural conditions necessary for rotational polar domains. For this, we utilize a range of X-ray diffraction (XRD and transmission electron microscopy (TEM))-based instruments and techniques, described in the Methods. Note that all Miller indices are given in the pseudo-cubic notation.

To first determine whether the T-layer is subject to an in-plane tensile strain from the underlying R-layer, we measured the out-of-plane lattice parameters using high-resolution XRD θ -2 θ measurements of the 001 and 002 Bragg reflections (Fig. 2.3(a)). The lattice parameters, detailed in Table 2.1, were extracted using a simulation program that accounts for interface effects from the multilayer structure ^[61] (fits given in appendix A1.2.1.). The out-of-plane lattice parameter (~ 0.399 nm) for the PZT-T phase is significantly less than the bulk value (~ 0.411 nm) and is concomitant to an imposed in-plane tensile strain. The R-layer, on the other hand, is completely relaxed, with a lattice parameter of ~ 0.410 nm.

Table 2. 1 Comparison of the in-plane and out-of-plane lattice parameters measured for the ultra-thin bilayer via different techniques.

	T PZT in-plane	T PZT out-of-plane	R PZT in-plane	R PZT out-of-plane
TEM	0.4110 ± 0.0002 nm	0.3980 ± 0.0011 nm	0.4060 ± 0.0025 nm	0.4060 ± 0.0025 nm
ARSM 103	0.4072 ± 0.0005 nm	0.3990 ± 0.0003 nm	0.4091 ± 0.0110 nm	0.4091 ± 0.0110 nm
ARSM 113	0.4064 ± 0.0004 nm	0.3983 ± 0.0001 nm	0.4090 ± 0.0050 nm	0.4090 ± 0.0050 nm
ARSM -103	0.4078 ± 0.0006 nm	0.3991 ± 0.0002 nm	0.4096 ± 0.0048 nm	0.4096 ± 0.0048 nm
HR XRD		0.4001 ± 0.0002 nm		0.4096 ± 0.0005 nm
Fitting		0.3991 ± 0.005 nm		0.4091 ± 0.002 nm

We can similarly conclude that the R-layer dictates this misfit strain on the T-layer by assessing asymmetric reciprocal space maps (ARSMS) around the 103 and 113 reflections (Fig. 2.3(b-d)). No satellite reflections, indicative of periodic domain modulation^[57], are evident, and inspection of the crystal truncation rods (CTRs) positions along the in-plane axis reveals that, whilst the PZT-T layer is pseudomorphically constrained to the PZT-R layer, the PZT-R layer itself is not constrained to the underlying LSMO/STO lattice. Electron energy loss spectra (EELS) mapping using an aberration-corrected scanning transmission electron microscope (STEM) of the Ti-L_{2,3} edges (Detailed in A1.2.2) was performed across the T/R layers to accurately identify the interface. The EELS mapping confirmed an atomic level sharpness of the T/R interface. (Fig A1.2). This means the structural details discussed below are purely from an epitaxial strain engineering perspective as opposed to chemical redistribution to relax the strain.

The ARSMs also shed light on the directionality of the T-layer polarization component: the in-plane *a*-axis lattice parameter (0.4015 nm) is larger than the out-of-plane *c*-axis lattice parameter (0.399 nm), implying that the T-layer possesses an induced in-polarization component. This constitutes the first structural requirement to cant the polarization moment. The symmetry reduction from tetragonal to monoclinic is evidenced in the slight difference between the out-of-plane lattice parameters extracted from the $\bar{1}03$ ARSM, given in Table 1 (for tetragonal or cubic phases they should have the same d-spacing). Note the marked asymmetry in the shape profile of the T-layer peak in the 103 ARSM. The “comet” like profile hints at more than one peak in the in-plane direction. This was previously shown to arise from a symmetry change to M_A type monoclinic phase,^[56, 62] however, the counts are insufficient to confidently fit the peak profile in this instance. We thus performed selected area electron diffraction (SAED)

analysis. Fig. 2.3(e) is the SAED pattern acquired for the bilayer along [310] zone. The T-layer shows clear peak splitting in the $1\bar{3}l$ family of reflections along the in-plane direction. The lattice parameter of the PZT (T) using SAED was calculated to be out-of-plane 0.3979 ± 0.0019 nm and 0.4107 ± 0.0002 nm (detailed in **A1.3**). Based on the XRD and the TEM SAED analysis we can conclude that the PZT-T layer is induced into a monoclinic M_A phase.

While these results strongly suggest the successful creation of an in-plane tensile strained PZT-T layer, one must be cautious. We have previously shown that, under certain thickness conditions, bilayers demonstrate a highly-dense tetragonal ferroelastic polydomain (either $c/a/c/a..$ or a_1/a_2) structure that can release the epitaxial constraint, while being difficult to detect by diffraction techniques due to size and strain effects^[63]. In such cases, the XRD profiles show a single, broad peak (as opposed to e.g. 00l/100 splitting) similar to the domain-free state.

To ascertain the absence of any tetragonal ferroelastic domains in our bilayer, we measured high-resolution reciprocal space maps of the 002 Bragg peak at beamline ID06 at the European Synchrotron (ESRF). The high brilliance and angular resolution in comparison to lab-based instruments enable such nano-domain topologies to be identified. The measurement sampled a 0.5×0.5 mm area of the sample. Fig. 2.3(f) shows a close-up of the T-layer peak, which is obliquely elongated with a non-uniform intensity distribution, characterized by two distinct sub-peaks. While this could be misinterpreted as evidence of c/a tetragonal ferroelastic domains, it is unlikely. A tetragonal structure described by these two peaks would have a tetragonality ratio of 1.00031, and thus a misorientation between neighbouring domains of 0.0176° , or $5.2 \times 10^{-3} \text{ \AA}^{-1}$ in Q_x or Q_z . Yet, the measured broadness of the peak is less than 1.5×10^{-4}

$\text{\AA}^{-1}$ – thirty-five times smaller. We therefore conclude that the T-layer does not outwardly exhibit any evidence of tetragonal symmetry from the 002 reciprocal space map, implying that the non-uniformity of the local peak structure is due to strain inhomogeneity across the relatively large sampling region. This strain is of the order of 0.1% and, although its inhomogeneity was not directly measured, we note that it is consistent with in-plane strain gradients. A similar behaviour was reported for trilayer superlattices where strain gradients were attributed to the 180° polydomain configurations^[56].

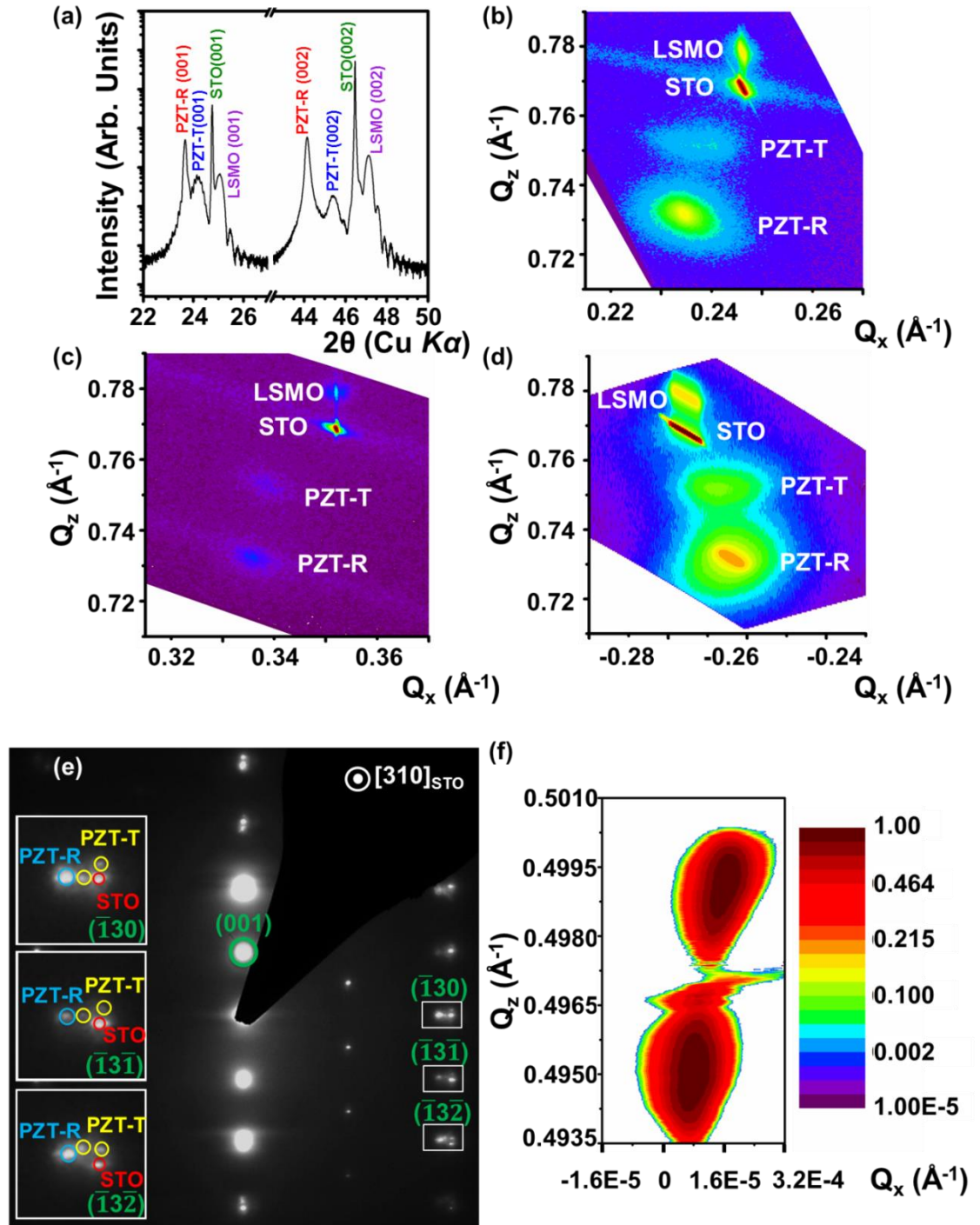


Fig. 2. 3D Diffraction analyses- (a) Normal coupled θ - 2θ XRD with Bragg 001 and 002 peaks. (b-d) Asymmetric Reciprocal Space Maps (ARSM) round (103), (113) and (103̄) reflections to investigate the in-plane and out-of-plane parameters of the bilayers (e) selected-area electron diffraction pattern along the [310] zone. The (13̄ l) family of reflections show peak splitting for the T-phase confirming M_A symmetry. (f) is a close-up of the T-layer peak in (002) Bragg acquired by high-resolution RSM at the European Synchrotron.

The structural measurements therefore imply that the strained T-layer should demonstrate both in- and out-of-plane polarization components. To confirm this, vertical and lateral piezoresponse force microscopy (PFM) phase and amplitude images were acquired (Fig. 2.4(a)). Although the individual domains are quite small (~30-50 nm), both the domain walls and any contrast within the domains are clearly resolvable. However we cannot resolve the striations predicted by the phase field studies, probably due to very fine domain periodicity.

The images acquired via PFM can be easily affected by cantilever-induced effects such as flexure^[44, 64], photo-detector cross-talk^[65] and the laser's location on the cantilever^[66]. Proving 3D polarization therefore requires: (i) rotating the samples so as to separate true out-of-plane signals from flexure, (ii) correctly positioning the laser on the tip to minimize cross-talk (which is dependent on both the type of tip and the beam geometry) and (iii) understanding the phase image both off and at resonance. To satisfy points (ii) and (iii), laser spot position dependent PFM images were acquired off and at resonance (see appendix A1.3.2), which allowed us to correct for any cross-talk or phase-related artifacts. Using the optimized imaging conditions thus obtained, Angle-resolved PFM images (shown in Fig. 2.4) were captured by rotating the samples to three different directions (0°, 45° and 90°) in the same manner used to deterministically identify variants of the monoclinic phase in bismuth ferrite (BiFeO₃)^[67]

To show that the contrast stems from ferroelectric polarization, we applied a DC bias (± 4 V) to write square domain patterns to the film and study its switching behavior. Larger area scans of the full written areas are given in appendix A3.3. Clear phase contrast for all three rotation directions in vertical (V-) and lateral (L-) PFM images indicate the existence of a piezoresponse. The individual directions were identified

using a protocol previously developed by for such bilayers.^[68] The external bias is expected to induce a change in the out-of-plane contrast due to domain switching along the c -axis, visible in Fig.2.4(a) between the regions subject to +4 vs. -4V bias. However, we also found some nanoscale regions that change phase contrast in the VPFM as function of sample rotation angle (see the white boxed region in Fig. 2.4(a)). Previous reports show that this originates from tip flexure induced by an in-plane component.^[44] On the other hand, we observe a change in the lateral PFM (LPFM) images depending on the orientation of the written bias (positive vs. negative), which gives the polarization information in the forwards and backwards in-plane directions. Based on the XRD analysis, we can make a schematic for the possible polar orientations as sketched in Fig. 2.4(b). The M_C or M_A phases should have a total of 16 variants. Of these, 8 variants with downward (upward) out-of-plane polarizations will be stable under a positive (negative) applied field. This then allows identification of the individual polarization components for each nanodomain, exemplified in Fig. 2.4(d), which is for the boxed regions in Fig. 2.4(a). Table 2.2 is a guide for interpreting the resulting PFM contrast. Crucially, it provides unequivocal evidence that these domains possess both, in-plane and out-of-plane polarization components.

Table 2. 2 A guide to the PFM contrast observed in Fig. 2.4.

Position	Polarization Axis	0° Scan Out-of-Plane/In-Plane	45° Scan Out-of-Plane/In-Plane	90° Scan Out-of-Plane/In-Plane
1	c'	Downwards/Onwards (Bright/Dark)	Downwards/Onwards (Bright/Dark)	Downwards /Onwards (Bright/Dar k)
2	b	Upwards/Backwards (Dark/Bright)	Upwards/Backwards (Dark/Bright)	Upwards/Ba ckwards (Dark/Brigh t)
3	c'	Downwards/Onwards (Bright/Dark)	Downwards/Onwards (Bright/Dark)	Downwards /Onwards (Bright/Dar k)
4	d'	Downwards/Backwards (Bright/Bright)	Downwards/Onwards (Bright/Dark)	Downwards /Onwards (Bright/Dar k)

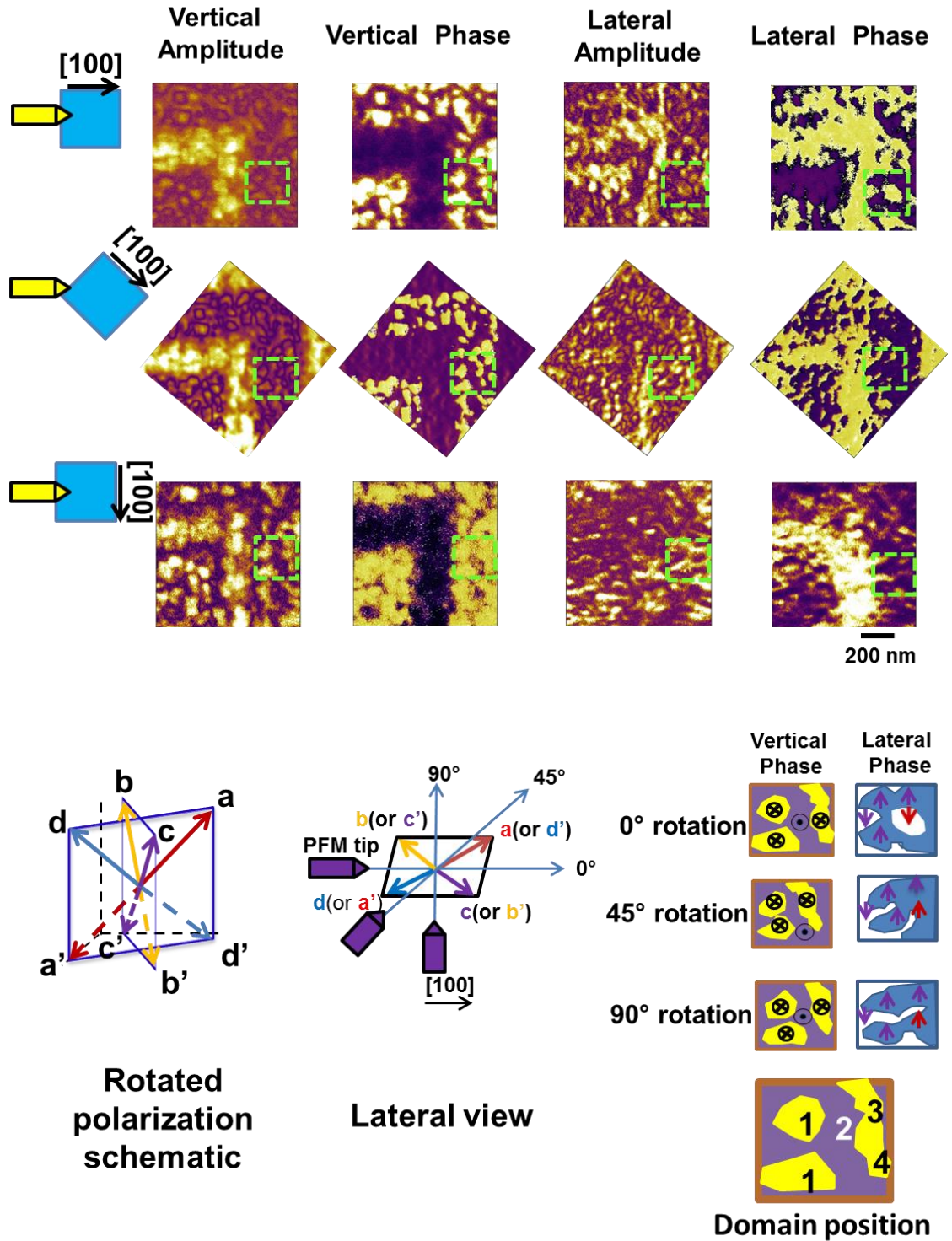


Fig. 2. 4: (a) Vertical and Lateral Piezoresponse Force Microscopy (VPFM, LPFM) images) of the bilayer after application of local bias as a function of rotation angle. The relationship between scanning direction and substrate is depicted on the left hand side. The scans are $\sim 800 \times 800$ nm in size. Full scans can be found in the appendix. (b) Schematic of the polarization rotation for a monoclinic cell. (c) Relationship between in-plane polarization and tip scanning direction (d) Fully-resolved vector polarization map for nanoscale region in the box of Fig. 2.4(a).

Clearly in-plane and out-of-plane domains are observed confirming the presence of a canted polarization state.

Finally, we demonstrate the effect of this induced symmetry lowering and polarization rotation on the measured functional properties. Fig. 2.5(a) shows the P-V hysteresis loops acquired for three samples: (i) the ultra-thin bilayer investigated here (red) and two control samples comprised of (ii) an (001)-epitaxial 100 nm thick single R-layer (blue) and (iii) a thick (001) epitaxial bilayer with the same PZT composition, but 100 nm thick R- and T-layers (black). Details of the synthesis, structure and behavior of the control samples can be found in ^[68]. The voltage is applied along the normal to film (i.e. along the *c*-axis). The ultra-thin bilayer has a robust P-V loop with square shape and full saturation, and is able to sustain an applied bias of 10V without breakdown. The remanent polarization is $35 \pm 5 \mu\text{C}/\text{cm}^2$ - in very good agreement with the theoretical predictions made in Fig. 2.2, but smaller than that of both control samples. This is expected because the single R-layer ($P_{r,\text{thin}}$ of $50 \pm 5 \mu\text{C}/\text{cm}^2$) is fully *c*-axis oriented, whereas the polarization response of the thick bilayer ($P_{r \text{ thick}} = 65 \pm 5 \mu\text{C}/\text{cm}^2$) originates from *c/a* domain switching ^[68]. The coercive voltage for the ultra-thin bilayer is also relatively high ($\sim 5\text{V}$) compared to the control samples. Given the predominantly in-plane polarization for the ultra-thin bilayer, the large coercive bias is a reflection of the energy barrier that needs to be overcome to induce switching from in- to out-of-plane polarization states. The large threshold bias relative to the phenomenological calculations can be accounted for by pinning effects (substrate-induced) that were not accounted for in the calculation. In order to avoid complications from spurious contributions, such as leakage or space-charge driven effects, positive-up negative-down (PUND) pulsed-polarization switching data (ΔP) was acquired as a function of applied voltage with 1 μs pulse width (inset to Fig. 2.5(b)). The measured (ΔP) reaches a maximum value of $60 \pm 5 \mu\text{C}/\text{cm}^2$.

To test the long-term stability of the polarization rotation mechanism, we subjected the ultra-thin bilayer to polarization fatigue testing using 100 μs pulse interval *via* PUND (Fig. 2.5(b)). The bilayer demonstrates high fatigue resistance despite the lack of a top oxide electrode. Robust switching behavior continued up to 10^8 cycles with a ‘wakeup’ process around 10^7 cycles where ΔP starts to increase. We are presently unable to explain this recovery process, and aim to address this in the near future. The square hysteresis behavior and the PUND data confirm the ultra-thin bilayer is able to achieve electric-field driven polarization rotation and in-plane to out-of-plane switching.

As a final comparison of the bilayer and control samples, we present the effective out-of-plane piezo coefficient (d_{33}) acquired via PFM (Fig. 2.5(c)). To ensure uniform electric field dependence and reduce tip-induced local effects, the d_{33} loops were acquired on capacitors with top electrodes identical to those used for the P-E and C-V tests. Although the use of PFM hysteresis to quantify the d_{33} response is subject to controversy^[69], we can make *qualitative* comparison using calibrated samples such as the single R-layer. We find that the ultra-thin bilayer demonstrates a piezoresponse $\sim 500\%$ of the single R-layer and comparable to the thick bilayer. The single R-layer is clamped to the substrate and a number of reports estimate its value to be $\sim 70 \pm 5$ pm/V. Thus, a direct simple extrapolation would estimate the piezoelectric coefficient of the ultra-thin bilayer to be in $\sim 200\text{-}300$ pm/V regime -remarkable considering the 25 nm total thickness. Despite its in-plane polarization vector, the strong out-of-plane d_{33} hysteresis response reinforces the observation of polarization rotation under an applied electric field. Other methods of quantification such as *in-situ* electric-field dependent XRD and interferometry are underway to complement the data presented here.

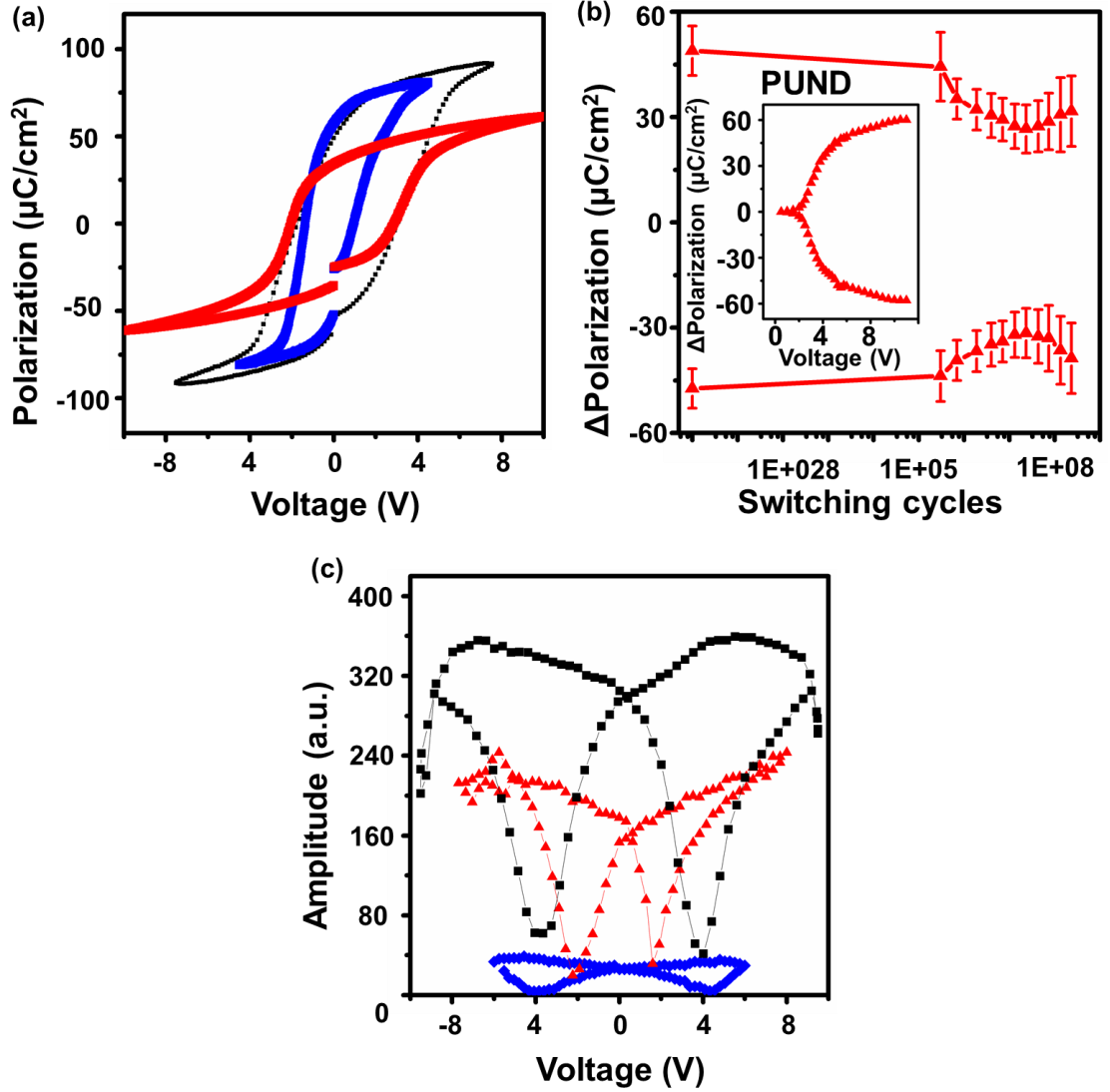


Fig. 2. 5 functional properties measurements, i.e. (a) is comparison of P-V loops of ultra-thin bilayer (red) with control samples of single R layer (blue) and thick bilayer (black), (b) Fatigue testing for the ultra-thin bilayer. The inset is the corresponding PUND measurement. (c) compares the d_{33} loops acquired via PFM for all three samples. To ensure uniform field distribution and mitigate local electromechanical effects the loops were acquired using a metallic top electrode.

2.3. Conclusion

In summary, we present theoretical, structural and electromechanical results that strongly indicate the presence of symmetry lowering and reversible polarization rotation domains in an ultra-thin epitaxial bilayer. We are aware that these three different experimental datasets, namely structural diffraction analysis, vector PFM and electric-

field driven switching hysteresis loops each have their own drawbacks and are often subject to either over-interpretation or erroneous conclusions. However, here the three techniques work in synergy to give complementary viewpoints- the general alignment of all three in conjunction is compelling.

The outcome that one can achieve polarization rotation in bilayer systems has several significant implications. Firstly, this approach is an elegant and simple way to induce rotational polar domains without the need for exotic substrates or superlattices. Second, the large electromechanical properties we observe are congruent with the prevalent notion that ferroelectric multilayers with intentional composition gradients can possess significantly enhanced susceptibility properties compared to a monolithic counterpart^[70] Finally, the ability to switch the polarization from in- to out-of-plane suggests the possibility of ferroelastic coupling - a key requirement for electromechanical and magnetoelectric switching devices^[71] Thus it further propels the burgeoning possibilities offered by interface-controlled ferroelectricity in the development of modern nanoelectronic materials.

2.4. Methods:

Thin film growth-The ultra-thin $\text{PbZr}_{0.30}\text{Ti}_{0.70}\text{O}_3$ (PZT-T)/ $\text{PbZr}_{0.55}\text{Ti}_{0.45}\text{O}_3$ (PZT-R) bilayer sample was grown on (001)-oriented SrTiO_3 (STO) via pulsed laser deposition (PLD) with a $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) as bottom electrode. We focused on a T-layer thickness of 5nm and R-layer thickness of 20 nm, as this combination was optimal in giving us a robust ferroelectric response yet at the same time, they are thin enough to avoid any complications arising from ferroelastic domain formations. During the entire deposition, oxygen pressure, laser frequency and substrate-distance were kept constant at 100 mTorr, 5 Hz and 15 cm, respectively. Deposition temperature and laser

energy were optimized to 700°C and 255 mJ for PZT-T, 550 °C and 225mJ for PZT-R and 800 °C and 225 mJ for LSMO layers. After deposition, the films were cooled at 20°C/min to room temperature under 450 Torr oxygen partial pressure.

X-ray diffraction:

Lab X-Ray diffraction measurements were carried out on a Bruker D8 with a rotating copper anode X-ray source of up to 4500 kW ($\lambda=1.54013 \text{ \AA}$) in order to measure high-resolution 2θ XRD and reciprocal space mapping as shown. In order to obtain high resolution the instrument was set up with a compound silicon strip detector (Lynx-Eye) in 0-dimension mode. The RSM for $(10\bar{3})$ was acquired under 1-dimensional mode of Lynx-Eye for fast measurement. All measurements were done at room temperature.

The synchrotron X-ray reciprocal space maps presented in this work were acquired using the reflection diffraction geometry at an X-ray energy of 17 keV(± 1 -2eV). 3D reciprocal space (q_x, q_y, q_z) , where q_y is parallel to the diffracted beam 002) was measured with a nominal q -space resolution of 5.1×10^{-5} , 6.0×10^{-5} , and 4.7×10^{-5} in q_x , q_y and q_z respectively, where q_z is parallel to $(002)_C$. Tungsten slits located 0.5 m upstream of the sample defined a square incident beam shape of dimensions 0.5mm x 0.5mm, impinging close to the centre of the sample. The data was acquired as 5001 2D images using a FReLoN CCD detector with an exposure time of 3 seconds each. Accounting for the experimental geometry, the 3D reciprocal space maps were then obtained by interpolating values at a 512x512x2048 point grid of query points in q_x , q_y and q_z , respectively.

Piezoresponse Force Microscopy Imaging:

A commercial scanning probe microscopy (SPM, Cypher, Asylum Research, US) was used to obtain the vector piezoelectric force microscopy (PFM) phase and amplitude images. Conductive Pt/Ir coated silicon cantilevers (PPP-CONTPT, NanoSensors, Switzerland) were used for PFM imaging studies. Switched domain patterns were made by applying a DC bias of $\pm 4\text{ V}$ on the film. Then three set of vertical and lateral PFM images were captured by first placing the film (001) orientation paralleled (0°) with the cantilever, followed by rotating the films by 45° and 90° . PFM images of the exactly same field were studied at above 3 rotated orientations to understand the crystal symmetry and polar domain structures of the ultrathin bi-layer PZT films

Device Measurements-The piezo coefficient was measured at room temperature using an Asylum DART module. Conductive Cr/Pt coated silicon cantilevers (Multi75E-G, BudgetSensors) were used during the tests. As PFM the images reveal significant domain at the local scale, metallic gold electrodes ($\sim 23 \times 23 \mu\text{m}^2$) were thermally evaporated to prevent electric field localization induced artifacts and capture an average piezoelectric response. The underlying film areas were initially activated using sine wave with step DC bias pulses ramping from -5 V . The first -5 V pulse was also applied to pole the ferroelectric film under top electrode. Then amplitude and phase loops were recorded via AC bias between each internal when the DC bias offset to zero. Electrical measurements (P-V loops, PUND and Fatigue) were acquired on a Radiant precision Premier on $35 \mu\text{m}^2$ top electrodes at room temperature. To obtain entire ferroelectric hysteresis loop, the tests were done at 10 kHz with 10 V as maximum voltage. Fatigue tests were carried out at 100 kHz as polarization switching frequency

and the applied voltage was 10 V to reach polarization saturation. Identical settings (10 V and 1 μ s) as PUND were employed to measure polarization after certain cycles.

Chapter 3 Positive effect of an internal depolarization field in ultrathin epitaxial ferroelectric films

Abstract

The effect of intentionally introducing a large depolarization field in (001)-oriented, epitaxial $\text{Pb}(\text{Zr}_{0.2}\text{TiO}_{0.8})\text{O}_3$ (PZT) ultra-thin films grown on $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) buffered SrTiO_3 (STO) substrates is investigated. Inserting between 3 to 10 unit cells of STO between two 3nm thick PZT films significantly influences the out-of-plane (c) lattice constant as well as the virgin domain state. Piezoresponse force microscopy images reveal a nanoscale (180°) polydomain structure in these films. In comparison, a “reference” single layer PZT sample (6 nm thick without STO spacer) exhibits an elongated PZT c -axis (0.416 nm) and is preferentially “down”-polarized with large regions of monodomain contrast. It shows asymmetric switching loops (i.e. imprint) coupled with sluggish domain switching under external bias. We show that the insertion of STO drives a monodomain to 180° polydomain transition in the as-grown state, which reduces the imprint by 80 %. The insertion of the STO also profoundly improves dielectric leakage and hence the distribution of the applied electric field. Consequently, the critical pulse duration of the electric field required to initiate domain switching is reduced by two orders of magnitude relative to the reference sample. These results demonstrate the possibility of manipulating the depolarization field in such a way that it has positive effects on the ferroelectric behavior of ultrathin PZT films.

3.1. Introduction

Recent advances in the field of thin-film oxide heteroepitaxy^[72, 73, 74] have enabled the synthesis of new artificially-layered materials with atomically-abrupt interfaces.^[75] This capacity for atomic level precision has opened new research avenues in ferroelectric oxide thin films, where the polar properties of the system can be adapted not just by changing the “bulk” ferroelectric, but by modifying the local interaction at the interfaces.^[74] The systematic tuning of the interface coupling either through modulating superlattices,^[76-78] strain,^[79] electronic termination,^[73, 74] and/or epitaxial orientation have yielded ferroic systems with domain patterns and functional properties that are either radically different, or even more intriguingly, completely absent in the constituent compounds. Ultimately these features point toward exciting new functional opportunities. Breakthroughs such as magnetoelectric control of polarization,^[80] polarization modulation of a two-dimensional electron gas (2DEG),^[75] and polarization-driven resistive-switching^[81] are eminent examples of functional phenomena made possible via atomic level heteroepitaxy.

In this study, we harness the growth control offered by pulsed laser deposition (PLD) to investigate one of the most critical concepts in nanoscale ferroelectrics, namely, the depolarization field. Perceived to be a “necessary evil”, it is an electric field that arises at a interface, stemming from the incomplete screening of the polarization charges. The abrupt breaking of the polarization at an interface is energetically prohibitive and the material may respond in many ways. The most natural scenario is for the ferroelectric to break into several domains (referred to as a “polydomain” state). However in ultra-thin (or nanoscale) ferroelectrics, the energy cost to create a domain wall may be quite large and thus a more efficient option can be either to smear out or even completely eliminate the ferroelectric polarization.

Although it is extremely difficult to directly measure the depolarization field, its manifestation on ferroelectric properties are clearly observed. It is particularly dominant on films between 1~10 nm thick, depending on the existing electrical boundary conditions, such as suppression of spontaneous polarization expressed via reduction of the lattice parameter^[82] and/or oxygen octahedra displacement within the perovskite unit cell.^[77, 83] In extreme cases, an uncompensated depolarization field can even completely eliminate the ferroelectric phase at room temperature.^[84] It is for these reasons that the discussions and investigations regarding depolarization field have always been about its detrimental and debilitating nature on the stability of the ferroelectric phase at a reduced length scale, and almost always focus on how it can be eliminated.^[85]

In this study, we turn this attitude on its head and ask (perhaps an oxymoronic question) — can the depolarization field be exploited to enhance ferroelectric polarization switching?

We intentionally enhance depolarization effects in a ferroelectric heterostructure by introducing a semiconducting STO dielectric spacer layer between two ultra-thin $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ (PZT) ferroelectric layers. We show that through spacer thickness tuning, it is possible to control the nanoscale domain structure in the PZT layers. The presence of a spacer promotes the formation of irregular 180° domains, as evidenced by piezoresponse force microscopy (PFM) scans. Our observations are supported by a simple phenomenological model which suggests that the electrostatic decoupling of the two ferroelectric layers with the formation of distinct 180° domains in both ferroelectric layers. Critically, when compared to a reference PZT sample, the introduction of the STO layer reduces the measured coercive voltage, decreases the built-in voltage

(imprint) by ~80% and shortens the nucleation time for a written domain under a biased PFM tip by two orders of magnitude. Furthermore, PZT heterostructures with spacer layers exhibit a robust leakage resistance. These observations can be attributed to a change in the defect distribution within the film through the introduction of the semiconducting STO spacer, and the change in depolarization field profile at the top and bottom PZT layers due to the different chemical environments.

It has been shown that the placement of a spacer between a ferroelectric and the electrode has a profound effect on the ferroelectric behavior and domain structure. [73, 86, 87] The recent efforts to exploit interface engineering of the depolarization field in thin film ferroelectrics motivated the present work. The key difference between those cases and here is that the dielectric spacer in our case is introduced between the two ferroelectric (FE) layers, and not between the FE layer and the electrode. This opens up new possibilities by which the system may choose to relax in response to the polar discontinuity.

3.2. Results

The following samples were fabricated using the procedure described in the methods section:

(a): PZT(6 nm)/LSMO/STO substrate: (PZT_reference) [Fig. 3.1(a)]

(b): PZT(3 nm)/STO(3u.c.)/PZT(3nm)/LSMO/STO substrate: (PZT_3ucSTO) [Fig. 3.1(b)]

(c): PZT(3nm)/STO(10u.c.)/PZT(3nm)/LSMO/STO substrate: (PZT_10ucSTO) [Fig. 3.1(c)]

The LSMO electrode is kept at 2 nm to ensure epitaxial registry across the entire film stack. We have shown in a previous study that LSMO remains conductive enough for PFM at this thickness^[88]; however Hall measurements revealed a very low carrier density of $10^{15}/\text{cm}^3$. The LSMO can thus be considered to be a “bad” metal with an effective screening length much larger than conventional oxide electrodes.

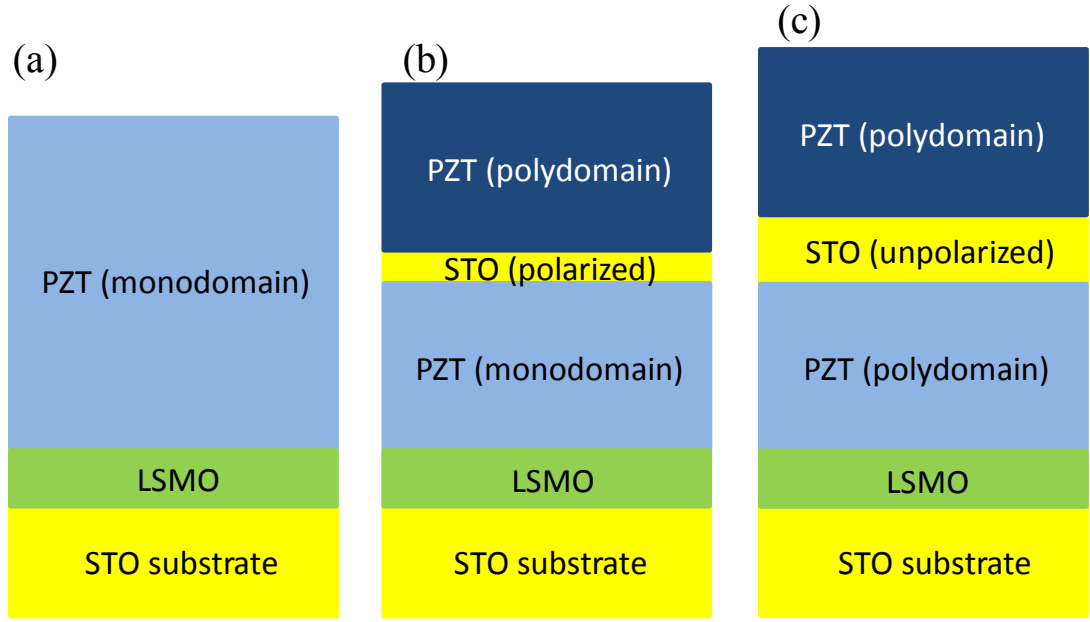


Fig. 3. 1 Schematic of the investigated thin film heterostructures for (a) PZT_reference, (b) PZT_3ucSTO and (c) PZT_10ucSTO with varying STO thickness.

Fig. 3.2(a-c) are X-ray asymmetric reciprocal space maps (RSM) acquired along (103) reflections for the three samples. Although the intensities for the PZT (103) peaks are low, the RSMs reveal that the PZT films grow fully constrained (as the crystal truncation rods for the substrate and the PZT layers are aligned perfectly with each other along $(00L)$). Thus epitaxial cube-on-cube growth is confirmed. High-resolution transmission electron microscopy of a representative sample [see A2.1] confirms that all ultra-thin layers are continuous with sharp interfaces.

Magnified normal coupled θ - 2θ scans around the (002) family of reflections is compared in Fig. 3.2(d). The peaks are quite broad – as expected for ultra-thin films. In order to accurately calculate the c -axis parameter, a custom-made MATLAB fitting script was employed. The script uses thickness and out-of-plane c -axis for each layer as the input variables. For all fits the thickness of the LSMO was kept constant at 2 nm with out-of-plane lattice parameter of 0.386 nm. In the case of the reference sample, the best fit was obtained for thickness of 14 ± 1 unit cells for PZT, with an out-of-plane c -axis of 0.416 ± 0.005 nm. This is $\sim 0.6\%$ larger than the bulk value of 0.4135 nm. Such an elongation of the c -lattice in ferroelectric thin-films fabricated via PLD has previously been reported in PZT^[83] and can be understood as an effect of the in-plane compressive strain ($\sim 1\%$) imposed by the underlying STO substrate. Full fitting details can be found in appendix section A2.2. The observation that the reference sample is able to sustain a full c -axis evidences that both the LSMO layer and the surface adsorbates are able to effectively screen the polarization-induced surface charge.^[89]

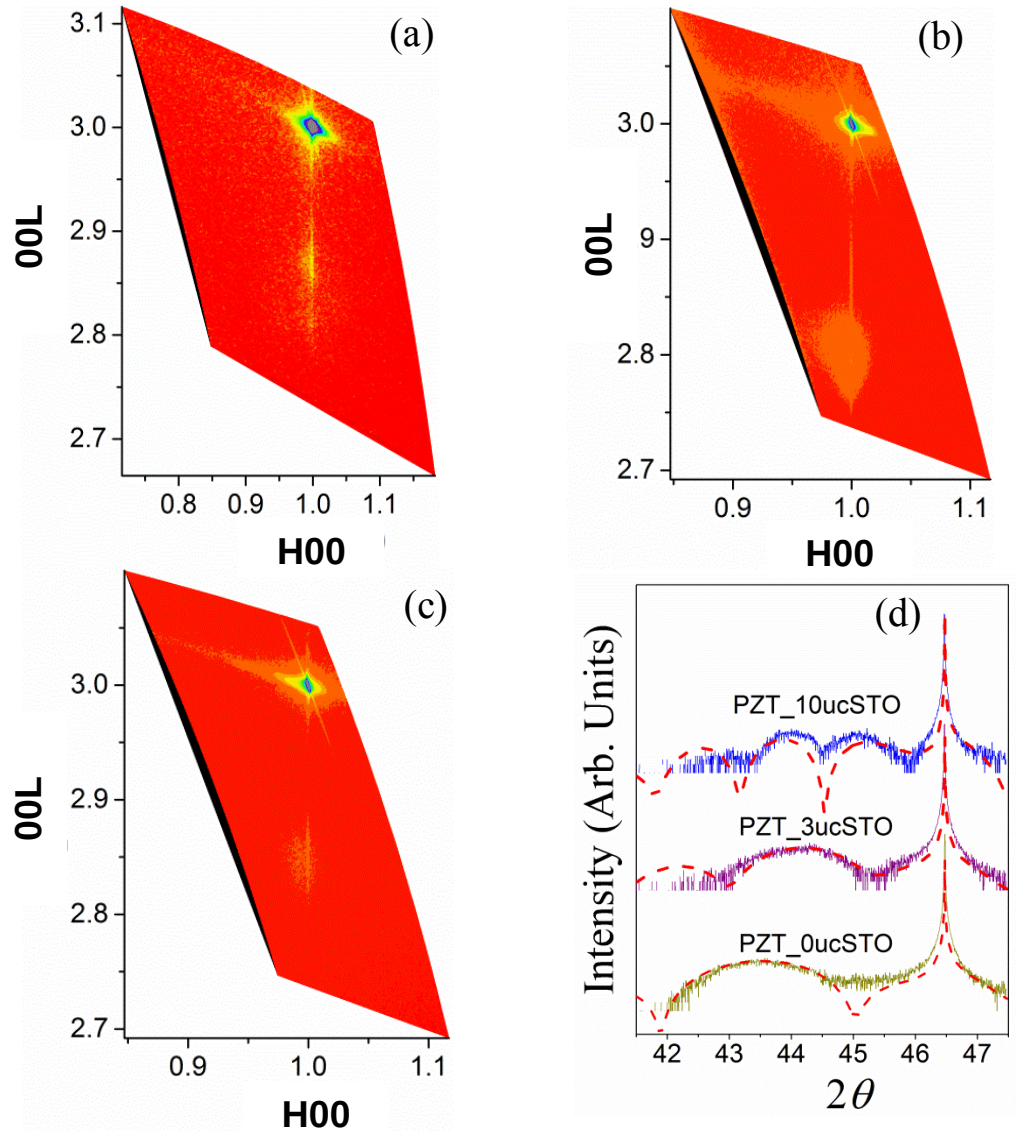


Fig. 3. 2 (a) (103) Asymmetric reciprocal space maps for (a) PZT_reference, (b) PZT_3ucSTO and (c) PZT_10ucSTO showing that the films are epitaxially constrained to the underlying STO substrate with their c-axis aligned in the [00L] direction. (d) θ - 2θ XRD comparison for samples with varying STO thickness and XRD peak simulation (red dotted lines).

In contrast to the reference sample, insertion of the STO layer has a dramatic effect on the lattice parameter of the PZT layers. For the PZT_3ucSTO sample, we observe that the (002) peak is broad and slightly asymmetric. We checked for all possible situations where both the lattice parameter and the number of unit cells were allowed to vary. (Screen shots of the program along with visualization of the parameters that can varied is given in A2.2.) The best fit to the PZT_3ucSTO sample was found with the following out-of-plane lattice parameters: top PZT with 0.416 ± 0.002 nm, STO-spacer layer with 0.402 ± 0.003 nm and bottom PZT with 0.409 ± 0.002 nm. The fits also confirmed that the thickness for each layer was 7 ± 2 uc of PZT, 3 ± 1 uc of STO and 7 ± 1 uc of PZT. These out-of-plane lattice parameters point to three key observations. First, the top PZT layer has fully recovered its *c*-axis, similar to the reference sample. Second, the middle STO layer has a significant out-of-plane elongation compared to bulk that might be attributed to a partial polarization of the STO layer induced by the neighbour PZT domains, and possibly additionally to the presence of defects^[90]. Finally, the bottom PZT shows a significant reduction in the *c*-axis lattice constant. Based on previous measurements on ultra-thin PbTiO₃ (PTO) films,^[82] this reduction in the *c*-axis can be attributed to a large depolarization field due to poor screening by the bottom LSMO layer compared to the top PZT layer with adsorbates on top. The fitted lattice constant for the bottom interface is compatible with a polydomain structure, with a smaller polarization within each domain.

For the PZT_10ucSTO sample, the peak shape changes completely with two separate peaks in the same 2θ space where previously there was a single broad peak. We found that the closest fit (within the limitations of the fitting software) was with a top PZT *c*-axis of 0.416 ± 0.002 nm. Importantly, the best fit for the STO was always 0.3905 ± 0.003 nm irrespective of the PZT lattice parameter. This means that for the

thicker spacer sample the STO is no longer polarized and the two PZT layers are effectively decoupled from each other. For the bottom PZT layer we obtained the best fit using 0.412 ± 0.002 nm.

It is also important to note that just taking the position of the two peaks (apart from the substrate) doesn't lead to the true individual lattice parameters of each layer. From the peak positions ($2\theta=44.03^\circ$ and 45.11°), one would get c-axis values of 0.411 nm and 0.402 nm respectively, clearly not the real values of the individual layers. As we work with heterostructures (here 4 alternating layers of different materials on top of a substrate), the XRD patterns become considerably complex, and only a proper simulation of the diffracted intensity can lead to meaningful conclusions regarding the structural characterization of the constituent layers.

To check if these dramatic changes in structure have any bearing on the domain behavior, out-of-plane Dual Amplitude Resonance Tracking (DART)-PFM images were acquired. Fig. 3.3(a) & (d) are amplitude and phase images of the as-grown state, obtained from the PZT_reference. The images show the film to be in a preferentially downward-polarized state; with small pockets of upwardly polarized domains embedded within a continuous negative domain. This preferential poling is typical of asymmetrical PZT heterostructures and has been discussed elsewhere.^[74, 91] In the PZT_3ucSTO sample, the insertion of a STO spacer changes the as-grown domain configuration, shown by the PFM amplitude and phase images [Fig. 3.3(b) & (e)]. The imaged domain configuration now changes to a polydomain state that shows both up and down polarized domains. The domain periodicity was evaluated to be between 22 and 24 nm using an Autocorrelation script as shown in the appendix A2.3. A similar effect was previously reported in 50 nm PbTiO_3 (PTO),^[87] where it was shown that the

insertion of 2 nm STO between PTO and the bottom electrode causes the film to go from a monodomain state to a polydomain state due to poorer screening conditions. PFM images of a sample which had no top PZT (i.e. terminated with the spacer STO) also displayed distinct polydomain contrast (not shown).

For the PZT_10ucSTO sample, the PFM amplitude and phase images, Fig. 3.3(c) & (f), show no distinct domain features in the as-grown state. However, positive and negative biases applied to the as-grown state are able to switch the film into downwardly and upwardly polarized states, respectively [see Fig. A2.4]. Cross-section analysis of the PFM image [Fig. A2.4] indicates the PZT_10ucSTO sample to be polydomain with a domain size at the limit of the PFM resolution. The switched regions also exhibit greatly enhanced piezoresponse compared to the as-grown state. These results, in conjunction with the theoretical model (discussed later), hint that the bottom layer in both spacer samples are also polydomain.

The presence of the STO layer should also influence the local switching behavior. To investigate this, Switching Spectroscopy Piezoresponse Force Microscopy (SSPFM)^[92] loops were acquired in order to compare and contrast the coercive behavior for the different samples [Fig. 3.3 (g-i)]. As the measured coercive voltage can be very different to the actual coercive voltage, as pointed out by Dawber *et al.*^[93], the voltages will therefore refer to the “measured” ones.

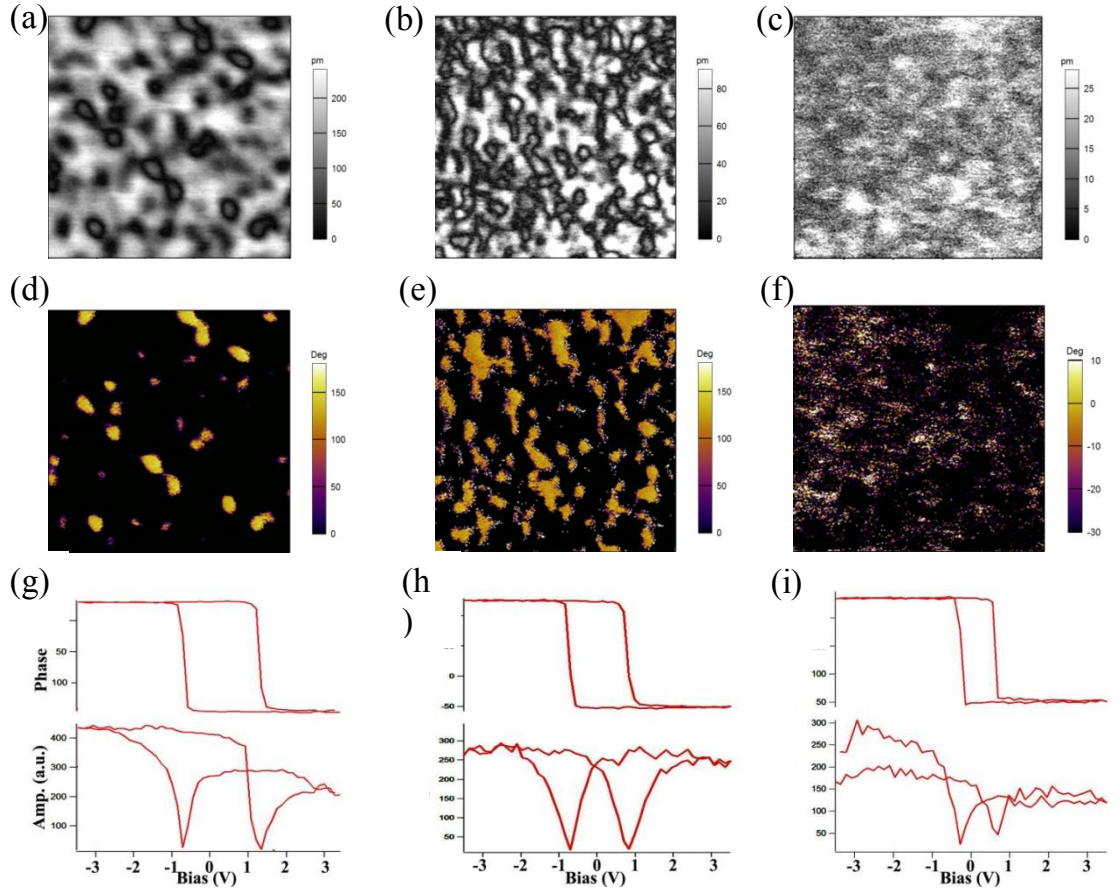
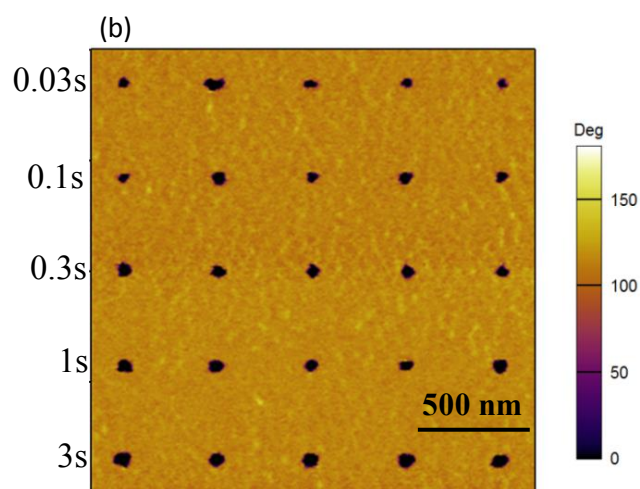
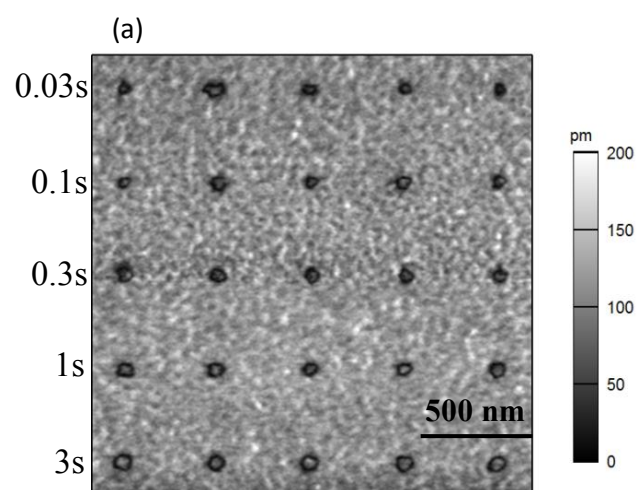


Fig. 3. 3 Dual Amplitude Resonance Tracking - Piezoresponse Force Microscopy (DART-PFM) amplitude (a, b and c) and phase (d, e and f) images on the as-grown PZT_reference (a,d), PZT_3ucSTO (b,e) and PZT_10ucSTO (c,f) samples respectively. The PZT_3ucSTO sample shows a marked increase in the density of 180° domains compared to the reference sample. The amplitude and phase images for PZT_10ucSTO ((c) & (f)) show no distinct domain pattern in the as grown state. Further analysis of the PZT_10ucSTO can be found in Fig. A2.4. Typical SSPFM hysteresis loops obtained from (g) PZT_reference, (h) PZT_3ucSTO and (i) PZT_10ucSTO samples.

For the reference sample, which is strongly down-polarized, the SSPFM loops are significantly shifted to positive voltages. The measured coercive voltages are $V_c^+ \sim 1.5$ and $V_c^- \sim -0.8$ V respectively, giving a built-in voltage $V_{shift} = \frac{V_c^+ + (V_c^-)}{2} = 0.35 \pm 0.03$ V. This built-in voltage leads to an electric field, referred to as imprint, which has been one of the key reliability issues in ferroelectric thin film devices.

Most interestingly, for the case of the PZT_3ucSTO and PZT_10ucSTO samples, both the coercive voltages as well as the built-in voltages are dramatically reduced. Note that the 3-layer structure, in addition to a poor electrode at the bottom, makes computation of the field non-trivial. Therefore we resort to directly-measured voltages. For the PZT_3ucSTO the coercive voltages are ~ 0.82 and -0.68 V respectively. This leads to a built-in voltage of $0.07 \text{ V} \pm 0.02$; ~ 5 times smaller than the PZT_reference case. Even the PZT_10ucSTO sample has a significantly lower average built-in voltage of 0.19 ± 0.08 V with respect to the reference sample. However, the loops obtained in this case are quite noisy, and the variance in the measured coercive voltages is large from one location to another, which is reflected in the large standard deviation.

Finally, we investigate if the modulation in the electrical boundary conditions has an effect on the switching dynamics. Fig. 3.4 plots the radius of domains formed under a +3V tip-bias for different pulse durations on a region homogeneously polarized into the upward state by a -3V bias on all samples studied here. We have also plotted data acquired for samples with 5 and 7uc thick STO spacers^[37]. PFM images and SSPFM analysis of these additional samples can be found in A2.5. Note that, under a +3V tip-bias, domain formation is in the direction of the downward-pointing built-in field, as found in the as-grown state for all samples. The plots show a lower bound of ~ 10 nm (limited by tip resolution) for domain radius size for all samples. However, the formation time for this metastable domain size is much longer in PZT_reference ($t = 1$ s) than in the samples with a STO spacer. In their case we observe a stable nucleus for as low as $t = 0.03$ s. This result is all the more remarkable when one considers that the built-in field, which is in the direction favoring domain growth, is ~ 5.5 times higher in PZT_reference compared to PZT_3ucSTO.



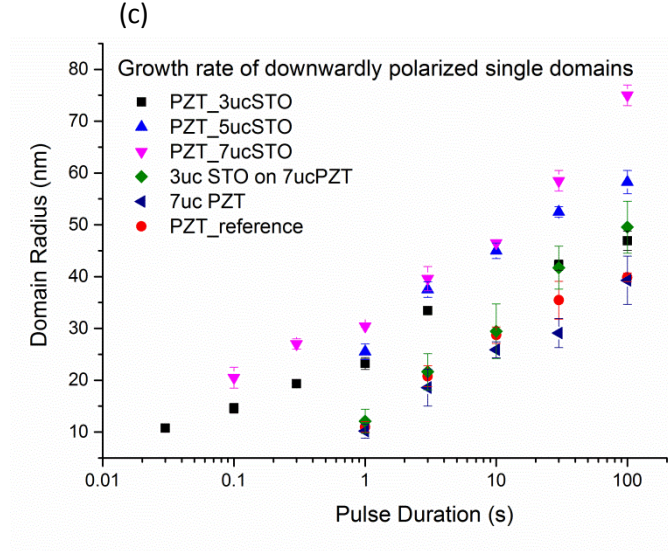


Fig. 3. 4 Domains formed under a +3V tip-bias for different pulse durations on a region homogeneously polarized into the upward state by a -3V bias. (a) & (b) PFM amplitude and phase of a domain array on PZT_3ucSTO sample drawn with different pulse duration on identical area. (c) Domain radius as a function of pulse duration.

To make the comparison complete we also investigated the pulse behavior of a 7 u.c. PZT sample (i.e. 7 u.c. PZT/LSMO/STO) and 7 u.c thick PZT sample with top STO spacer 3 u.c. thick. The writing experiments performed on these thinner PZT samples only reinforce the trend observed. The PFM images (see A2.5) show that the domains are at near limit of the imaging resolution, hence the larger errors associated with the domain radius measurement.

We have examined the retention of these written domains (see A2.6) and find that they are able to be imaged even after 12 hours. Table 1 summarizes the key experimentally measured characteristics of the three systems studied here.

We conclude the experimental section by pointing out one more advantage of having the STO spacers. It was previously shown by Dawber et al.,^[94] that the insertion of STO in PTO/STO superlattices drastically reduced leakage current compared to single-layer PbTiO₃ films. Similarly it has been found that heterostructures consisting of dielectric or ferroelectric bilayers between two high- T_c superconducting films possess greatly reduced leakage current^[95]. This is also true here with the insertion of STO between just two layers of PZT [see Fig. A2.7]; the PZT_reference exhibits a diode-like behavior and started to conduct at +3V, while the PZT_3ucSTO and PZT_10ucSTO samples show no conduction even at $\pm 4V$. There are electrostatic potential and stray fields at the two STO/PZT interfaces^[96] that allow the interfaces to become trapping centers for mobile charged defects, impeding their movement across the film. This would dramatically improve the field distribution as more of the applied field would drop across the ferroelectric as opposed to being lost via resistive leakage. It is likely then that this more intense field would then help domain nucleation.

3.3. Theoretical model

To rationalize the experimental observations described above, we have developed a very simple phenomenological model that takes into account different mechanisms to screen the depolarization field^[85] together with the Helmholtz free energies of the FE and the STO layer, previously introduced by Dawber and coworkers in Ref.^[94]. Note that for simplicity we simulate using parameters for PTO,^[97] as the primary effect of the 20% Zr alloying is simply to slightly shift the transition temperature and magnitude of the spontaneous polarization.

The first scenario considered assumes a continuous polarization within the FE/STO/FE stack. The insertion of a STO layer disrupts the homogeneous dipole-dipole

environment from within the bulk. The electrostatic cost of having a discontinuity of the normal value of the polarization at the FE/STO interface is enormously high. For a sufficiently thin paraelectric layer, one way to minimize the electrostatic energy at a ferroelectric/paraelectric interface might be to induce a polarization in the paraelectric layer, with the same normal component as the neighboring ferroelectric.^[77, 94] Then the presence of the bottom electrode and the effects of the adsorbates on the top surface is introduced through an effective screening length, as described in Ref ^[98]. The second mechanism is the breaking into 180° domains; in this case the reduction of the electrostatic energy compensates the extra domain wall energy.

In this model, we calculate the energy of a PTO/STO/PTO stack with a thickness of 3 nm for both the top and bottom PTO layers, and with varying STO thickness. We make a distinction between the top and the bottom layer, accounting for the different chemical environments. Further details of all parameters used can be found in the methods section.

For the top layer, the adsorbates provide efficient screening of the polarization charges, as was pointed out in Ref. ^[89]. Therefore, the electrostatic energy is highly reduced with respect to that computed from the periodic domain structure alone. Consequently domains wider than those predicted from the Kittel law are expected. The combination of the screening provided by the wider domains and the adsorbates implies a polarization at the center of the domains that amounts essentially to the PTO bulk-strained spontaneous polarization (0.765 C/m² within our model) and thus, due to the polarization-strain coupling, the out-of-plane lattice constant enhances up to 0.418 nm in good agreement with the experimental fit (0.416 nm). The energy of the polydomain configuration is obtained by adding the energy of the domain wall ($\sigma = 132$ mJ/m²) from

Meyer and Vanderbilt^[99] for the top FE layer, and by fitting the scaling of the electrostatic energy with respect to the one evaluated by Ozaki and Ohgami^[100] to reproduce the observed domain periodicity from the PFM images. The energy of the polydomain structure is then very similar to that of the monodomain configuration (of the PTO/STO bilayer) under *perfect* screening conditions [see Fig. 3.5(a)], and the polydomain becomes the ground state for thicknesses of the STO layer larger than 4 unit cells. Of course, more realistic screening conditions drive this transition to even lower thicknesses of the spacer, in good agreement with the experimental observations.

For the bottom layer, the screening of the polarization charges is poorer since, as discussed above, the conductance of the LSMO bottom electrode corresponds to that of a “bad” metal. In fact, the tetragonality deduced from XRD results suggests that the polarization in this layer is reduced to about 50% of the bulk value. Assuming that the domain wall energy scales roughly linearly with the polarization, we use $\sigma = 66 \text{ mJ/m}^2$ to obtain the energy of the polydomain structure of Fig. 3.5(b). We see that for the bottom STO/PTO bilayer the energy of the polydomain structure is again essentially degenerate with a monodomain configuration for the sample with 3 u.c. of STO under perfect screening conditions, suggesting that, in practice, the former should be more stable in a realistic sample.

If we add together the previous two energies for the polydomain configuration, and compare with the limit of coupled PTO layers, in which the full stack of PTO/STO/PTO is in a monodomain configuration, the former is again the most stable phase for thicknesses of the STO spacer larger than 5 unit cells (still assuming perfect screening in the monodomain case) [Fig. 3.5(c)].

If we add to the model a reasonable value of the screening length, $\lambda_{\text{eff}} = 0.1 \text{ \AA}$, then the polydomain structure becomes the ground state of the system for any thickness of the STO spacer [Fig. 3.5(d)], and only the absence of the dielectric stabilizes the monodomain configuration, as experimentally observed in the reference structure.

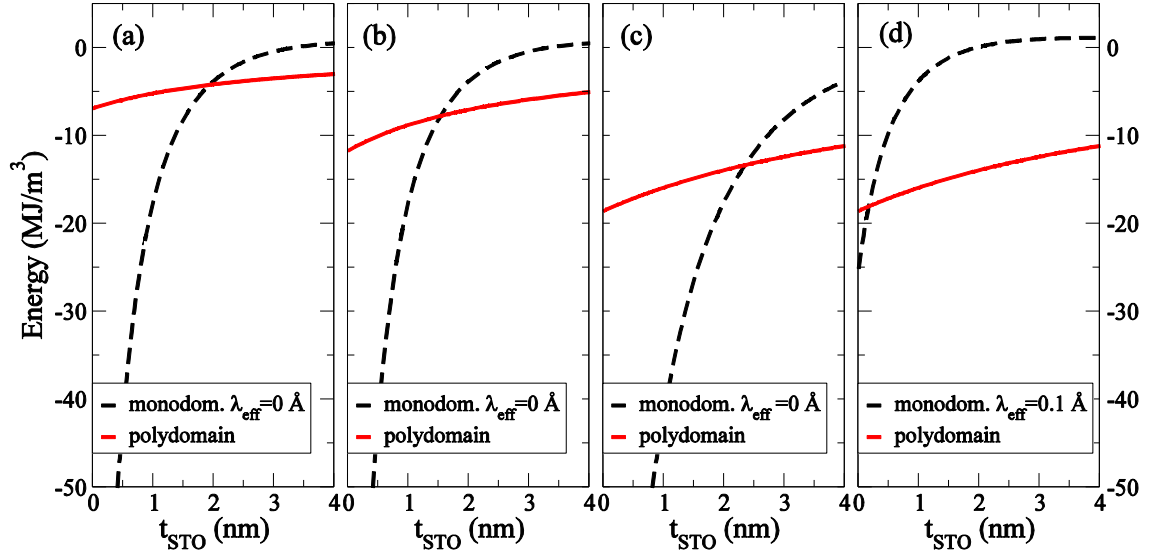


Fig. 3. 5 Energies of the PTO/STO/PTO stack as a function of the thickness of the STO layer obtained with the phenomenological model described in the text. In (a) and (b) we consider the top (a) and bottom (b) PTO layers as electrostatically decoupled and compare the energy of a polydomain phase (solid red lines) with a monodomain one (dashed black lines), which is penalized by the polarization of the STO spacer. In (a) and (b) perfect screening is assumed for the monodomain phase, since for such thickness of the PTO layer, any realistic value of the screening length yields a paraelectric structure. In (c) and (d) the configuration with two polydomain, decoupled PTO layers (solid red) is compared with the limit of coupled regime, for which the whole stack is polarized homogeneously (black dashed). Ideal screening is assumed in (c). In (d) a realistic value of the screening length drives the transition from monodomain to polydomain to very small thicknesses of the STO spacer.

3.4. Discussion

With this model, we found that the introduction of the STO spacer layer in a PTO/STO/PTO stack makes the polydomain configuration for both the top and bottom PTO layers more stable, and that the monodomain configuration is stable only for the

case without STO spacer. This is in very good agreement with experimental observations for our PZT/STO/PZT heterostructures.

In the PZT_3ucSTO sample, a large tetragonality of the STO layer is observed (0.402nm), suggesting that the spacer layer is partially polarized, in agreement with previous first-principles studies on PTO/STO superlattices which observed that the STO layer was polarized even in the presence of domains in the ferroelectric films ^[101]. This, together with the likely presence of charged defects in this layer, supports the experimental finding of a significantly enhanced out-of-plane lattice constant for the STO spacer.

As the thickness of the STO spacer increases, the energy cost of polarizing the STO increases. For the PZT_10ucSTO sample, we found that the c-axis value of STO goes back to the bulk unpolarized value (0.3905 nm), suggesting that the two PZT layers are then decoupled. This may also explain the large variations and high noise level in the piezoresponse for the PZT_10ucSTO sample, as the measured piezoresponse signal is now a sum of the responses from three decoupled layers. The decoupling makes the interpretation of the PFM data extremely complicated as discussed in the findings of Jo et al. ^[102] and Chen et al. ^[76] Additionally, the decoupling leads to smaller domain sizes as each PZT layer is seen individually, and the domain size is governed by the individual film thickness rather than by the thickness of the whole PZT/STO/PZT heterostructure as for the case in which the layers are coupled. Certainly the intrinsic characteristics of the electromechanical coupling within the PZT_10ucSTO sample require further investigation.

Having understood how the STO spacer influences the PZT layer lattice parameters, we next rationalize the surprisingly positive switching behavior found in

Fig. 3.4 for the samples with the STO spacers. Before performing the switching experiments, the full stack is poled to a monodomain configuration with a voltage of -3V, resulting in a uniformly up-polarized region. In this configuration, there is now a depolarization field that opposes to the polarization, i.e. pointing down. During the switching experiments, a +3V is applied to the AFM tip, inducing a field pointing down, and the depolarization field present in this pre-poled region therefore adds to it. The depolarization field being larger for the samples with the thicker STO layers, the effective field at the time of switching is larger with thicker STO, resulting in larger written domain sizes under otherwise equal conditions. Additionally, in the pre-poled region the magnitude of the polarization is reduced by the larger depolarization field (which is not compensated by the presence of domains anymore). The energy required to switch this reduced polarization is therefore decreased, so that it is easier to switch the samples with the larger depolarization field, i.e. with the thicker STO.

We would like to conclude the paper by proposing a speculative model to address the question of the imprint. To do so, we trace back to the first appearance of spontaneous polarization as the samples are cooled below the Curie temperature T_c , and to the subsequent charge migration inside the samples in response to the polarization. High temperature XRD carried out using a lab source for the samples studied here (not shown) confirmed that the T_c in these samples is in fact lower than the growth temperature (720°C). As the PZT_reference sample drops below the T_c , a transition from paraelectric cubic phase to a ferroelectric tetragonal phase occurs, and a spontaneous polarization is established in the c -axis direction (Fig. 3.6(a) and (b)). Though there are two possible polarization states along the c -axis, they are not degenerate, due to the asymmetrical electrical boundary conditions. However, the formation of a uniformly polarized film is energetically costly and thus, internal

screening occurs. Namely, the movement and accumulation of positively and negatively charged carriers towards the top and bottom interfaces takes place to screen out the oppositely charged surface bound charge. As illustrated in Fig. 3.6(c), this internal alignment of charged species creates a net field within the film that further stabilizes the domain alignment in the preferred direction (i.e. stronger imprint). Finally, the preferentially polarized as-grown state is further stabilized by the attachment of charged adsorbates on the surface as the sample is under an ambient environment. The end result is a strongly preferentially polarized as-grown domain state.

Fig. 3.6(d) and (e) show that in the case of the system with spacers (the example sketched here is the PZT_3ucSTO sample), as the film is cooled below T_c , the driving force for a downward polarization stemming from the PZT/LSMO interface is still present. However, there now exists a non-negligible source of depolarization within the center of the film. Note that particularly for the bottom layer, there is poor screening on both interfaces (a bad metal on the lower side and polarized STO above). The formation of 180° domains emerges as an energetically-favorable mechanism for screening the depolarization field^[103], also leading to the reduction in the net drift of charged defects to the top and bottom interfaces. For the bottom layer, the driving force for positive and negative defect segregation towards the top and bottom interface is further impaired by the suppressed spontaneous polarization. The end result is a large reduction in the built-in field and the formation of an as-grown domain state with 180° domains.

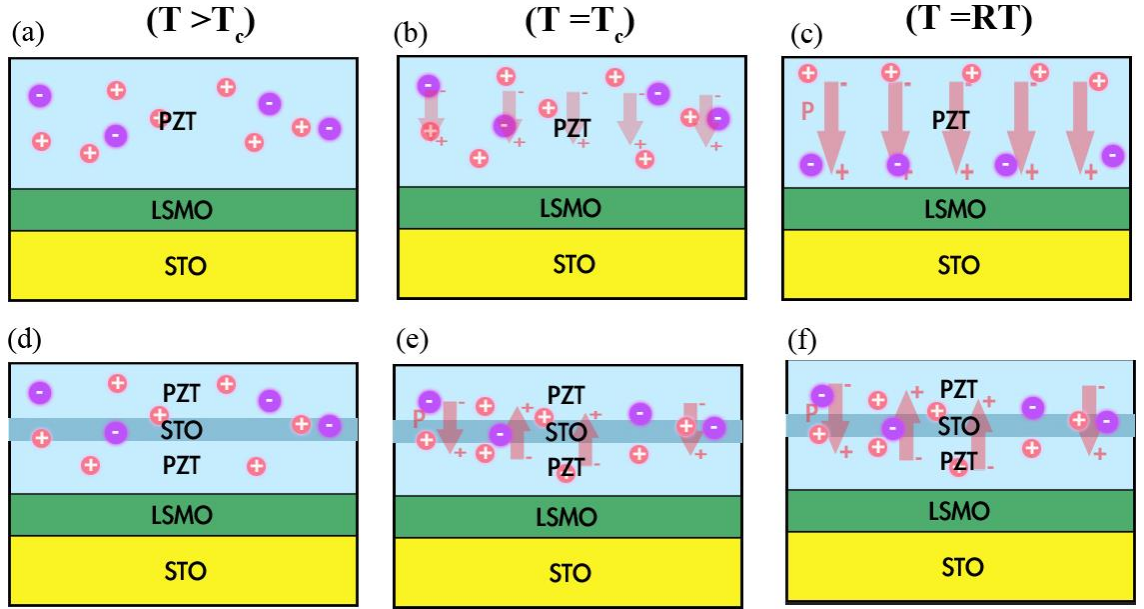


Fig. 3. 6 Illustrations of our speculative model to describe possible scenarios in our samples, showing the domain formation and internal charged defect movement as a function of temperature in PZT_reference (a-c) and PZT_3ucSTO (d-f).

3.5. Conclusion

In conclusion, we have shown that by intentionally introducing an STO layer between two ferroelectric PZT thin films it is possible to induce a depolarization field and tune its effect by modulating the thickness of the STO layer. Starting with a monodomain PZT 14 u.c. thin film, the introduction of a 3u.c. STO layer between the two 7 u.c. thick PZT layers results in the formation of domains, with the STO layer being polarized and the two 7 u.c. PZT layers being coupled. By increasing the STO thickness, the coupling between the two PZT layers decreases in agreement with previous work on PTO/STO superlattices ^[77], where a transition from a coupled to decoupled state around 3-4u.c. of STO was found. Accordingly, we find that our sample with 10u.c. STO is fully decoupled with two PZT layers that are ferroelectric and

polydomain, and the STO layer that is paraelectric with a *c*-axis relaxed to the bulk paraelectric value. Combining XRD and PFM measurements with theoretical estimations, we were able to characterize the different samples and follow their evolution as a function of the STO thickness. These results show that at the appropriate length scale, the depolarization phenomenon can result in a large improvement of ferroelectric properties, such as lower measured coercive voltages, faster nucleation speed, reduced imprint, and reduced leakage current.

3.6. Methods

3.6.1 Experimental

Growth - Epitaxial SrTiO₃ (STO) and Pb(Zr_{0.2}TiO_{0.8})O₃ (PZT) films were deposited on (001) etched stepped SrTiO₃ (STO) substrates (Shinkosha, Japan) buffered with a La_{0.67}Sr_{0.33}MnO₃ (LSMO) bottom electrode using a pulsed laser deposition system (PLD). All targets used for PLD were acquired from Kurt J Lesker. The oxygen pressure during ablation was maintained at 20 mTorr (STO) and 100 mTorr (PZT and LSMO), respectively. The deposition temperature for all layers was fixed at 720°C. The substrate-target distance was 15 cm, with fluence ranging from 2~2.5 Jcm⁻² and the laser repetition rates used were 3 and 10 Hz for STO and PZT, respectively. The cooling of the films was carried out at a rate of 20 °C/min to room temperature in 450 Torr of oxygen partial pressure.

X-ray diffraction - Asymmetric reciprocal space maps around the (103) reflection were performed for all samples using a Bruker D8 to verify the growth orientation and epitaxial quality.

Atomic-force microscopy - Surface topography and piezoresponse measurements were performed using a commercial AFM system (Cypher, Asylum Research). As the films are relatively thin (<10nm), Dual AC resonance tracking (DART) piezoelectric force microscopy (PFM) mode was employed to resolve the fine domain structure in the as-grown and switched states. An AC bias of 0.2 V at ~350 kHz was supplied to the tip for piezoresponse hysteresis loops and images measurements. Pt/Cr coated, conductive AFM tips (ElectriMulti 75G, BudgetSensors) with an average radius of 25nm were used throughout this study. Local hysteresis loops for all samples were obtained using Switching Spectroscopy Piezoresponse Force Microscopy (SSPFM). Multiple hysteresis-loops were taken over a $4 \times 4 \mu m^2$ area using a 0.2Hz, 3.5V_{peak-peak} triangle pulse bias. For the domain growth study, a region was firstly poled into the positively polarized state with a -3V writing bias before an array of circular domains was created by applying a 3V writing bias for different pulse durations. To extract an average value and to ensure the domain size data are statistically reliable, several domains were drawn for each pulse-duration/amplitude combination to minimize the contribution from experimental artifacts such as tip-drift and tip/sample contact variations.

3.6.2 Theoretical

We base our theoretical predictions for the out-of-plane lattice constant and polarization of the PZT/STO/PZT superstructure on the Devonshire-Ginzburg-Landau model fully explained in Ref. ^[94] For the monodomain case, the model is modified to take into account the electrostatic energy penalty due to the depolarization field through including an extra term in the energy expression, $\lambda_{eff} P^2 / \epsilon_0 t$, where λ_{eff} is the effective screening length, ϵ_0 is the vacuum permittivity and t is the thickness of the

polarized layer [the PTO/STO bilayer for Fig. 3.5(a) and 3.5(b), and the PTO/STO/PTO sandwich for Fig. 3.5(c) and 3.5(d)]. For the polydomain structures, in addition to the Helmholtz free energy inside the domain, we add the energy of the domain wall ($\sigma = 132 \text{ mJ/m}^2$, from Meyer and Vanderbilt^[99] for the top FE layer, where the polarization at the center of the domain is expected to attain the PTO bulk strained value, and reduced to $\sigma = 66 \text{ mJ/m}^2$ for the bottom FE layer due to the reduced value of the polarization) and the electrostatic energy of a 180° domain structure as derived in Ozaki *et al.*^[100] that might be scaled to account for the extra screening due to the adsorbates in the top layer. In the expression for the electrostatic energy, we used again the equations and parameters in Pertsev *et al.* to obtain the permittivity tensor of the ferroelectric material.^[97] In all cases we are calculating the energies per unit volume, where the volume considered is that of a PTO/STO bilayer [for Fig. 3.5(a) and 5(b)] or a PTO/STO/PTO sandwich [Fig. 3.5(c) and 3.5(d)].

For the curves in Fig. 3.5(a) and 3.5(b) we assume a regime in which both PTO (PZT in the experiment) layers are electrostatically decoupled. We compare the energy of a polydomain 3nm-thick PTO layer with that of a monodomain phase in which both the PTO and the STO spacer layer polarize. In this case, we assume a vanishing effective screening length since otherwise the monodomain case becomes unstable for any thickness of the STO. Two different domain configurations for the top and bottom FE layers are considered due to the different chemical environment, as explained in the main text.

For Fig. 3.5(c) we consider the coupled limit where the whole stack is in the monodomain configuration. The incomplete screening by the real metallic electrodes has been introduced through an effective screening length of $0.10 \text{ \AA}$ in Fig. 3.5(d). The

energy of the monodomain configuration, assuming a continuous polarization in the 6nm-thick PTO layer (3nm from the top and 3nm from the bottom FE layer) and STO spacer, is compared with that of a polydomain configuration where we consider that the 3nm-thick PTO layers are decoupled and break into 180° domains, while the STO layer remains unpolarized.

Chapter 4 Nano-bubble domains in epitaxial ultra-thin PZT film

4.1. Introduction

In the previous chapter, the possible effects of depolarization field, especially in terms of the benefits for potential devices, on ferroelectric properties are discussed. The thickness of inserted STO spacer varies from 3 to 7 unit cells to enable the depolarization field-induced modification on T-PZT layer domain and c lattice parameter. Additionally, with purposeful introduction of STO spacer into PZT layer, it shows that the domain configuration can be tuned by the thickness of inserted spacer and the PZT heterostructure shows reduced coercive field and significantly decreased imprint compared with PZT ferroelectric film without STO spacer. It is also noticeable that the screening effect also plays an important role to the behaviors of ferroelectric thin film. Piezoresponse force microscopy (PFM) results indicate that STO spacer turns PZT domains from monodomain into 180° polydomain via stripe-like domain configuration. Critically, the 2 nm bottom electrode (LSMO) which was employed in depolarization field investigation was a ‘bad’ metal. In this chapter, epitaxial PZT thin films with STO spacer heterostructures on metal-like bottom electrode are prepared and investigated by high resolution x-ray diffraction (HRXRD) and PFM.

The general concept is that if the depolarization field is suppressed sufficiently, the homogenous ferroelectricity with monodomains can be achieved in nanoscale thickness. However, the depolarization field within ultra-thin film is often significant because of incomplete screening from bottom electrodes ^[24, 84]. Typically researchers pursue methods to reduce the field by engineering heterostructure at film-electrode

interface^[104, 105]. By contrast, we have demonstrated the positive effects by enlarging the depolarization field. So it offers new possibilities to get desirable polarization in ferroelectric films through tuning the depolarization field

In ultra-thin ferroelectric films, the reactions of whole heterostructure system to the depolarization field are complicated. Except creating 180° domains to reduce depolarization field, there are several responses to minimize depolarization field in order to reach energetic favorite. For example, intrinsic polarization through oxygen suppression of displacement has been^[83].

In this chapter, PZT heterostructures have been prepared on 15 nm LSMO bottom electrode, which is more metallic-like electrode compared with 2 nm LSMO. In this case, the large depolarization field stemmed from ferroelectric (PZT)/paraelectric (STO) interface breaks the top PZT monodomain into nano bubble-like polydomain. Under the sufficient free charge carriers from the bottom electrode, the small bubble domains (<10 nm) of anti-parallel polarization are observed. The observed tiny 180° domains are consistent with other studies by Thompson et al, and Lichtensteiger et al.^{[106] [107, 108]}. Using the thicker LSMO buffer layer, it is found that the increasing thickness of STO spacer leads larger proportion of polydomains in PZT thin film, although the domains still retain in the bubble shape. In addition, it is noticed that the as-grown state of bubble domains is metastable state, such that PFM AC signal (<300 mV) leads redistribution within film and promotes the bubble-like to stripe domain transformation, consistent with theoretical computations^[109, 110].

4.2. Results

$\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films with STO spacer of various thicknesses were deposited on 15 nm LSMO buffered (001) TiO_2 terminated STO substrates (Shinkosha Co., Ltd., Japan) using pulsed laser deposition system (Neocera Co., Ltd., USA). Thickness of STO spacer varied from 1 monolayer to 10 monolayers. Ambient oxygen pressure was for 100 mTorr LSMO and STO and 120 mTorr for PZT during deposition. The substrate-target distance was 15 cm with laser fluency at approximately $2 \text{ J}\cdot\text{cm}^{-2}$. The laser frequencies used for deposition of PZT and STO were 5 Hz and 3 Hz, respectively. After deposition, the films were cooled to room temperature in 450 Torr partial oxygen pressure at a cooling rate of $20 \text{ }^\circ\text{C}/\text{min}$.

Using above conditions, the following samples were fabricated in this chapter. The Film configuration is shown in Fig. 5.1.

(a): PZT (3 nm)/1 monolayer STO/PZT (3 nm)/LSMO (15 nm): PZT_1_{ML}STO [Fig. 5.1 (a)]

(b): PZT (3 nm)/3 monolayer STO/PZT (3 nm)/LSMO (15 nm): PZT_3_{ML}STO [Fig. 5.1 (b)]

(c): PZT (3 nm)/5 monolayer STO/PZT (3 nm)/LSMO (15 nm): PZT_5_{ML}STO [Fig. 5.1 (c)]

(d): PZT (3 nm)/7 monolayer STO/PZT (3 nm)/LSMO (15 nm): PZT_7_{ML}STO [Fig. 5.1 (d)]

(e): PZT (3 nm)/10 monolayer STO/PZT (3 nm)/LSMO (15 nm): PZT_10_{ML}STO [Fig. 5.1 (e)]

Although LSMO film is much thicker, the epitaxial quality remains through the entire structures according to HRXRD and transmission electron microscopy (TEM) observations. The carrier density of 15 nm LSMO bottom electrode attains $10^{20}/\text{cm}^{-3}$, which is 5 times magnitude higher than STO spacer series in Chapter 4. Such carrier density of bottom oxide electrode facilitates effective screening in a much shorter length.

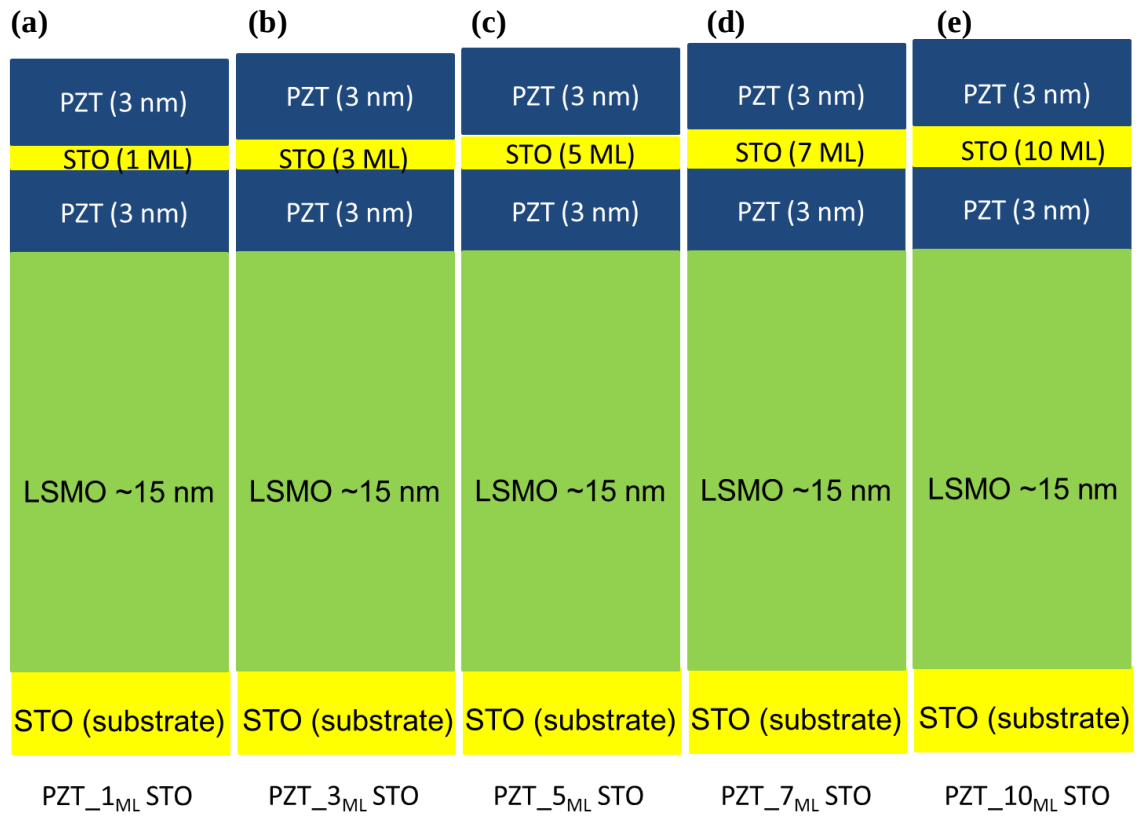


Fig. 4. 1 Schematic of PZT/STO/PZT heterostructures for (a) PZT_1_{ML}STO, (b) PZT_3_{ML}STO, (c) PZT_5_{ML}STO, (d) PZT_7_{ML}STO, (e) PZT_10_{ML}STO with increasing STO spacer thickness

Fig. 5.2 shows comparison of the high resolution XRD data of (002) peaks for all PZT_ X_{ML} STO samples on 15 nm LSMO electrodes. Epitaxial growth is assured as no other peaks appear from 40° to 50° (2theta). Broad PZT peak around 43° confirms the ultra-thin nature of all five films. Here the LSMO (002) peaks appear higher and sharper as they are thicker than samples in previous chapter. The d -spacing of LSMO is $3.850 \text{ \AA}$ which is close to its bulk value. In addition, the varying of PZT (002) peaks from 42.842° to 43.874° indicates d -spacing of each PZT layer is greatly modulated by

the inserted thickness of STO spacer, i.e. the depolarization field. As we noticed, the splitting of PZT (002) peak emerges with the increase of STO spacer thickness, that two peaks can be observed for PZT_{10ML}STO thin film because of the decoupled top and bottom PZT layers. The out-of-plane *d-spacing* of in PZT_{10ML}STO is approximately 4.05 Å which greatly suppresses the polarization.. Moreover the out-of-plane lattice parameter reduces as the decrease of STO thickness. That is, 4.1428 Å for PZT_{3ML}STO and 4.146 Å for PZT_{1ML}STO. Since the polarization value is proportional to tetragonality of PZT, this suggests that the ferroelectricity is modulated by tuning of depolarization field..

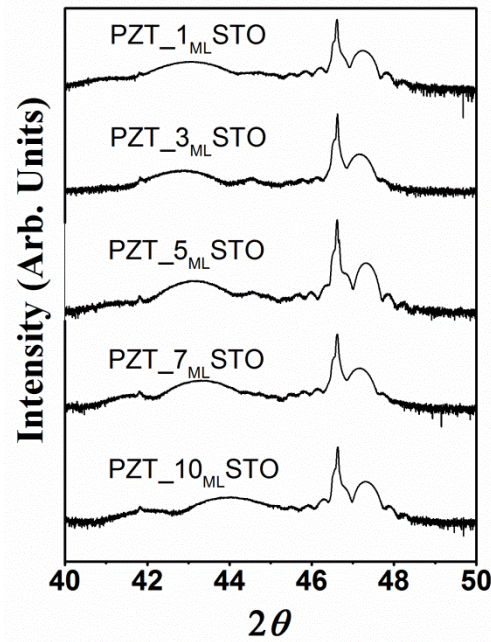


Fig. 4. 2 high-resolution of θ - 2θ XRD comparison for all PZT_{xML}STO samples. With developing the thickness of STO spacer, PZT peak gradually splitted into two peaks as the two PZT layers fully decoupled.

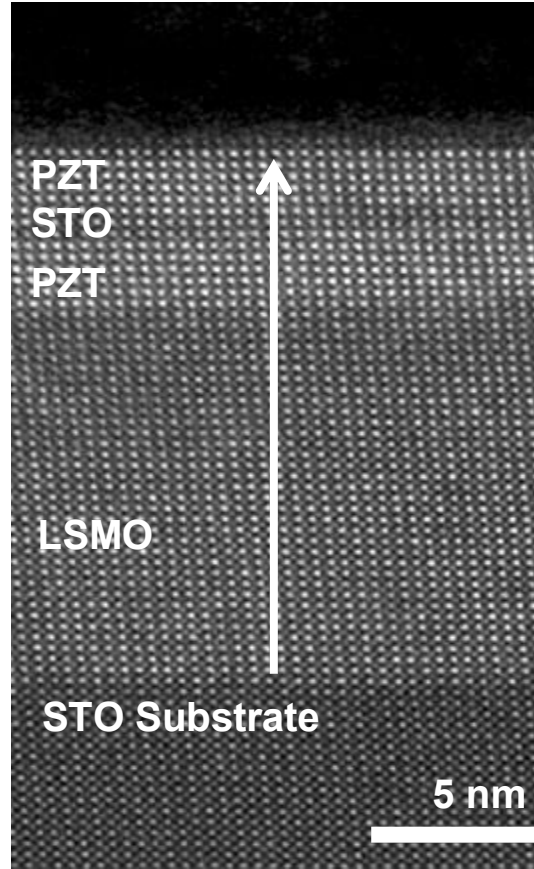


Fig. 4. 3 TEM cross-section of PZT_{3ML}STO confirms good epitaxy of triple layers on STO substrate with sharp interface formation. The thickness of PZT (7 u.c) and STO (3 u.c) totally agree with the deposition rate of last chapter.

In order to analyze the effect of altering layered structure on ferroelectric domain configuration of top PZT, DART-PFM (dual amplitude resonance tracking) was employed to investigate the vertical ferroelectricity. Fig. 5.4 (a)-(e) show the PFM amplitude evolution as a function of increasing STO spacer thickness in as-grown state. There is no distinct domain structure observed in the PZT_{10ML}STO sample. Except the PZT_{10ML}STO, all other films consist of monodomain matrix with out-of-plane piezo-response and tiny spots without detected response. The density of ‘bubble domain’ increases as depolarizing field increased. The out-of-plane responses also follow the tendency that piezo-response decreases with increasing STO spacer thickness. The phase evolution in virgin state is shown in Fig. 5.4 (f)-(j). Although the bubble domain size in the amplitude images appeared bigger than in the phase images, the unclearness

of PZT_1_{ML}STO spots in phase image can be caused by weak response and smaller size. . What is worth mention is that the accurate imaging of small bubble domains is challenging due to the PFM probe's scanning limit, which is approximately 20 nm. This probe limit causes the zero amplitude of inside of bubbles, which is interrupted by the bubble domain walls. . When STO spacer increases to 3 and 5 monolayers, phase images give distinct nano-domain spots which agree with the amplitude images for the location of bubble domain.. More spots are shown up from PFM results in PZT_7_{ML}STO due to the further enhanced depolarizing field. In PZT_10_{ML}STO sample, there are no clear domain features in as-grow state, as shown in figure 5.4 (e) and (j).

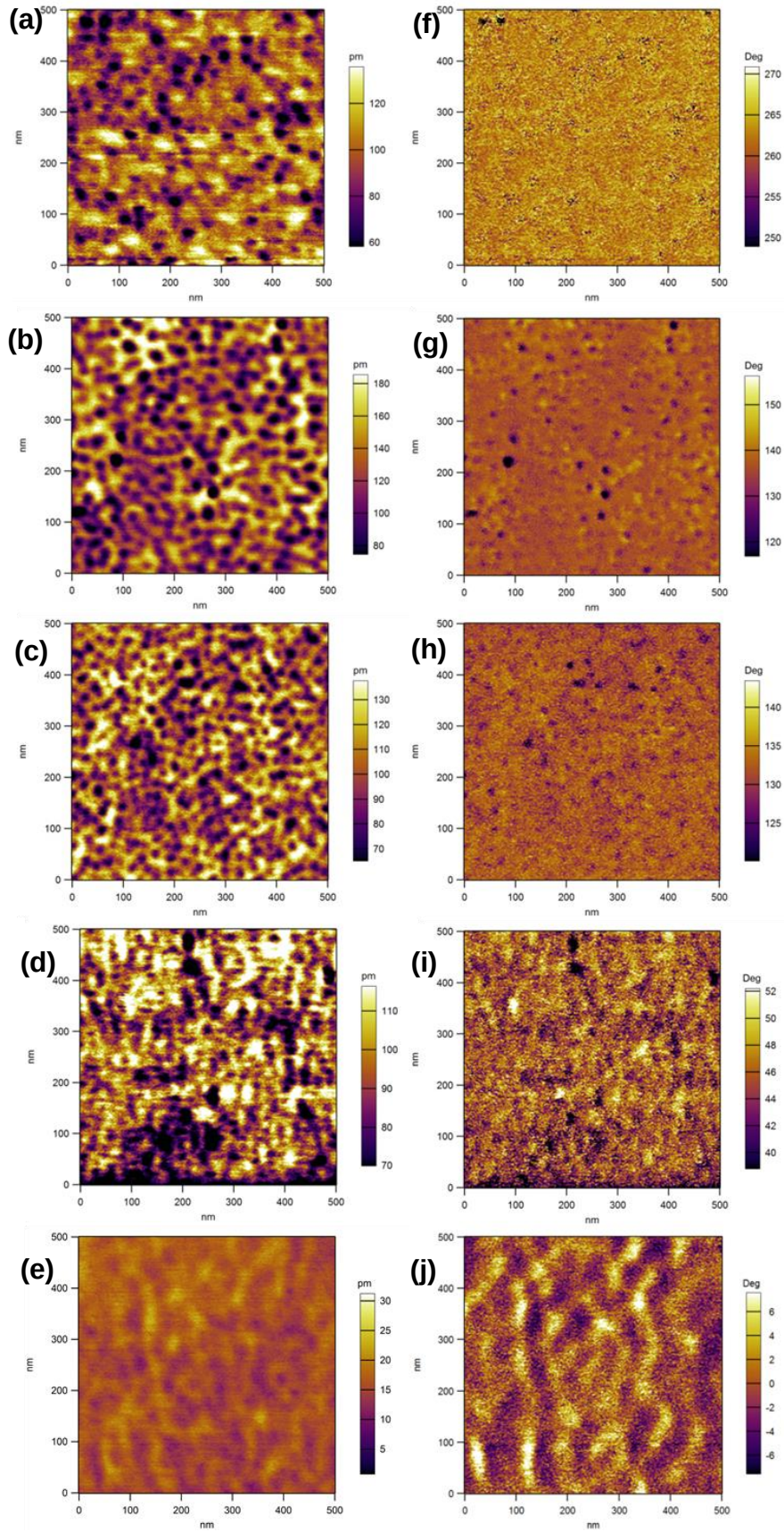


Fig. 4. 4 The as-grown state PFM amplitude and phase of PZT_{1ML}STO to PZT_{10ML}STO

To understand the nano-domain in as-grown state, PZT_3_{ML}STO was scanned in selected 200×300 nm² area using DART-PFM as shown in Fig. 5.5. (a) and (b). As mentioned above, the ferroelectric films are combined with matrix domains in a downward-polarized state and nano-scaled domains distributed all over the image. By employing DART technique, the nanodomains are in upwardly polarized state and 180° domain walls are clearly observed.

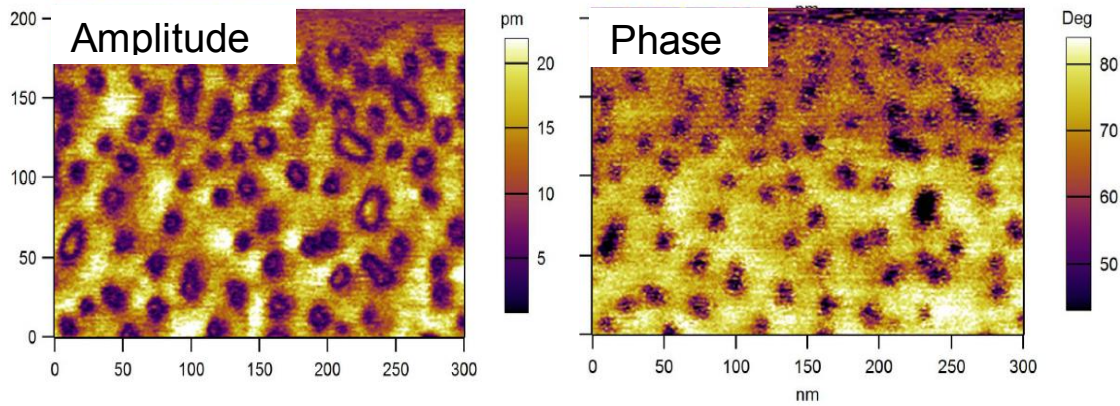


Fig. 4. 5 DART-PFM amplitude and phase for PZT_3_{ML}STO in selected area

It is noticed that the size of nano-domains keeps increasing during scanning when 150 mV AC bias is applied. It is surprising that the domain relaxation happens at such low electric field. To investigate the size-increasing phenomenon of nano-domains, a small area (200 nm x 200 nm) are imaged first before increasing the scan size to 500 x 500 nm² on PZT_1_{ML}STO. The increased magnitude of small domains can be observed for the comparison between the centre double-scanned area and the single-scanned neighbouring area. The nano bubble domain diameter widens by approximately 3 times (from ~10 nm to ~30 nm) after only one more PFM reading scanning at 150 mV. In addition, the nearby bubble domains start merging together (as marked in orange region). The nano-domain growing process is further detected via continuously scanning at selected 150 x 150 nm² region as shown in Fig. 5.7. The marked areas

indicate the same region as a reference to the drifting images. After several scanings, the original bubble-like domains transfer into stripe-like polydomains which are consistent with polydomain structure in PZT_X_{ML}STO thin bottom electrode ^[61].

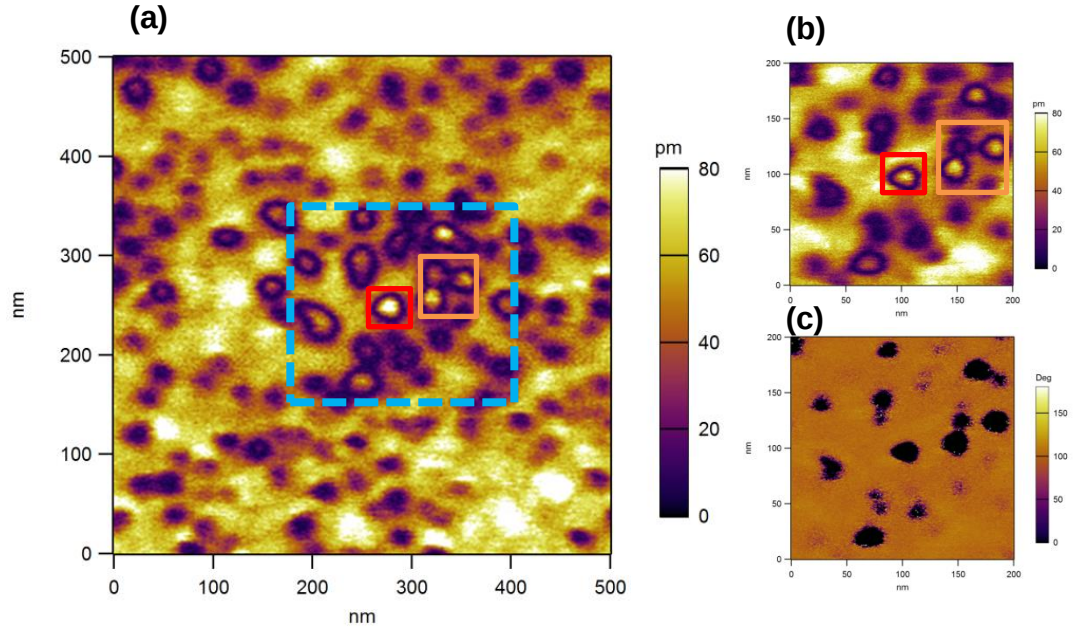


Fig. 4. 6 (a) is amplitude image of PZT_1_{ML}STO with 200 nm² double scanned centre region inset. (b)&(c) are amplitude and phase of 200 nm² at initial imaging. The red marked domain indicates that the diameter increased from ~11 nm to ~30 nm.

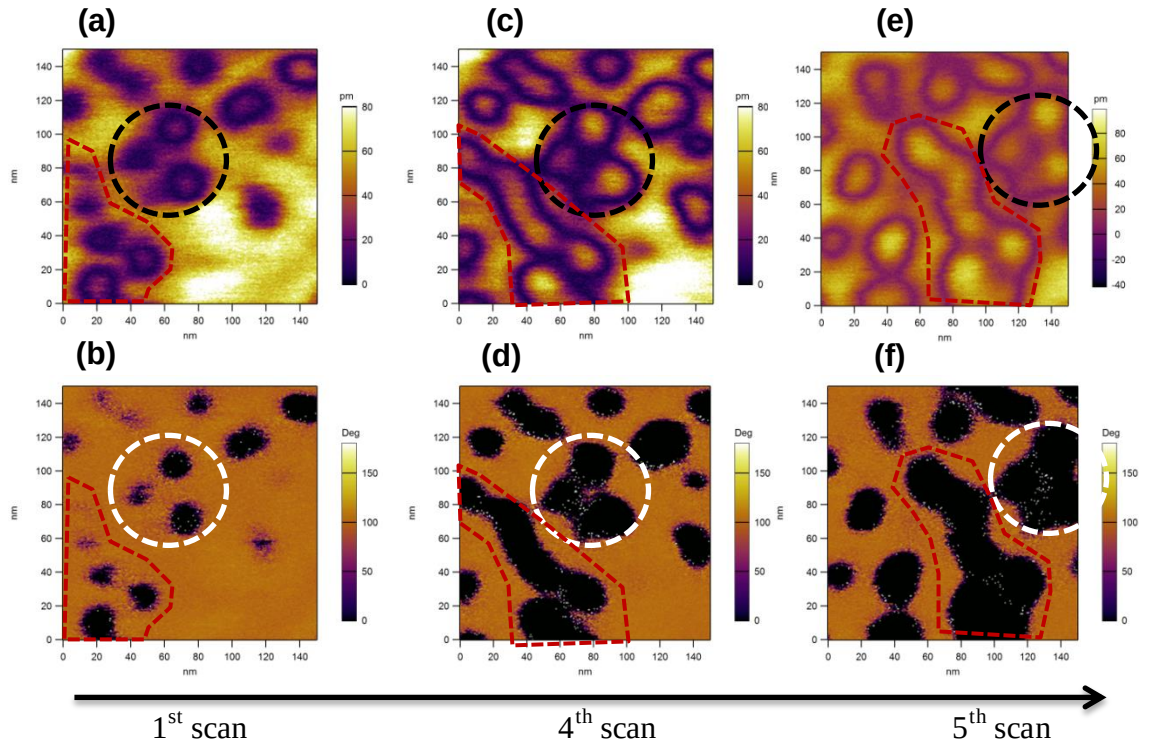


Fig. 4. 7 the amplitude and phase of nano bubble domains growing process in 150 nm² on PZT_1_{ML}STO. The marked areas finally combined together after 5th scans and bubble domain configuration turned into 180° polydomain.

4.3. Discussion:

For a pure ferroelectric film, the charge carriers from metallic electrodes or surface adsorbates can compensate the depolarizing field at ferroelectric interface ^[111]. In particular, for PZT and STO interface, the ferroelectric/conductive interface is replaced by ferroelectric/paraelectric interface and the thickness of STO spacer varies from 1u.c to 10u.c. Due to the small thickness, the inserted thin STO spacer makes the screening less effective thereby increasing the depolarization in the PZT film ^[107]. However, it is also energetically costly for the large depolarizing field to persist in ferroelectric layer. As a result, the ferroelectric layer is electrostatically coupled with STO spacer to eliminate depolarization field throughout the PZT/STO/PZT heterostructure. In this way, the ultra-thin paraelectric STO spacer is charged to appear the same polarization as neighbouring PZT layer, and leads polarization reduction in

PZT ferroelectric layer as well ^[104, 105]. Another response to this is that the monodomain configuration in ultra-thin epitaxial film breaks into 180° polydomains with an opposite ferroelectric polarization, which reduce the depolarizing field.

The next step is to investigate the formation of polydomain configuration with nano-bubble-like polarization upward domains. Fig. 5.8 shows the comparison of two samples with identical heterostucture (PZT_3_{ML}STO) on 2 nm and 15 nm thickness bottom LSMO electrodes. Both of two samples present polydomain configurations, but the domains transferred from stripe-like domains in samples of 2 nm LSMO into bubble-like domains in sample of 15 nm LSMO layer. In addition, the significant reduction of domain size (diameter of domain is ~10 nm in our study) is observed in comparison with other ultra-thin ferroelectric films studies (the domain diameter is ~100 nm in ^[107], for example) ^[106, 110].

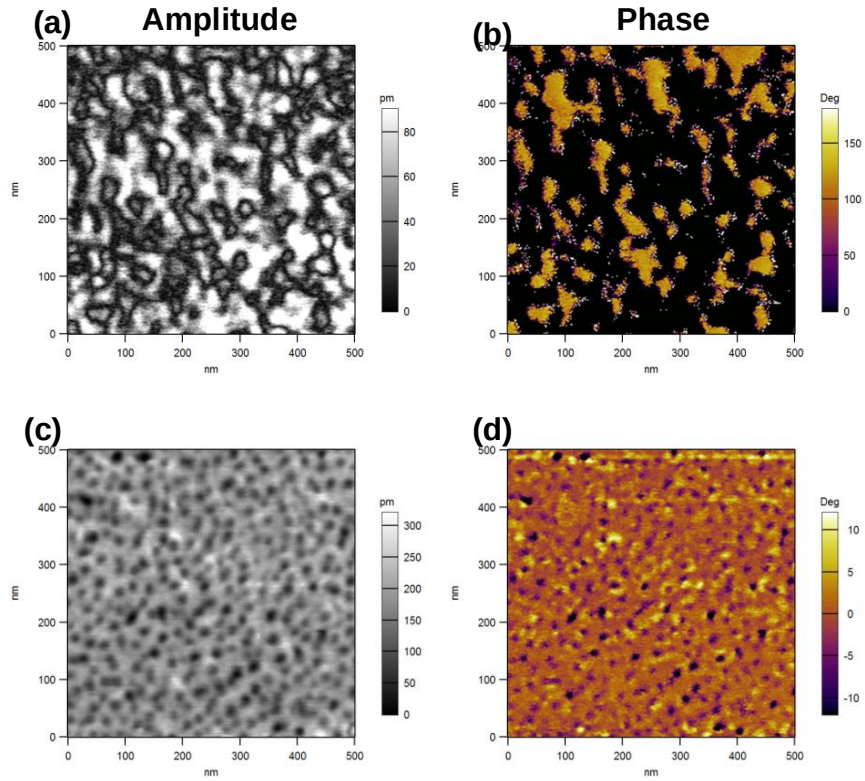


Fig. 4. 8 PFM amplitude and phase images of PZT_{3ML}/STO on 2 nm thick LSMO ((a) & (b)) and on 15 nm thick LSMO ((c) & (d)) in 500 nm² area. The transition from stripe-like to bubble-like configuration is clearly presented.

The domain evolution of PZT/STO/PZT films from stripe-like to bubble-like is not uncommon as many studies have examined in magnetic ultrathin films (i.e. Pt/Co/Pt films)^[112] and BiFeO₃ multiferroelectric films^[113]. Here we start with the discussion on the possible driving force for the size reduced domain formation in as-grow state. In the magnetic system, the comparable transformation from stripe to bubble domain configuration has been investigated theoretically by Cape et. al.^[114]. They confirmed that both of the stripe and bubble domain are in similar energetic state in terms of demagnetizing field in their study^[114]. Similar transition from stripe domain into bubbles domain in ferroelectrics has been studied by Lai et al.^[115]. According to their study, stripe-like domain configuration mainly comes from the depolarization field

while nano-bubble domain is formed as a result of the depolarizing field and applied external field. They also pointed out that compressive strain on film can decrease the external field and thus obtaining the stripe to bubble transition. In our study, the possible external driving force is built-in bias. Among all our samples on thick LSMO bottom electrode, the built-in bias effect promotes bubble domain over stripe domain with sufficient free charge carriers. The model by David J. ^[109], the presence of depleted layer may change built-in potential and therefore affecting as-grown domain state. The relationship between depletion layer width w and carrier density C_D is expressed as :

$$w = I/C_D^{1/2} \quad (1)$$

where I refers to ferroelectric-electrode interface property. The simulation of this study shows the domain pattern transition occurs under high the carrier density. Further, the domain state splits into striped reverse domains with uncompensated bound charge at electrodes in film predicted by ab initio calculations ^[116].

The built-in field E_b can be expressed as

$$E_b = -E_c * 0.5 * 3\sqrt{3}r(1 - r^2) \quad (2)$$

Where E_c means the coercive field for film without depletion layer and r can be deduced by rescaled thickness d' as

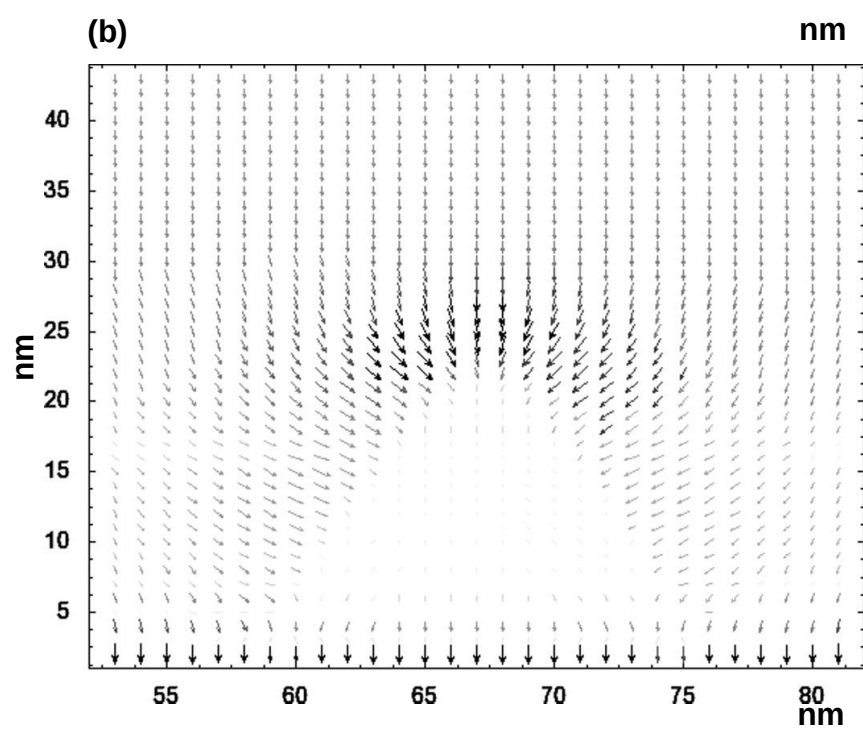
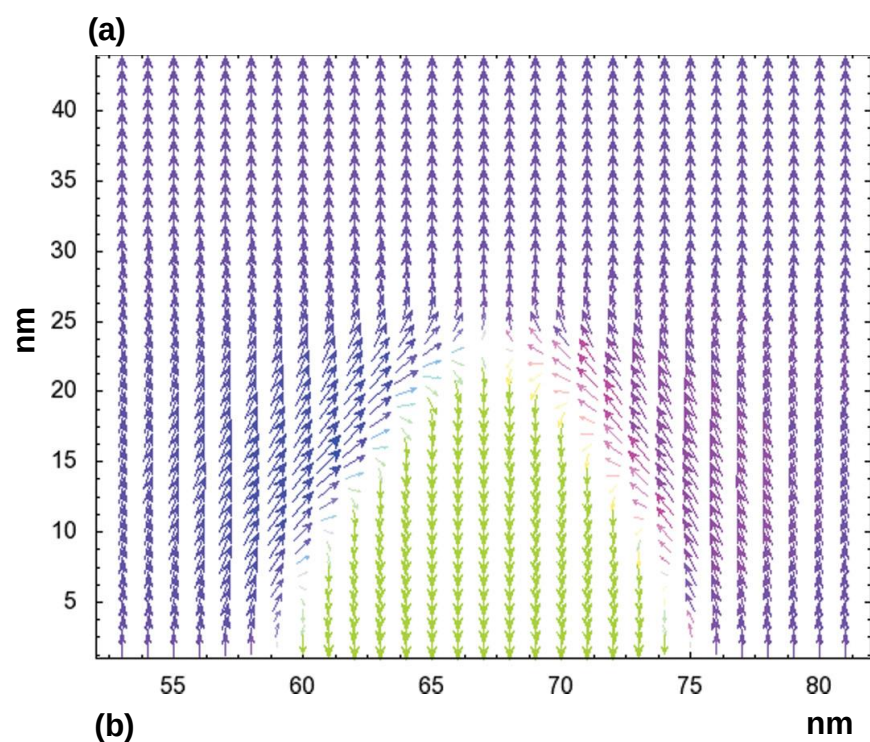
$$r = \sqrt{1 - 2/(3d')} \quad (3)$$

the expression for d' is

$$d' = \frac{d}{C_D^2(1-(\alpha_1\epsilon_0)^{-1})w^3b^2} \quad (4)$$

By combining the equation (1), the built-in field is proportional to carriers density C_D under the same thickness of ferroelectric film.

With low C_d , the built-in field is not sufficient enough to switch any region in the film thus monodomain is preserved. When the carrier density increases above critical value of coercive field, reverse domain starts nucleating at the bottom of ferroelectric layer. During the nucleation process, the electric field concentrates from the bottom interface of ferroelectric layer at the beginning. Accordingly, there is a tip-like domain formed to favour the depolarization field at the top of reversible domain in nucleation process. The distributions of polarization and electric field during the domain reversing have been systemically studied by David ^[109]. Fig. 5.9 (a) and (b) illustrate polarization and electric field distribution in the vicinity of an intermedia reversed domain during the 180° domain growth. To gain electrostatic energy favourite, the polarization vectors should avoid head to head or tail to tail domain configuration[ref]. Hence, the neighbouring polar vectors slightly rotate around the growing 'domain' under polydomain forming processes and result in tip-like reverse domain vertically which is illustrated in Fig. 5.9 (a). To screen electric field at the top region of tip-like domain with rotated polarization, the electric field out of tip-like region is enhanced as shown in Fig. 5.9 (b) (the darker arrows illustrate stronger electric field). For the interior region of 180° domain, the net electric field effectively reaches to zero. The growth of reverse domain processes is shown in Fig. 5.9 (c). With the growth of the reverse domains, the monodomain to bubble domain transition is realized. It is important that the carrier density is high enough to generate sufficiently larger electric field in vertical tip-like region than internal coercive field.



(c)

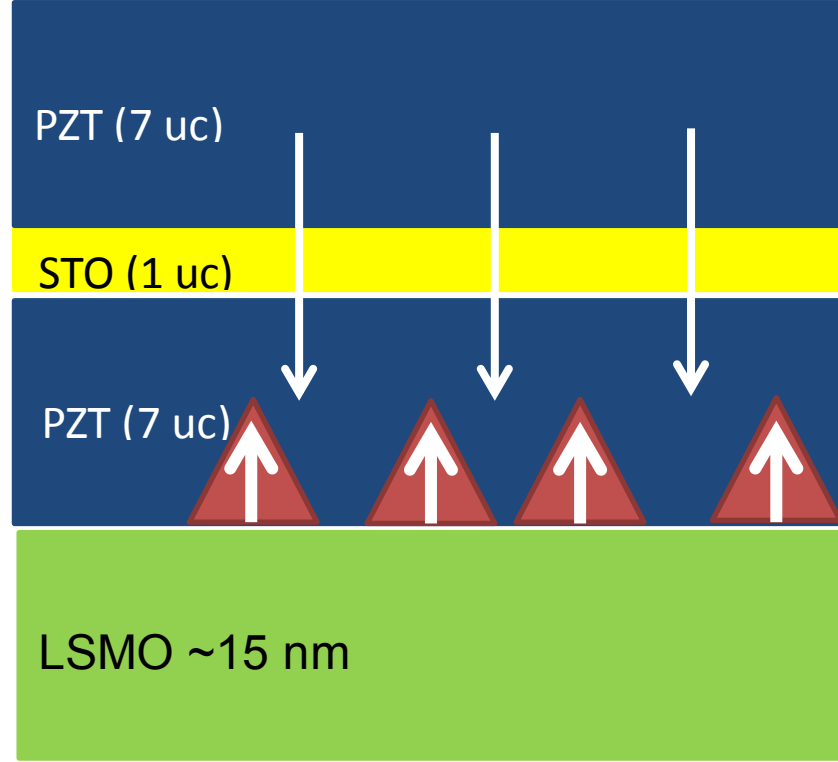


Fig. 4. 9 (a) indicates the distribution of polarization and (b) is electric field layout during the process of 180° domain developing. To minimize the electrostatic energy, the tip-like forms at the top of reverse domain ^[109]. (c) is the schematic for reverse domain growth in bubble domain samples. The white arrow presents polarization direction in the heterostructure.

However, the explanation of electrostatic energy is not enough to solve bubble domain configuration completely. The defects within the film also contribute to the 180° nano bubble domain shape evolution. Fig. 5.10 (a) and (b) show the high resolution cross-section TEM for PZT_{5ML}STO on thick bottom electrode, and the corresponding polarization distribution, respectively. In the Fig. 5.10(a), the defect is found at the interface in the marked area. The growing tip-like domain is also observed in polarization mapping (Fig. 5.10(b)) at identical area. This indicates that defect at

interface between PZT and LSMO is related to the bubble domain formation. The defect-induced fluctuation potentially breaks the long-term build-in electric field. Hence, intrinsic defect structure plays an important role to promote the bubble domain transition over stripe domain. In conclusion, there is a complicated mechanism to drive the nano bubble domain formation. This underlying driving force includes electrostatic consideration, enhanced screening effect by increased free carries, depolarization field and defect promoted domain nucleation.

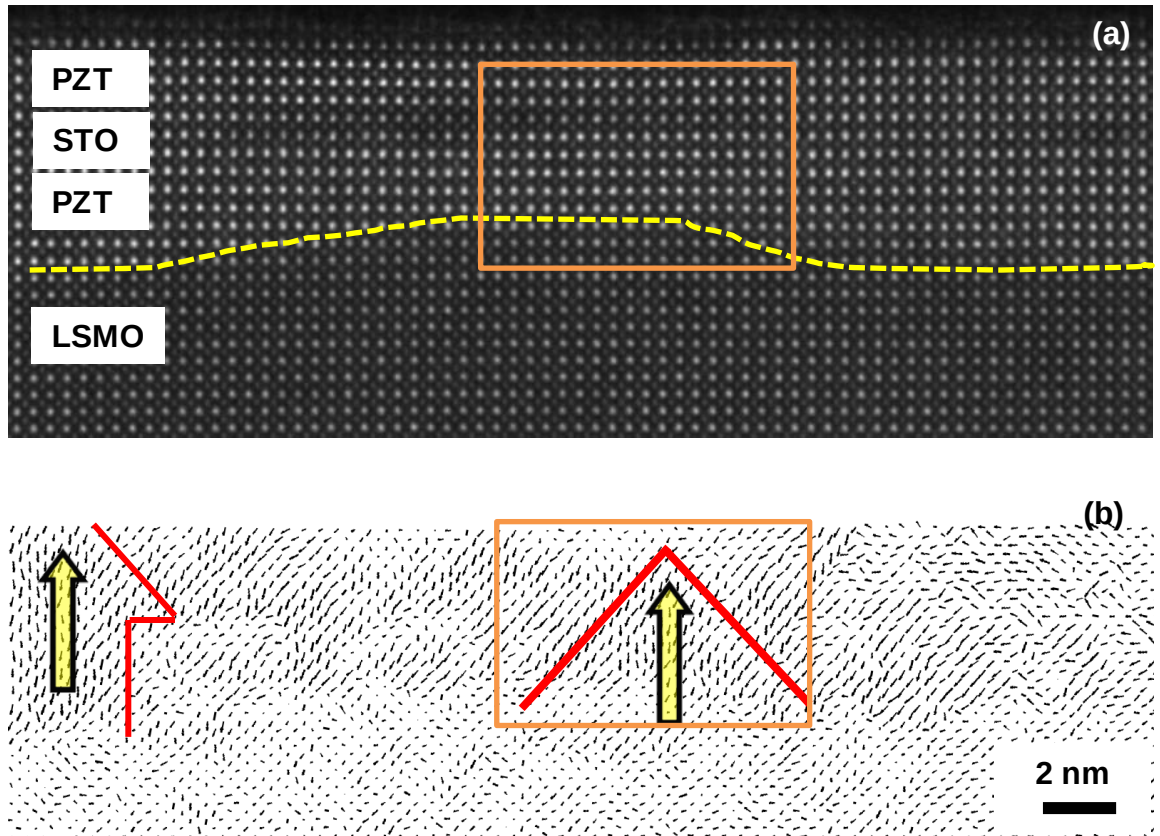


Fig. 4. 10 Cross section TEM of PZT_{5ML}STO (a) and the corresponding polarization mapping

Although bubble domain configuration is observed in many studies, our samples demonstrate ultra-small size^[85, 105, 107]. The bubble domain size is assessed for PZT_{3ML}STO according to its PFM phase images shown in Fig.5.11 (a). For this

estimation, we employed same approach as study^[107]. By fittings of bubble-like domain radius along (110) and (1 $\bar{1}$ 0) are 5.41 ± 0.28 nm and 4.79 ± 0.23 nm, respectively, as shown in figure 5.11.. Our PZT_3_{ML}STO sample has isotropic tiny bubble domains according to the result. This isotropic distribution indicates that our engineered STO spacer samples are more likely to attain enhanced electrostatically coupling with bottom electrodes^[117] and the build-in bias to remain the bubble-like domain structure over stripe-like domain structure is acquired in films^[115].

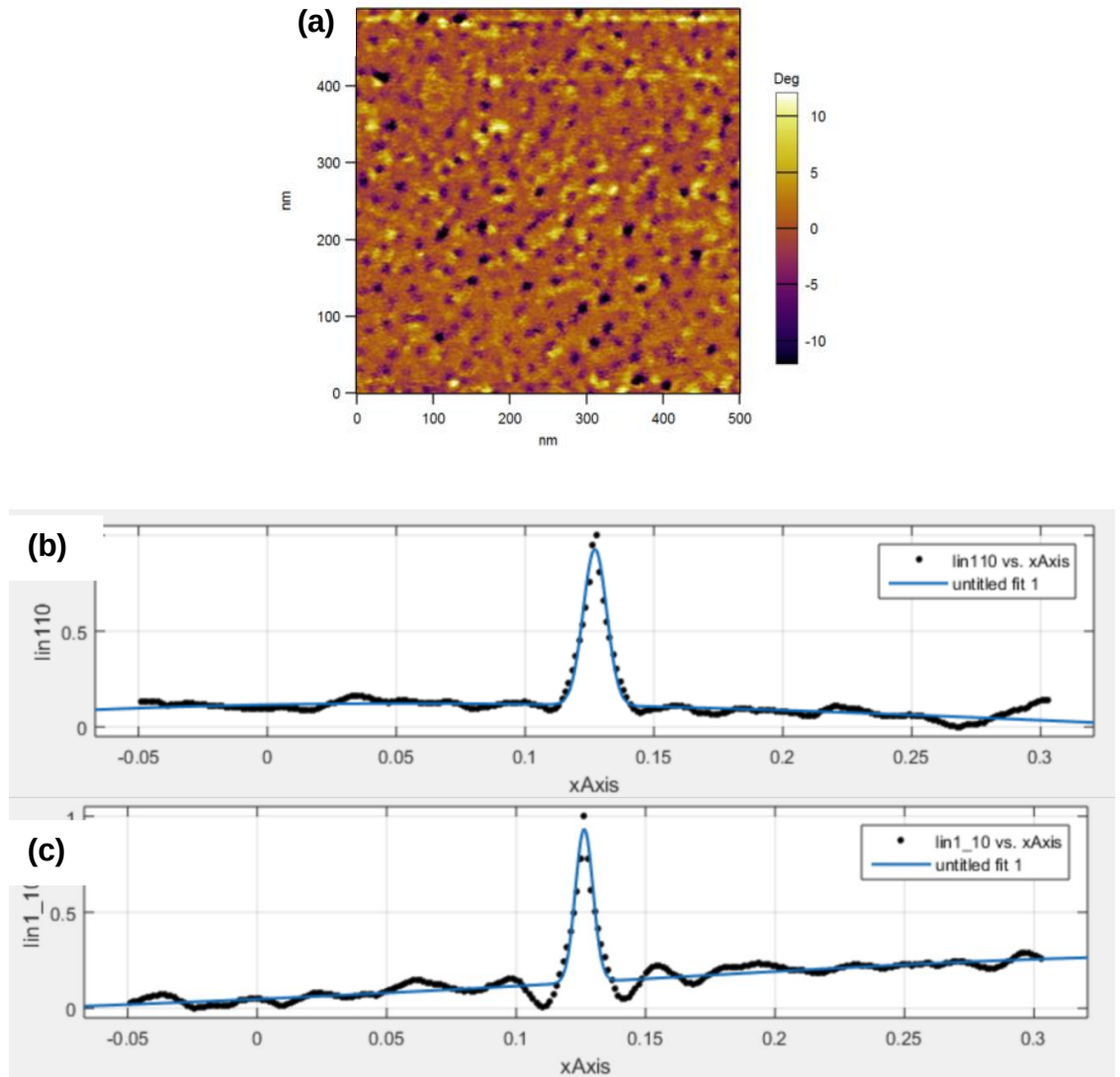


Fig. 4. 11 (a) PZT_3_{ML}STO PFM phase image for domain size fitting; (b) and (c) are the domain size fitting pattern according to LLK approach on (110) and (1 $\bar{1}$ 0), respectively.

The relaxing processes from bubble-like domain to stripe-like domain can occur under external electric field, as discussed previously in Fig. 5.7. Thus, the bubble domain evolution can be due to the charge redistribution caused by external field. The bubble-like domains were formed in as-grown state and , the intrinsic net filed is close to zero and thus achieving the metastable state bubble-like domain configuration. However, By applying external bias on the sample, the polarization vectors are partially or fully switched in the applied regions and an unstable state to this region is created since the as-grown electrostatic scenario is disturbed ^[118]. According to study of Gruveman ^[119], the retained polarization as a function of time-dependence is expressed as:

$$P(t) = P_0 - m \log(t/t_0) \quad (5)$$

P_0 refers to initial polarization and m is a decay rate ^[120]. The log-time relation indicates that relaxation from charges redistribution is in a wide time range. In our study, the relaxing process and domain evolution are quite fast as the scanning duration is around 10 mins. In addition, the irregular development of domain shape is observed because spatial variation of domain wall velocity. From Fig. 5.7, our enhanced depolarization field samples experiences similar tendency of retention relaxation ^[118, 119]. The marked red region shows a different relaxing rate compared with the black region (while dash line in phase images) and they evolved into two different domain shapes after continuous scans. To be specific, the red region relaxed into strip-like domain similar to the virgin domain state in ultra-thin bottom electrode spacer samples in chapter 4 while the black regions merged together and formed a large circle domain. As the depolarization field is enhanced by the introduction of STO spacer, it is possible that the build-in field is sensitive and can be easily disturbed by oscillation amplitude of the

cantilever. Then redistribution of charges occurred at bubble domain regions after scanning with AC signal (200.mV). Subsequently, the domain transferred from bubble-like into stripe-like after charges redistribution to obtain electrostatic stable state. Another necessity for the charge redistribution which responses to detection AC signal is the sufficient charge carriers at electrode interface. This is the major difference between samples in this study and that in chapter 4. Compared with the conductive thick LSMO, the ultra-thin LSMO presents the nature of semi-conductivity[ref], which makes it energetic costly and slower to redistribute the carries within LSMO electrode.. Besides, the growth of reverse bubble domain to stripe domain results in less required charges of electrode to screen build-in bias in film.

The domain wall mobility is another possible origin for irregular reverse domain growth. As we discussed that one of driving forces to form bubble domains is the effect of defects. . Defect-induced effect also plays a key role to determine the domain size and shape evolution during scanning relaxation. In addition, it can be observed that domain wall mobility is suppressed between pinning centres and causes reverse domain bending around pinning points as the Fig 5.7 indicated.

In conclusion, we have shown that not only the introduction of paraelectric STO layer affects the ferroelectric properties but also the 180° domain is adjustable by the underlying conductivity of bottom electrodes. The tiny bubble domains over stripe-like domains are gained by the combined effect of polarization field and appreciated screening in ultra-thin ferroelectric film. In addition, with increased deposition field which led by thicker STO layer, there are increasing number of ‘bubbles’ , but the bubble domain size keeps similar . Therefore, the new possibility of tuning the 180° domain pattern is revealed by careful design of ultra-thin ferroelectric structure.

Chapter 5 Conclusion and Future work

5.1 Conclusion

With advanced thin film deposition technologies such as PLD, high quality ferroelectric thin films are successfully deposited on selected substrates down to a few nm. At nano-scale thickness region, the boundary conditions and the presence of interfaces become extremely critical. This dissertation provides an in-depth investigation and understanding on ultra-thin epitaxial ferroelectric films, focusing on the effect of mechanical and electrical interfacial conditions on polarization and domain behaviour in classical ferroelectric $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) system.

The key topics investigated are:

- 1, the dielectric and electromechanical responses of a ferroelectric bilayer which consists of ultra-thin tetragonal PZT/rhombohedral PZT layers;
- 2, the positive effects of depolarization field on the ferroelectric behaviours of ultra-thin PZT/STO/PZT heterostructure grown on a semi conductive electrode;
- 3, the characterisation of metastable nano bubble domain pattern and the nucleation dynamics for the bubble domain configuration in ultra-thin PZT/STO/PZT on a metallic bottom electrode;

The outcomes of the projects in the thesis are listed as follows:

1. Firstly, the symmetry reduction and polarization rotated domains in ultra-thin PZT-T/PZT-R epitaxial bilayer are studied from a structural and theoretical aspects. Synchrotron XRD, electrons diffraction pattern, in-/out-of-plane PFM and electric-field-induced hysteresis loops confirm the bilayer system achieve a rotational polar states in

T-layer. A largely enhanced electromechanical d_{33} is observed attributed to reversible polarization rotation. Finally, the ferroelastic coupling is demonstrated for the bilayer sample via switching polarization from in-plane to out-of-plane, a key result required potential memory devices.

2. By purposely introducing a large depolarization field using SrTiO_3 (STO) spacer, the epitaxial heterostructure $\text{PbZr}_{0.2}\text{TiO}_{0.8}\text{O}_3$ /X u.c. STO/ $\text{PbZr}_{0.2}\text{TiO}_{0.8}\text{O}_3$ on (001)-oriented STO substrate was investigated. The inserted STO spacer, ranging from 3 unit cells to 10 unit cells strongly affects the as-grown domain pattern and the out-of-plane lattice parameter. The transition from monodomain to 180° polydomain is observed via PFM at the top 3 nm thick PZT layer in these samples with increasing thickness of STO spacer. In the sample of single 6 nm PZT (reference sample), the c constant is 0.416 nm and the main area shows monodomain with polarization downward. Under external bias, the reference sample gives asymmetric loops. However, this imprint behavior reduces by 80% by middle STO spacer. In addition, the domain switching reaction speed is accelerated by 2 orders of magnitude compared to the reference sample.

3. As a follow up to the precious study of on depolarization field on ferroelectricity, a study focuses on tuning the 180° polydomian structure is presented. It demonstrates that the 180° polydomain pattern is adjustable by the combined effect of depolarization filed and bottom electrode. The metal-like 20 nm thick $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (carrier density $\sim 10^{20}/\text{cm}^{-3}$) was deposited as bottom electrode to replace the 2nm LSMO in the previous chapter. PFM images illustrate the tiny bubble-like domain form an opposed polarization at top PZT layer in the STO spacer samples. The amount of nano bubble domain (radius is around 10 nm) increases with stronger depolarization field which is brought by thicker STO spacer. Furthermore, the bubble domain structure

is metastable in the virgin state. It is found that a repeatable scanning can modulate this nanodomain virgin state into stripe-like domain pattern as the 180° polydomain structure.

5.2 Future work

The bilayer project presents a simple way to modify the polarization rotation through insertion of a bilayer. We have demonstrated that the a/c domain structure exists in 100 nm PZT-T/100 nm and a_1/a_2 domain structure exists in 30 nm PZT-T/100 nm PZT-R bilayer in previous studies. More importantly, we observe structure symmetric reduction and polarization rotation in our ultra-thin bilayer. Further study can be developed on the interreaction between top PZT-T layer and bottom PZT-R layer. By varying the thickness of the underlying PZT-R layer, the structure symmetry and polar rotation can be progressively adjusted in the top PZT-T layer or the bilayer as whole.

In the study of depolarization field, the 180° polydomain configuration is extremely compelling in terms of physical and industrial interests. According to XRD simulation results, the inserted STO spacer strongly affects the out-of-plane lattice constant. It is valuable to visualize the polarization distribution of heterostructure via TEM unit cell polarization mapping. In addition, *in-situ* aberration-corrected STEM can be employed to analyse the domain growth process with external bias, especially the interfacial reaction between PZT and STO. The further focus of bubble series can be the understanding for relaxing mechanism from bubble-like to stripe-like domain configuration. In-situ aberration-corrected STEM technique can help to show the evolution of domains would be exciting. Moreover, the conductivity and dielectric properties of the samples with controllable domains are also interesting. These understanding are highly important for ferroelectric functional device engineering.

Appendices

A1 Reversible polarization rotation in epitaxial ferroelectric bilayers

A1.1 Phase-field simulations:

The spontaneous polarization vectors P_i ($i=1,2,3$) are chosen as the only order parameters. The polarization evolution is governed by the Time-dependent Ginzburg-Landau equations^[121]:

$$\frac{\partial P_i(\vec{r}, t)}{\partial t} = -L \frac{\delta F}{\delta P_i(\vec{r}, t)} (i = 1, 2, 3) \quad (\text{Eq.1})$$

Where r is the spatial position vector, t is the evolution time step, L is the kinetic coefficient, F is the free energy density of the system which includes the contributions from bulk, elastic, electric, gradient energy densities:

$$F = \int (f_{\text{Bulk}} + f_{\text{Elastic}} + f_{\text{Electric}} + f_{\text{Gradient}}) dV \quad (\text{Eq.2})$$

Detailed expressions of the energy density as well as method of solving the phase-field equations can be found in literature^[122].

The simulation system is discretised into a three dimension box of 128 grids×128 grids×50grids, with each grids represent 1 nm. Where the thickness direction is composed of 15 nm of substrate, 20 nm of R-PZT ($\text{Pb}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$), 5 nm of T-PZT ($\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$) and 10 nm of air layer. Periodic boundary condition is applied along the two in-plane dimensions while a superposition method is employed in the out-of-plane dimension.

Following the work by Fei et al.^[123], the effective in-plane average strain is defined as the difference between the substrate strain and lattice strain. From the

Reciprocal space mapping (RSM) of lattice parameter, the R-PZT is considered to be fully relaxed with respect to the SrTiO_3 substrate, while the T-PZT layer is fully coherent to the R-PZT layer. With R-PZT as the reference state, the substrate strain is effectively zero for the whole film, while the lattice strain is 0 and $\frac{a_T - a_R}{a_T}$ for R-PZT and T-PZT layers, respectively, where a_T and a_R are the pseudocubic lattice parameters for R-PZT and T-PZT layers^[60]. To account for the difference in elastic constants of the T-PZT and R-PZT, the elastic iterative method is used^[124]. All the parameters are taken from Haun et al.^[125]. As is shown in Fig.S1, metastable rhombohedral domains grow to the tetragonal top layer upon the application of external field, forming large R domains throughout the thickness direction. The metastable R domains can be switched by the reverse bias. Whereas the fine tetragonal a_1/a_2 twin domain can be nucleated and grown back during the removal of the applied bias. The nucleation process starts from the curved domain walls and expands to the rhombohedral domains.

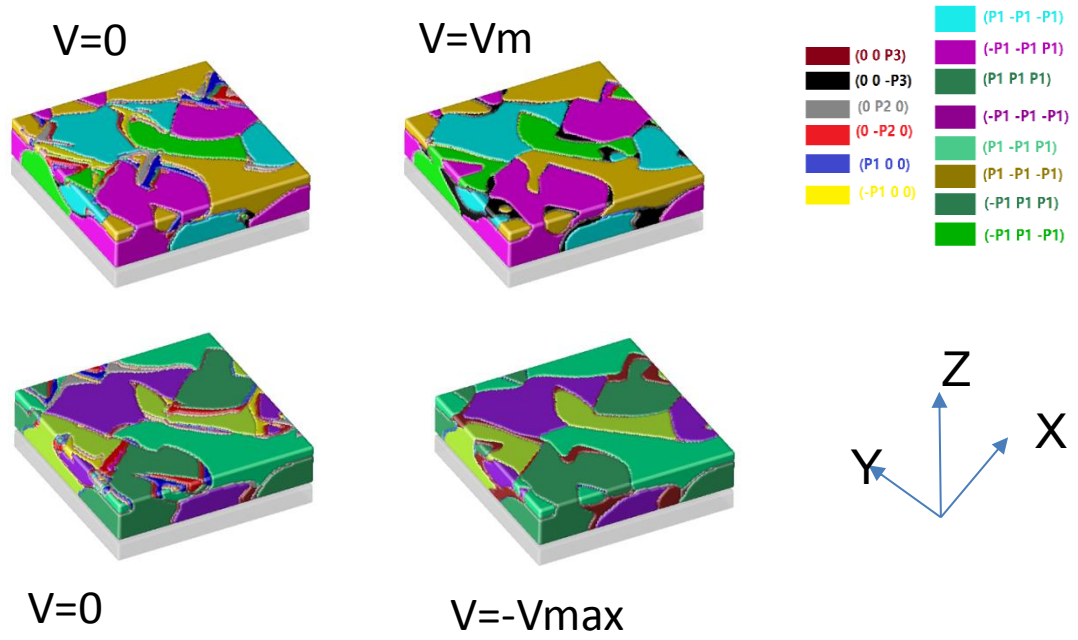


Fig. A1. 1 shows domain development with applied bias. The tetragonal domain with polarization in- plane can be re-orientated into rhombohedral domains by external electric field.

A1.2 Structural analysis of the epitaxial bilayers

A1.2.1 HR-XRD simulation (Similar to Liu G., Chen J., Lichtensteiger C., Triscone Jean-Marc, Aguado-Puente P., Junquera J., Valanoor N. (2016). Positive Effect of an Internal Depolarization Field in Ultrathin Epitaxial Ferroelectric Films. Adv. Electron. Mater., 2: 1500288. doi: 10.1002/aelm.201500288)

We have employed a custom-made Matlab program to simulate XRD patterns of a bilayered structure along (00L) truncation rods. The atomic scattering factors f are calculated using the formula :

$$f = \sum_{i=1}^4 a_i \exp \left(-b_i \cdot \sin^2 \left(\left(\frac{\theta}{\lambda} \right)^2 \right) \right) + c \quad (\text{Eq.3})$$

and the values for a_i , b_i and c found in the international tables for crystallography ^[126], where θ is the diffraction angle and λ the wavelength of the diffracted beam (here $\lambda = 0.15406$ nm). This is done for the different atoms present in the sample, nameley La,

Mn, O, Pb, Ru, Sr, Ti and Zr. Where there is alloying on the A- or B-site, an effective atomic scattering factor is created by taking the weighted average of the atomic scattering factors for individual atoms respectively.

All the materials used here have a perovskite structure ABO_3 . The structure factor is then obtained for each perovskite unit cell by using the Wyckoff positions within this cell, i.e. A at $(x,y,z)=(0,0,0)$, B at $(0.5,0.5,0.5)$, O at $(0.5,0.5,0)$, $(0,0.5,0.5)$ and $(0.5,0,0.5)$ in lattice parameter units. Since we are looking at the $(00L)$ truncation rods, we only need the z value for the different atoms and the c -axis parameter of the corresponding material. The structure factor is then

$$F = f_A \exp(iQz_A c) + f_B \exp(iQz_B c) + f_{O1} \exp(iQz_{O1} c) + f_{O2} \exp(iQz_{O2} c) + f_{O3} \exp(iQz_{O3} c) \quad (\text{Eq.4})$$

where $Q = 4\pi \sin(\theta)/\lambda$ is the momentum transfer.

The scattering amplitude g for the whole heterostructure is then obtained by adding the contributions from each layer following :

$$g = \sum_{\text{all layers}} F \cdot \exp(iQ t_{\text{below}}) \cdot \exp\left(-\frac{t_{\text{above}}}{\mu}\right) \quad (\text{Eq.5})$$

where t_{below} and t_{above} are the thickness of the heterostructure below/above the position of the layer considered, and μ is the penetration depth. The first exponential term takes into account the correct phase depending on the position of the considered layer in the structure. The second exponential term takes into account the penetration depth reducing the intensity of the contribution of the deeper layers. We use a penetration factor $\mu = 1.5 \times 10^4$.

The scattered intensity is then just $I = g \cdot g^*$, and is then renormalized to a maximum intensity equal to 1, allowing comparison with the measurements that are also renormalized.

The substrates used in this study are STO and are 0.5 mm thick, corresponding to $1.3 \cdot 10^6$ layers. In the program, we use only $2 \cdot 10^4$ layers with a c-axis of 0.3905 nm, in order to decrease the calculation time. As the deeper layers contribute much less, this is an acceptable approximation. We have checked that including more layers for the simulation of the STO substrate does not affect the resulting fit noticeably.

In this program, the quantities of unit cells and c-axis parameters can be adjusted within individual layers. Compositions are fixed for top T-PZT layer and bottom R-PZT layer. By adjusting the simulated pattern to the measurements, the optimized fitting curve can be obtained.

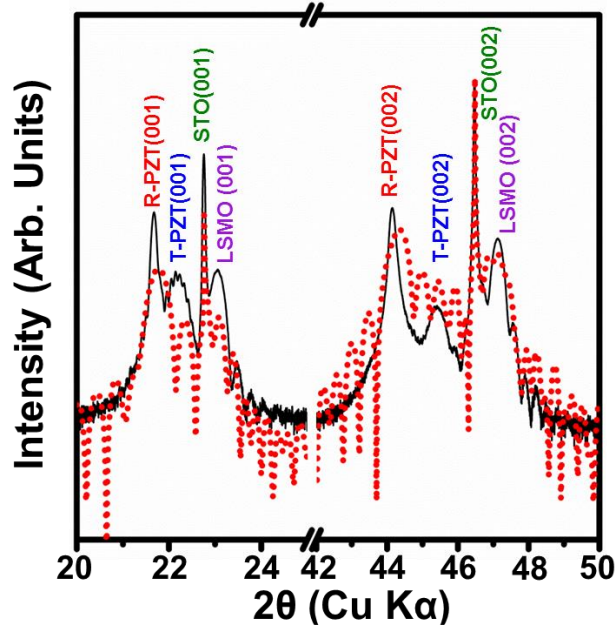


Fig. A1. 2 the comparison with simulation XRD pattern (red dot) and measurement (black line). Both of intensity are normalized to 1 so two STO (002)s are identical high in the figure. Simulated (001)s obtain better agreement with the measurement, including main peaks and oscillation.

Table A1. 1 Fitting Parameters

	Unit cells	Lattice parameter (c)
T-PZT	11	3.991 Å
R-PZT	50	4.091 Å

A1.2.2 Transmission Electron Diffraction analysis

Electron energy-loss spectroscopy (EELS) was carried out to identify the position of the interface between the PZT (T) and PZT (R) layers, as shown in Fig. A2.3. A HAADF STEM image (Fig. A2.3 (a)) was taken from the area near the outer surface of the sample, including the PZT (T) layer and part of the PZT (R) layer. Fig. A2.3 (b) shows a series of EEL spectra for the Ti-L_{2,3} edges collected along the direction of the arrow shown in Fig.A2.1 (a). The normalized intensity profile for Ti (Fig.A2.3 (c)) shows a stronger signal from point 1 to point 4. On the other hand, a weaker signal is observed from point 5 to 8. According to the deposition conditions, there should be more Ti in the PZT (T) (PbZr_{0.30}Ti_{0.70}O₃) layer compared to the PZT (R) (PbZr_{0.55}Ti_{0.45}O₃) layer. Therefore, the spectra at the top of the figure (point 1-4) correspond to the PZT (T) film and the bottom spectra (point 5-8) correspond to the PZT (R) layer. The interface is thus positioned between point 4 and point 5 with roughness of ~ 1 unit cell.

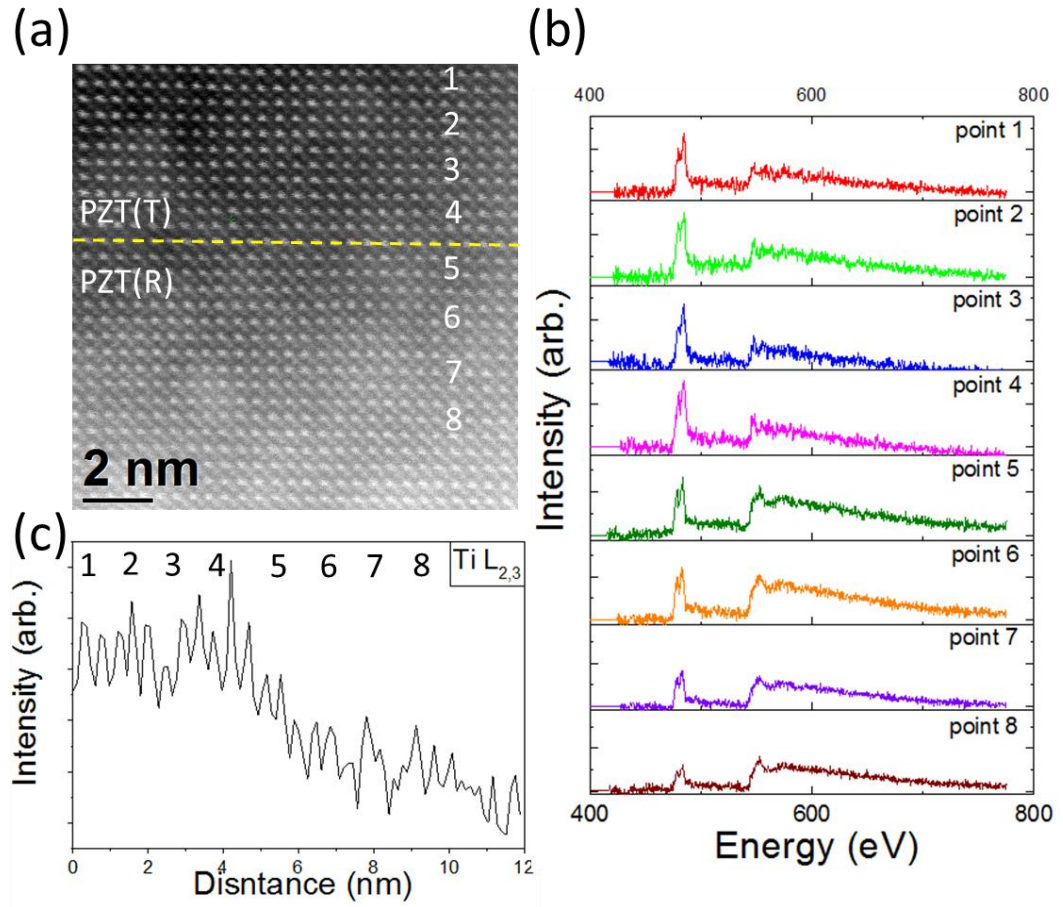


Fig. A1. 3 (a) The HAADF-STEM image was taken along the [100] beam direction. (b) A series EELS spectra were acquired in the energy loss range of 400 to 770 eV across the PZT (T)/PZT (R) interface, as denoted from point 1 to 8. (c) The normalized intensity profile for the Ti-L_{2,3} peak acquired across the interface shows a stronger signal from point 1 to 4, while a weaker signal at point 5, 6, 7 and 8. The interface between the PZT (T) and PZT (R) layers is identified.

A2 Positive effect of an internal depolarization field in ultrathin epitaxial ferroelectric films

A2.1 Cross-section TEM analysis:

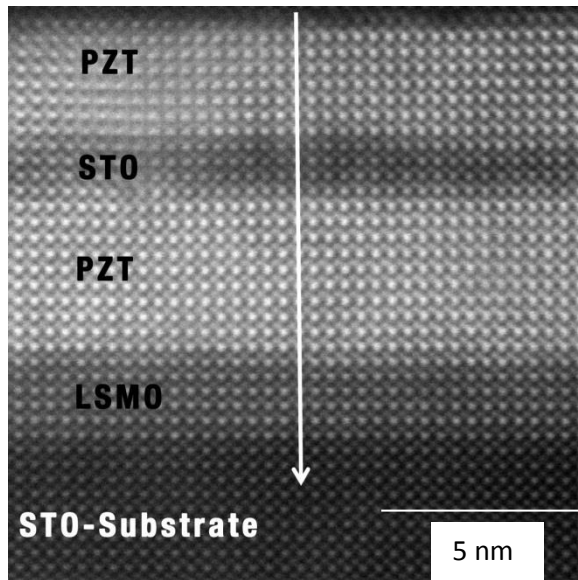


Fig. A2. 1 TEM images of PZT_3ucSTO showing the layers are continuous, with sharp interfaces, and without dislocation. The arrow shows the A-site atoms are perfectly aligned, confirming epitaxial registry across all layers.

A2.2 XRD Fitting

To simulate the XRD patterns measured for the different samples in the paper (Figure 2), we have used a custom-made Matlab program that simulates the (00L) truncation rods of heterostructures.

The atomic scattering factors f are calculated using the formula :

$$f = \sum_{i=1}^4 a_i \exp \left(-b_i \cdot \sin^2 \left(\left(\frac{\theta}{\lambda} \right)^2 \right) \right) + c$$

and the values for a_i , b_i and c found in the international tables for crystallography [P.J. Brown, A. G. Fox, E. N. Maslen, M. A. O'Keefe and B. T. M. Willis, International Tables for Crystallography (2006) Vol.C ch.6.1], where θ is the diffraction angle and λ the wavelength of the diffracted beam (here $\lambda = 0.15406$ nm). This is done for the different atoms present in the heterostructure, namely La, Mn, O, Pb, Ru, Sr, Ti and Zr. Where there is alloying on the A- or B-site, an effective atomic scattering factor is created by taking the weighted average of the atomic scattering factors for individual atoms respectively.

All the materials used here have a perovskite structure ABO_3 . The structure factor is then obtained for each perovskite unit cell by using the Wyckoff positions within this cell, ie A at $(x,y,z)=(0,0,0)$, B at $(0.5,0.5,0.5)$, O at $(0.5,0.5,0)$, $(0,0.5,0.5)$ and $(0.5,0,0.5)$ in lattice parameter units. Since we are looking at the (00L) truncation rods, we only need the z value for the different atoms and the c -axis parameter of the corresponding material. The structure factor is then

$$F = f_A \times \exp(i \times Q \times z_A \times c) + f_B \times \exp(i \times Q \times z_B \times c) + f_O \times \exp(i \times Q \times z_{O1} \times c) + f_O \times \exp(i \times Q \times z_{O2} \times c) + f_O \times \exp(i \times Q \times z_{O3} \times c)$$

where $Q = 4\pi \sin(\theta)/\lambda$ is the momentum transfer.

The scattering amplitude g for the whole heterostructure is then obtained by adding the contributions from each layer following :

$$g = \sum_{all\ layers} F \cdot \exp(i \cdot Q \cdot t_{below}) \cdot \exp\left(-\frac{t_{above}}{\mu}\right)$$

where t_{below} and t_{above} are the thickness of the heterostructure below/above the position of the layer considered, and μ is the penetration depth. The first exponential term takes into account the correct phase depending on the position of the considered layer in the structure. The second exponential term takes into account the penetration depth reducing the intensity of the contribution of the deeper layers. We use a penetration factor $F = 1.5 \times 10^4$.

The scattered intensity is then just $I = g \cdot g^*$, and is then renormalized to a maximum intensity equal to 1, allowing comparison with the measurements that are also renormalized.

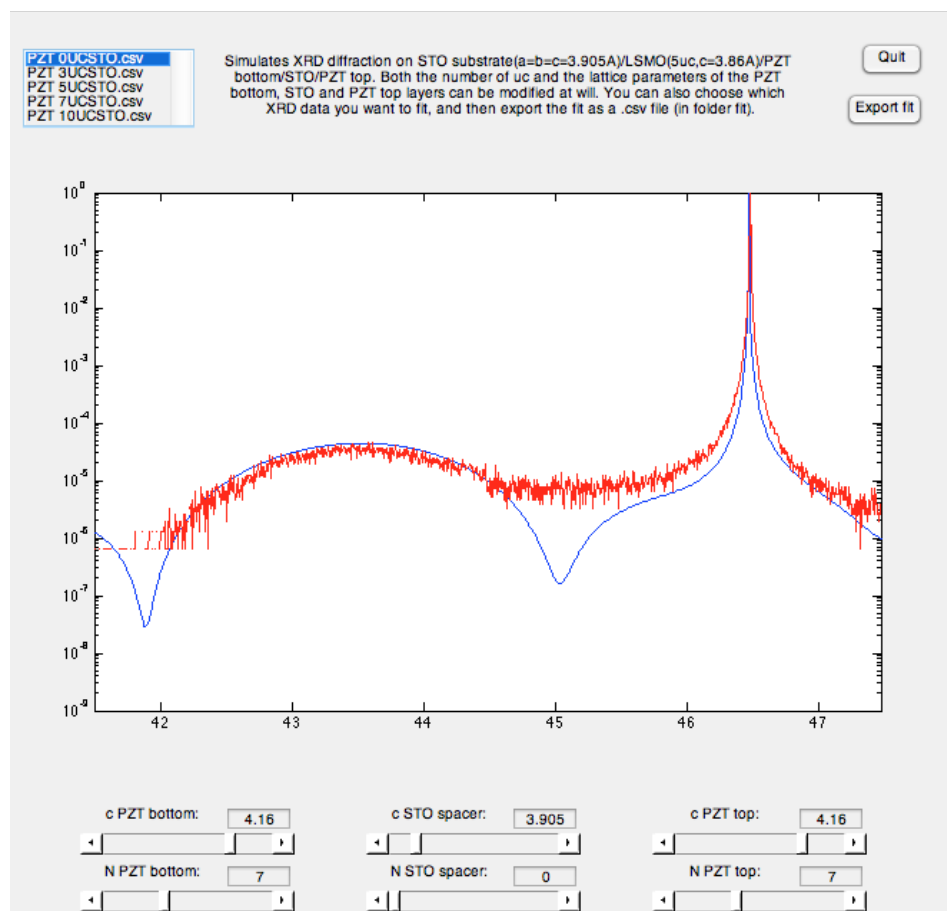
The substrates used in this study are STO and are 0.5mm thick, corresponding to 1.3×10^6 layers. In the program, we use only 2×10^4 layers with a c-axis of 0.3905 nm, in order to decrease the calculation time. As the deeper layers contribute much less, this is an acceptable approximation. We have checked that including more layers for the simulation of the STO substrate does not affect the resulting fit noticeably.

The LSMO layer is then composed of 5 unit cells with a c-axis of 0.386 nm.

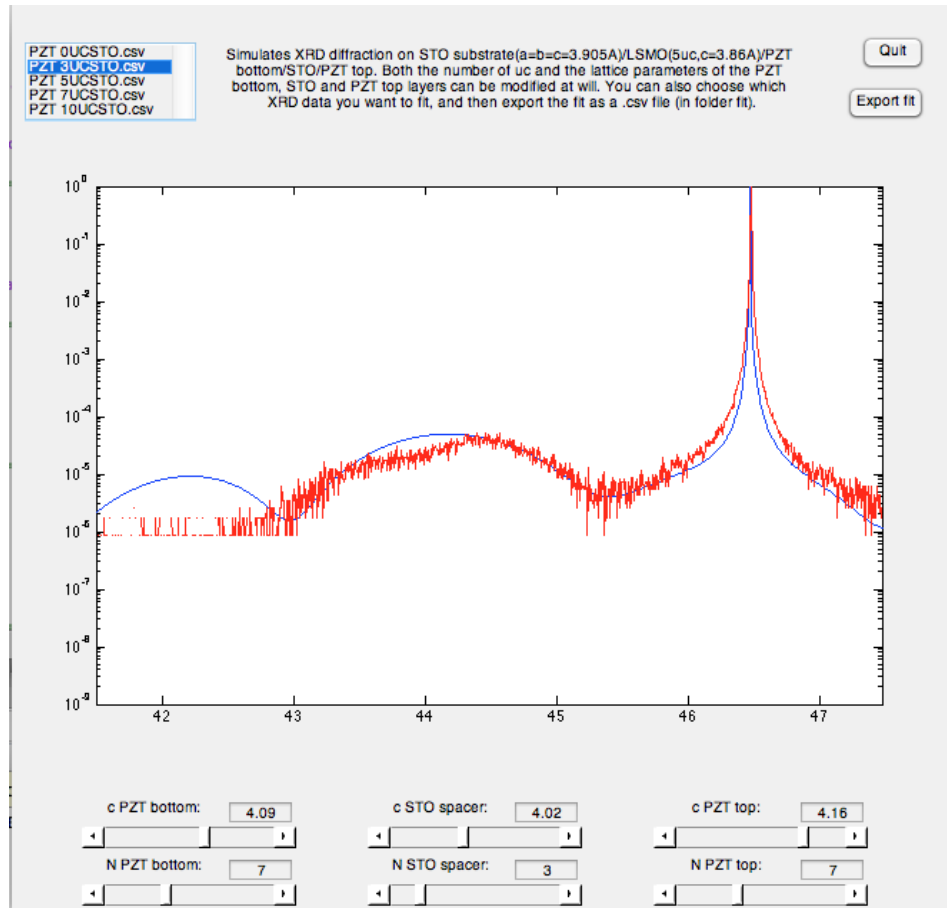
7 uc of PZT are then added, followed by 0, 3, or 10 uc of STO, and again 7 uc of PZT. In the program, the values of the c-axis parameters for the PZT bottom and top layers, as well as for the STO spacers can be varied.

By comparing the intensity curves obtained by this program to the measurements, we were able to fit the c-axis parameters for each layer in the different heterostructures.

For the sample without an STO spacer (PZT_reference), the best fit is obtained for a PZT c-axis of 0.416 nm (14uc of PZT, no STO).

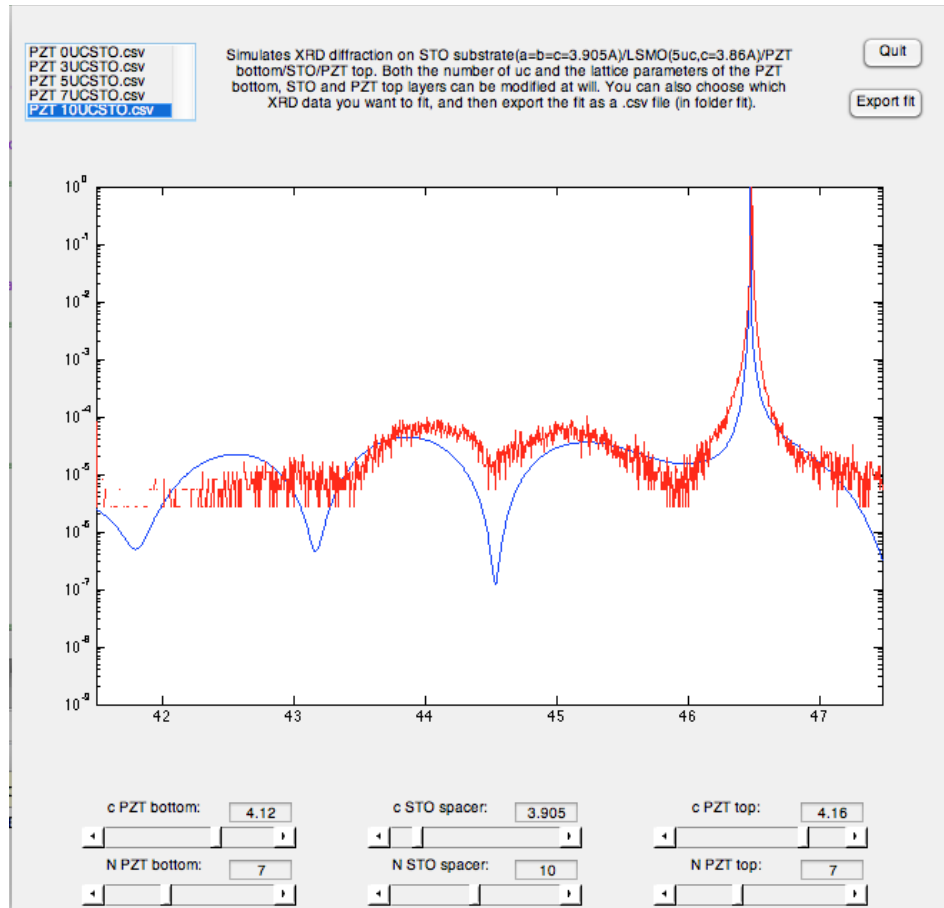


For the sample with 3uc of STO (PZT_3ucSTO), we found that it was impossible to get a good fit when the c-axis value for the STO was kept at 0.3905 nm, its bulk value. Only by increasing this value were we able to obtain a satisfactory fit. We also had to use different c-axis values for the top and bottom PZT layers. The best fits were found for a value of 0.409 nm for the bottom PZT, 0.402 nm for the STO spacer, and 0.416 nm for the top PZT.

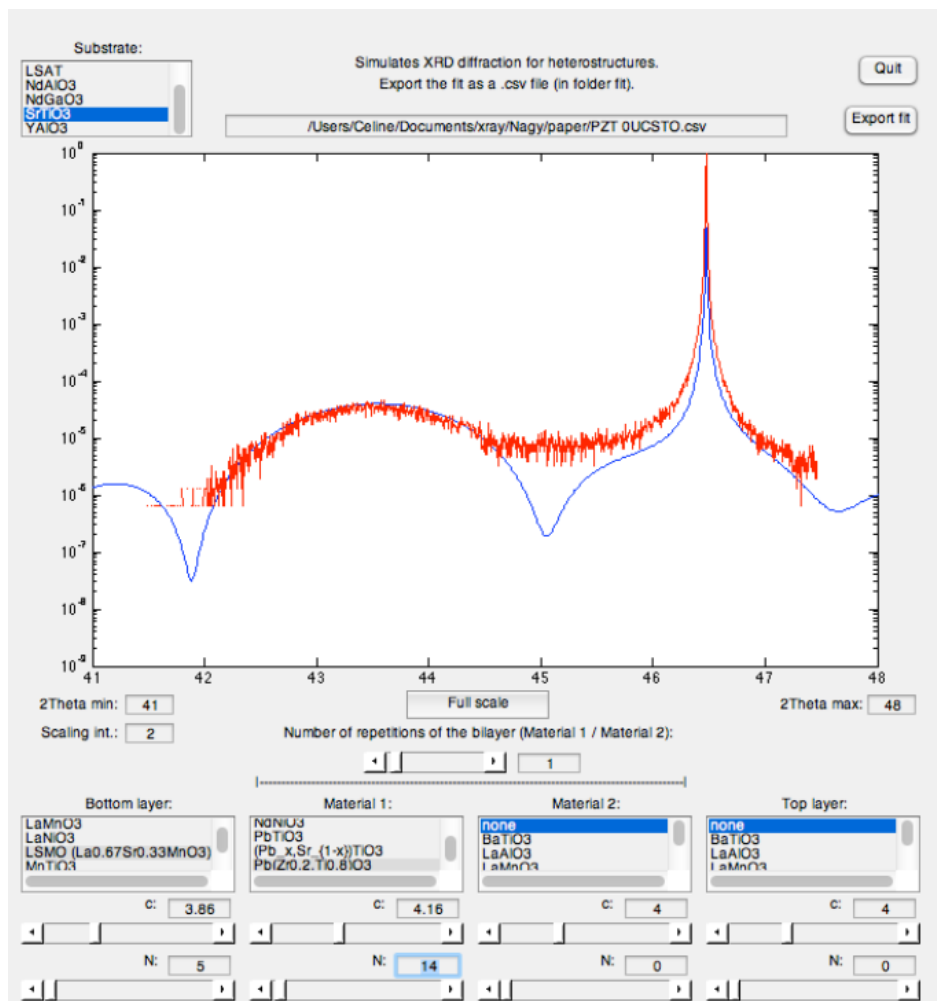


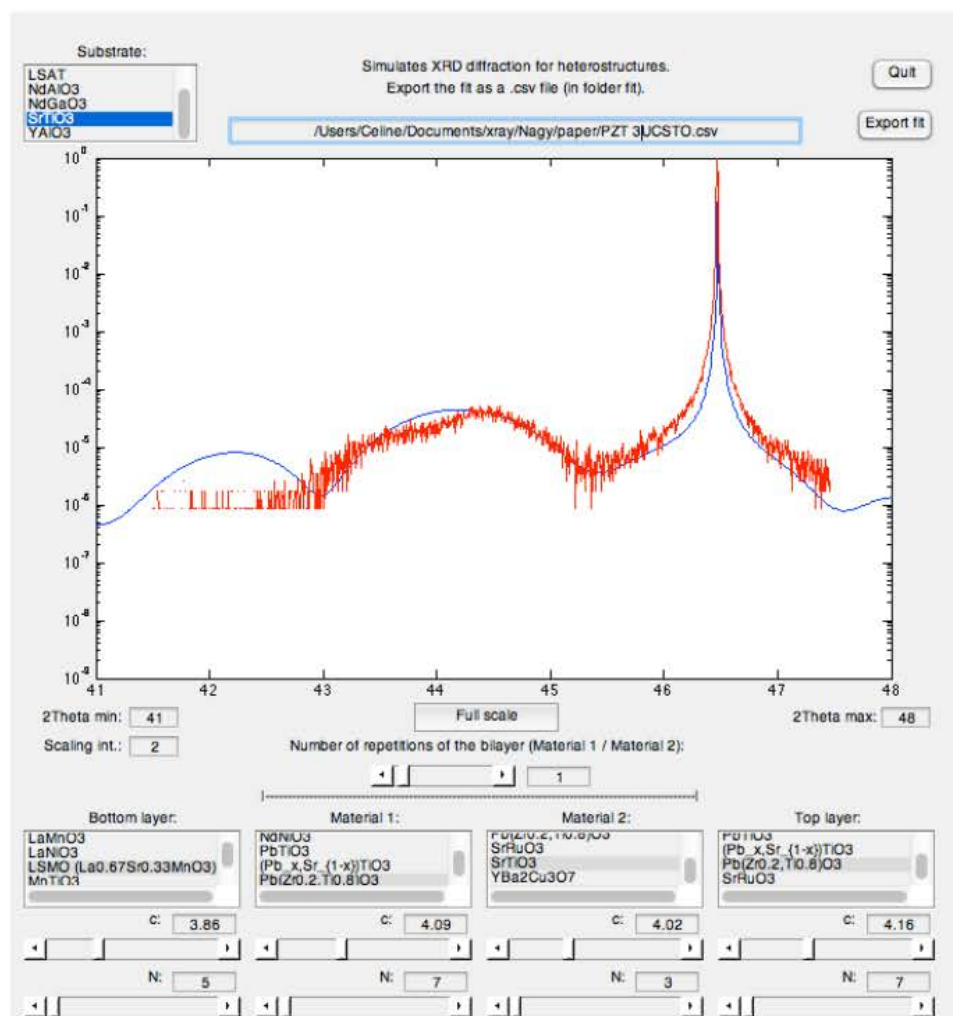
For the sample with 10 uc of STO (PZT_10ucSTO), the c-axis value had to be reduced to its bulk value again to get a better fit. The best fit was obtained with 0.412 nm for the bottom PZT, 0.3905 nm for the STO, and 0.416 nm for the top PZT. Note that this fit is still not fully satisfactory. This could be due for example to variations of

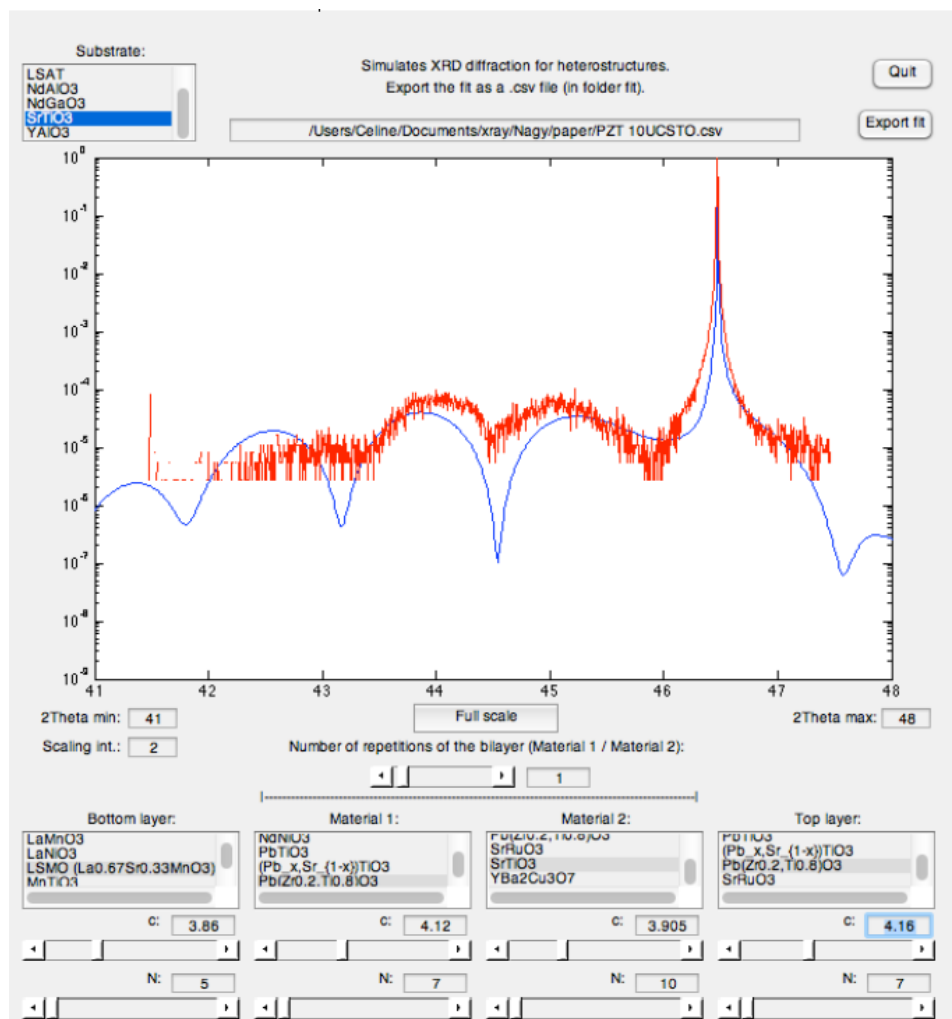
the c-axis value within one layer, which is not taken into account in the program. Fits of similar quality were obtained by putting the c-axis value of the top PZT layer at 0.412 nm and the bottom at 0.416 nm, or by having both top and bottom PZT layers at an intermediate value of 0.414 nm.



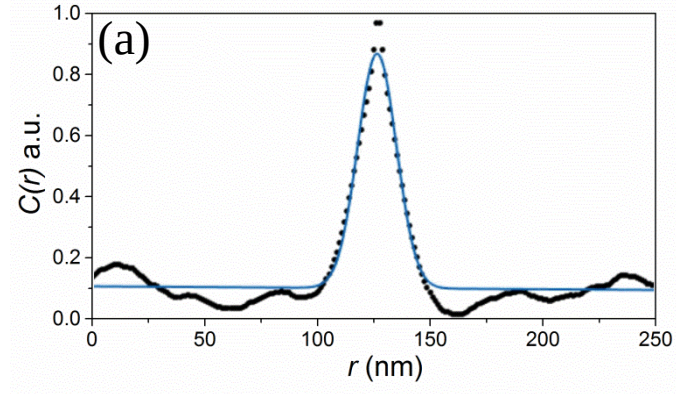
The choice of 0.412 nm for the bottom and 0.416 nm for the top layer follows the observation that the top layer was recovered to the full bulk value in the PZT_3ucSTO sample, so it is reasonable to assume that this is also the case for the PZT_10ucSTO.



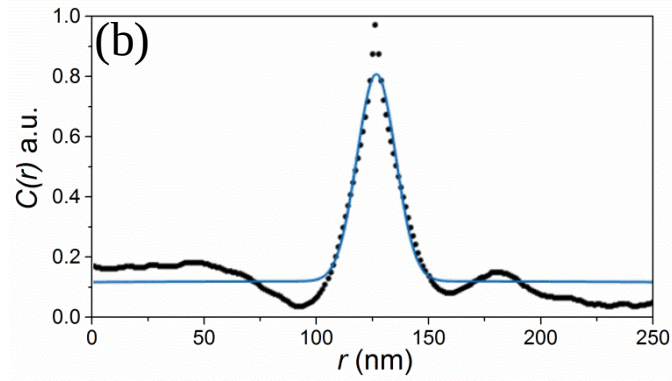




A2.3 Domain periodicity



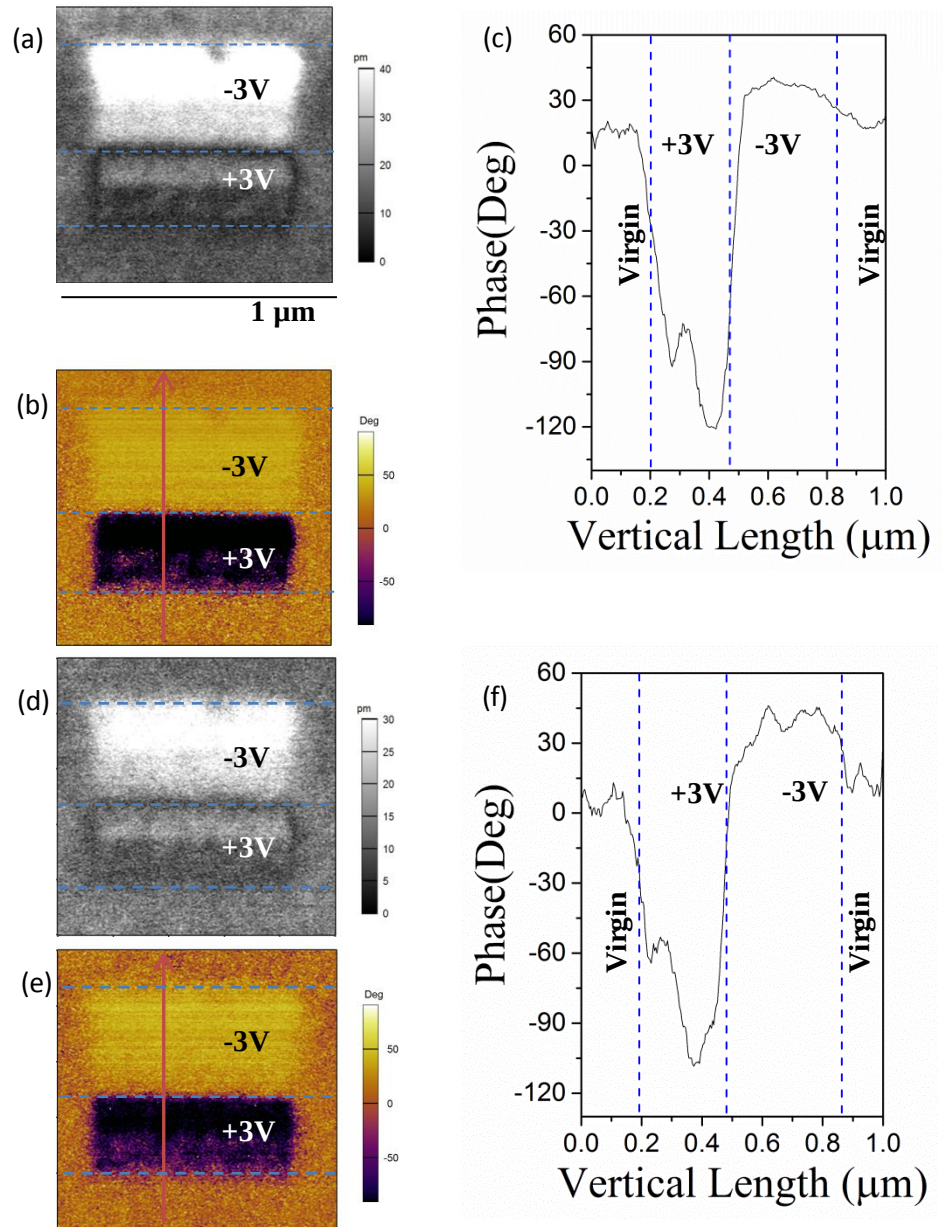
Domain periodicity (110) = 24.48 ± 1.08 nm



Domain periodicity ($1\bar{1}0$) = 24.5 ± 1.5 nm

Fig. A2. 2 (a) & (b) are autocorrelation scripts of PZT_3ucSTO along (110) and ($1\bar{1}0$) according to Fig. 3(e) in chapter 5

A2.4 PFM of domain writing and cross-section analysis on PZT₁₀ucSTO



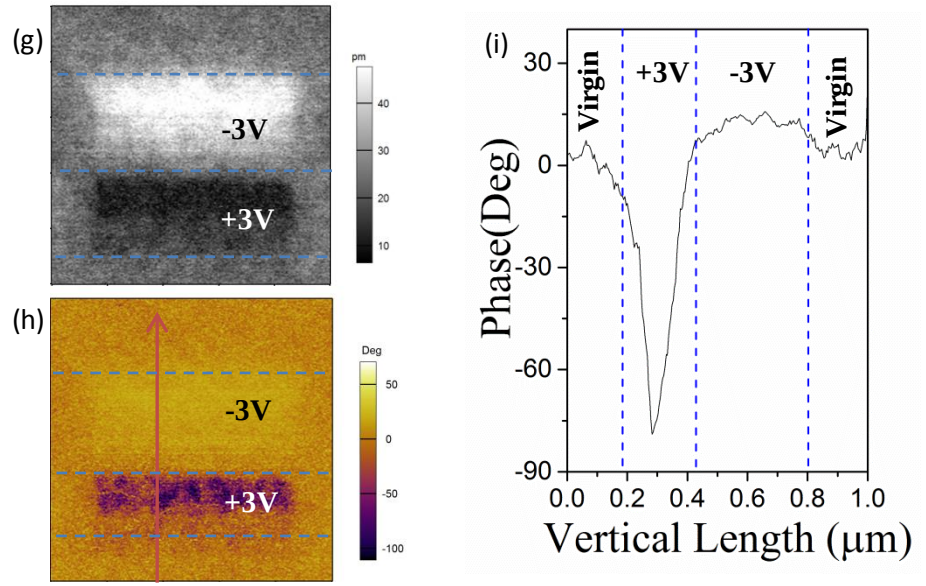
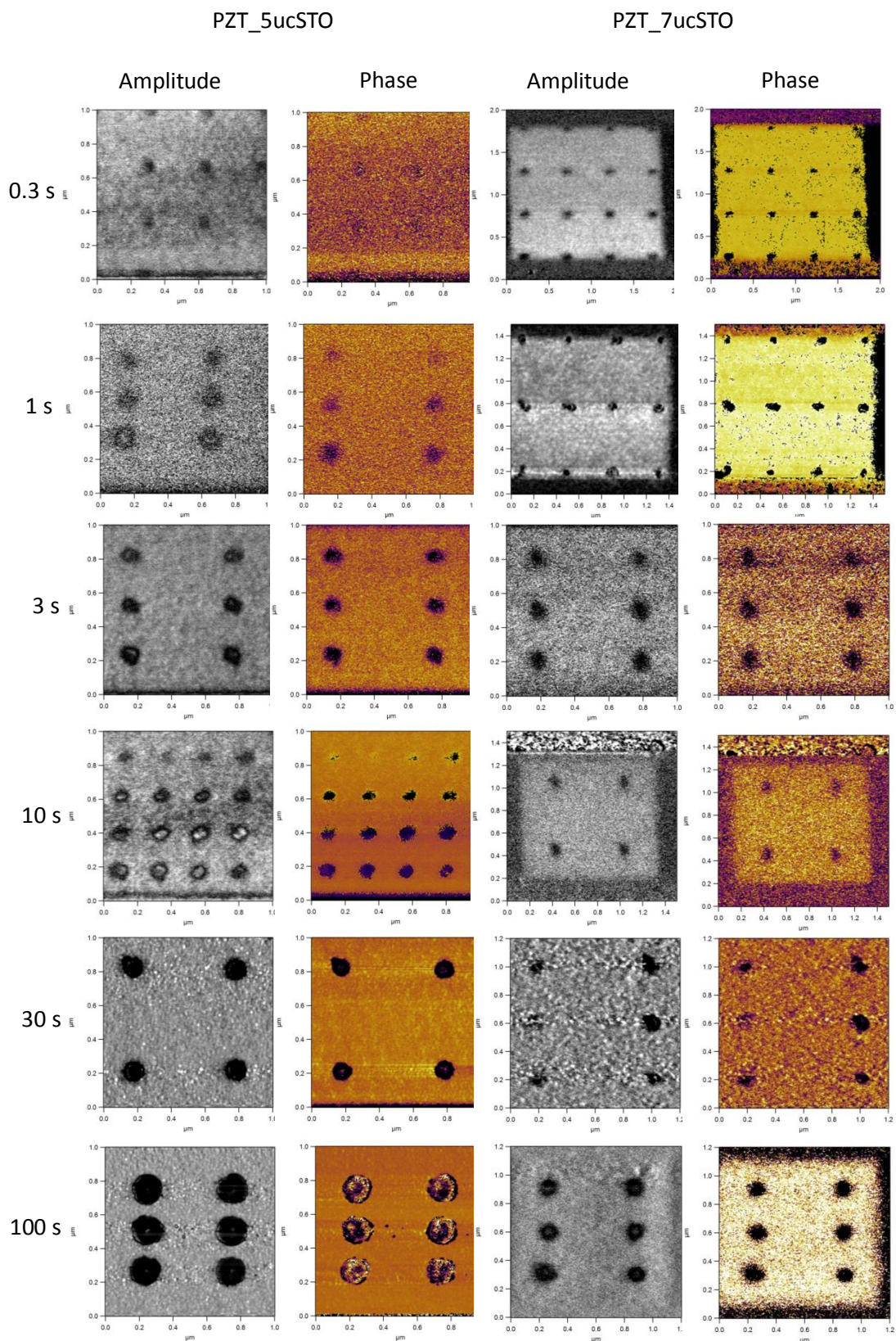


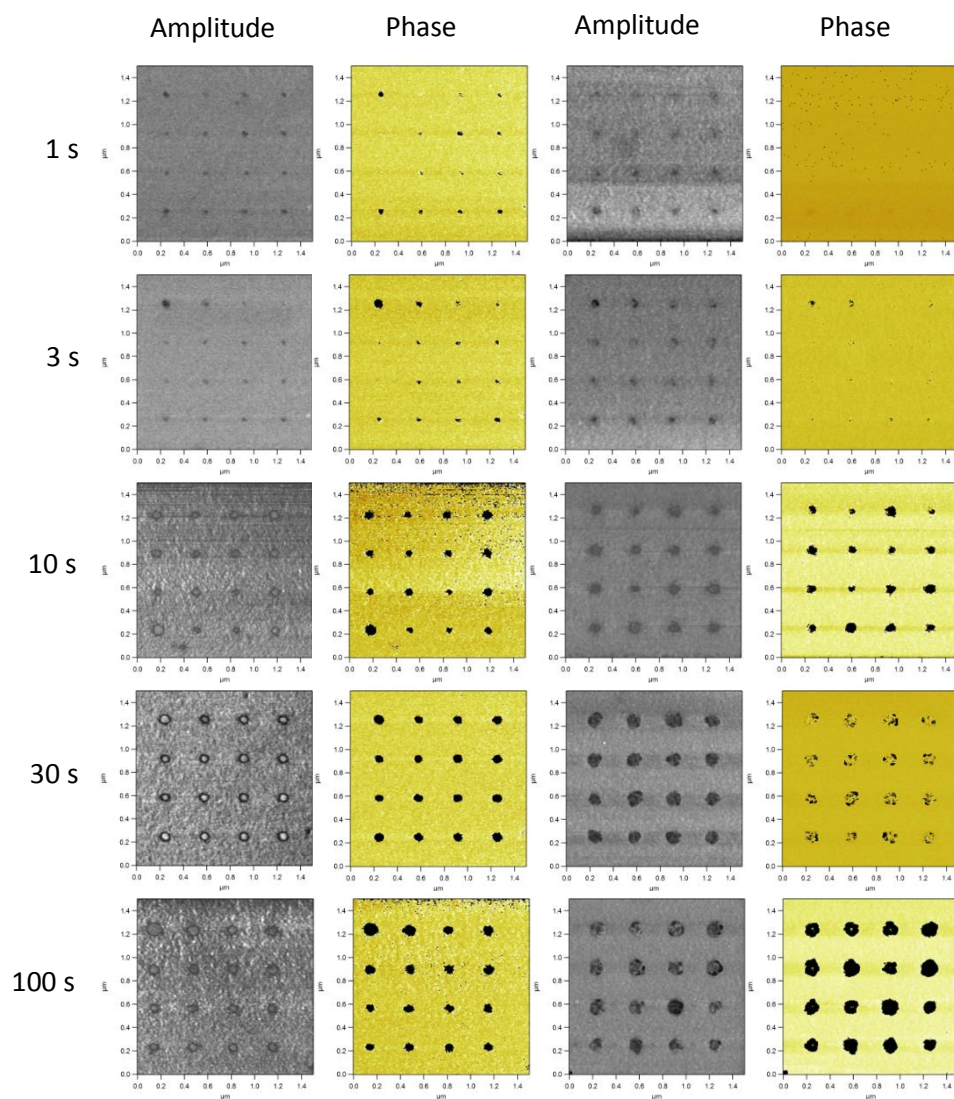
Fig. A2. 3 (a) & (b) are out-of-plane phase and amplitude images of PZT_10ucSTO after +3V and -3V bias application, respectively. (c) is the corresponding smoothed cross-section profiles along highlighted line of phase image. (d), (e) and (f) are the PFM results in identical area after 1 hour; (g), (h) and (i) are those after 12 hours.

A2.5 PFM data of PZT_5ucSTO, PZT_7ucSTO, 7ucPZT and 3ucSTO on 7ucPZT samples as a function of pulse width.



7ucPZT

3ucSTO on 7ucPZT



A2.6 Retention of written domains on PZT_3ucSTO

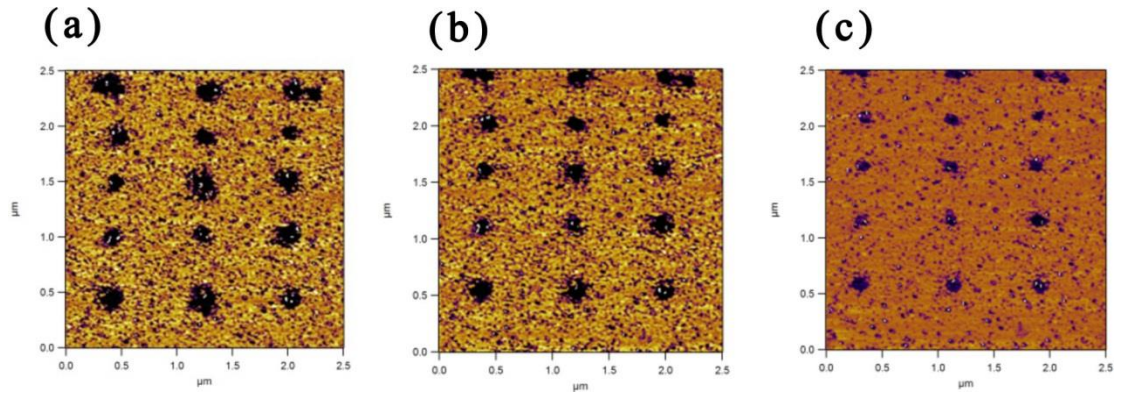


Fig. A2. 4 PFM phase images of circular domains written on PZT_3ucSTO using +3.5V bias (a) after writing, (b) after 4 and (c) 12 hours

A2.7 I-V measurement

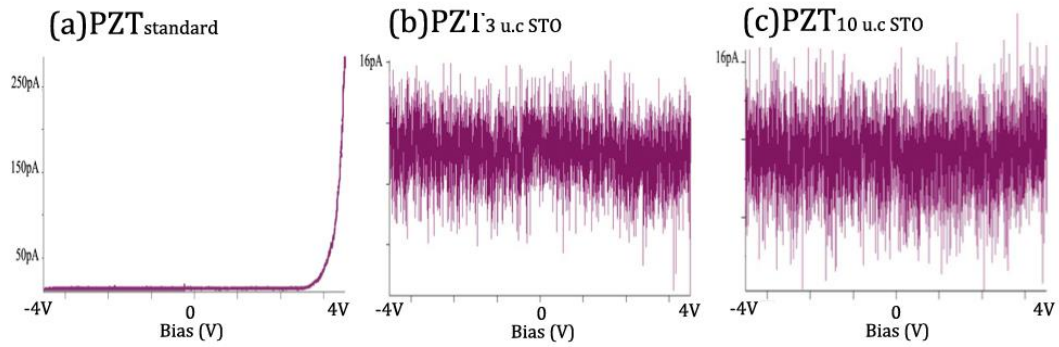


Fig. A2. 5 Typical I-V measurements obtained from (a) PZT_{reference}, (b) PZT_{3ucSTO}, and (c) PZT_{10ucSTO}; showing the improvement in leakage property with the insertion of STO layer.

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