Maxim Plekh

FERROELECTRIC PERFORMANCE FOR NANOMETER SCALED DEVICES
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The work deals with the experimental study of ferroelectric (FE) performance scaling for nanometer-sized devices. In the emerging and advanced devices, it is desirable to couple FE performance with other functions. This requires integration of nanoscale FEs with other materials, which is especially promising in epitaxial heterostructures. Such heterostructures inevitably possess a large lattice mismatch, the effect of which on FE properties is unknown and is in the focus of the present work.

In the study, heteroepitaxial thin and ultrathin films and superlattices of ABO₃-type perovskite structure FEs were used, with A = Pb, Ba, Sr, K, and N, and B = Ti, Zr, Nb, and Ta.

FE domains and local polarization switching were explored on the nanometer scale using piezoresponse force microscopy. The experiment was modified that allowed achieving images with high contrast and lateral resolution, and also allowed analysis of nanodomains in lateral capacitor configuration. Local properties were related to a macroscopic response. For this, the method of simultaneous on-wafer low-frequency impedance measurements was optimized allowing studies of thin and ultrathin (to 5 nm) films in a broad range of conditions and regimes.

Experimental studies have revealed phenomena which cannot be explained in the frame of the existing theories. The observed new effects are important for applications such as multistate memory devices, storage capacitors, and FE tunnel junction devices.

Keywords: PFM, domain dynamics, ferroelectrics, polarization switching, thin films
Acknowledgements

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<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>ε</td>
<td>Relative permittivity</td>
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<tr>
<td>AC</td>
<td>Alternating Current</td>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<td>BTO</td>
<td>Barium Titanate</td>
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<td>dB</td>
<td>Decibel</td>
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<td>DC</td>
<td>Direct current</td>
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<td>E</td>
<td>Electric field</td>
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<tr>
<td>$E_c$</td>
<td>Coercive field</td>
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<td>FE</td>
<td>Ferroelectric</td>
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<td>FeRAM</td>
<td>Ferroelectric random access memory</td>
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<td>FTJ</td>
<td>Ferroelectric tunnel junction</td>
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<tr>
<td>LPFM</td>
<td>Lateral piezoresponse force microscopy</td>
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<tr>
<td>LSCO</td>
<td>Lantanum strontium cobalt oxide</td>
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<tr>
<td>MFC</td>
<td>Mass flow controller</td>
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<tr>
<td>PFM</td>
<td>Piezoresponse force microscopy</td>
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<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
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<td>PMN</td>
<td>Lead magnesium niobate</td>
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<tr>
<td>PST</td>
<td>Lead Strontium Titanate</td>
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<td>PZT</td>
<td>Lead Zirconium Titanate</td>
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<tr>
<td>$P_r$</td>
<td>Remanent polarization</td>
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<tr>
<td>$P_s$</td>
<td>Spontaneous polarization</td>
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<td>SPM</td>
<td>Scanning probe microscopy</td>
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<td>SRO</td>
<td>Strontium ruthenate oxide</td>
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<tr>
<td>STO</td>
<td>Strontium titanate oxide</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Curie temperature</td>
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<tr>
<td>VPFM</td>
<td>Vertical piezoresponse force microscopy</td>
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</table>
List of original papers

I. Plekh M & Tyunina M (2010) Ferroelectric domains in epitaxial PbZr$_{0.65}$Ti$_{0.35}$O$_3$/La$_{0.5}$Sr$_{0.5}$CoO$_3$ heterostructures. Appl Phys Lett 97: 062902.

II. Tyunina M, Plekh M & Levoska J (2008) Dynamics of Nanodomains in Epitaxial Thin-Film PbZr$_{0.65}$Ti$_{0.35}$O$_3$. Ferroelectrics 373: 44–50.

III. Plekh M, Narkilahti J, Levoska J & Tyunina M (2010) Polydomain configuration in epitaxial Pb$_{0.5}$Sr$_{0.5}$TiO$_3$/La$_{0.5}$Sr$_{0.5}$CoO$_3$ heterostructures. Manuscript.


The Papers I and II are devoted to studies of domain configuration and dynamics in heteroepitaxial films of PbZr$_{0.65}$Ti$_{0.35}$O$_3$. The author has performed piezoresponse force microscopy experiments and dielectric characterization of the films in the broad range of conditions. In the films, random arrays of 0.1–1 μm sized FE domains were found. The lateral inhomogeneity of the switching fields and of the field induced strains was detected. The deviation from the Rayleigh law, hysteresis, and dependence on temperature, frequency, and time were revealed in the dynamic response. The results were discussed in terms of island growth and film-electrode clamping.

The Paper III is focused on a peculiar polydomain configuration in Pb$_{0.5}$Sr$_{0.5}$TiO$_3$ film with fully relaxed misfit strain. The author has performed piezoresponse force microscopy studies and impedance measurements. Here, random arrays of 0.1–0.5 μm sized $a$- and $c$- domains were also found. In the capacitors, a step-like switching of polarization was observed. The results were discussed in terms of island growth and different switching mechanisms in $a$- and $c$-domains.

The Paper IV deals with microstructure controlled change of properties in BaTiO$_3$ films. The author contributed to the work with piezoresponse force microscopy studies of ferroelectric domains. The experiment was modified for
analysis of domains in lateral capacitor configuration. The author has also performed some of impedance measurements.

In the Papers V–VIII, the author has concentrated his efforts on optimization of on-wafer impedance measurements in the broad range of conditions and regimes. The low-frequency dielectric characterization of ultrathin films is especially demanding, and it has been successfully realized in the Papers VII and VIII.
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1 Introduction

1.1 Ferroelectrics

A crystal is said to be ferroelectric (FE) when it possesses a spontaneous polarization below a transition temperature ($T_c$), with two or more polarization orientation states and possibility to switch the spontaneous polarization between these states by applying an external electric field [1].

The spontaneous polarization in a FE crystal is not uniformly distributed throughout the whole crystal, but rather forms regions in which polarization is uniform, or domains. The polarization direction of each domain is determined by the crystal symmetry of the FE crystal. The process of applying an electric field to orient all domains in bulk FE crystal of ceramics toward the field direction is often termed as poling. Under applied field, the switching of polarization direction to other orientation involves hysteresis, as it schematically shown in Fig. 1. The reversing electric field is known as the coercive field ($E_c$). The spontaneous polarization ($P_s$) is found by extrapolating the linear saturating portion back to the polarization axis. The value of polarization which remains in FE after the poling field is withdrawn is called remanent polarization ($P_r$), which is always smaller than the $P_s$.

![Polarization – electric field hysteresis loop of ferroelectrics.](image)

Fig. 1. Polarization – electric field hysteresis loop of ferroelectrics.
For most FEs, there is a certain temperature, above which spontaneous polarization disappears. This temperature marks the FE - non-polar paraelectric phase transition, which is signaled as a dielectric constant peak [2].

(However, in the so-called relaxor FEs, or relaxors, such as lead magnesium niobate (PMN), the dielectric constant maximum does not correspond to a transition from non-polar phase to a FE polar phase [3].)

Many FE materials are of the perovskite structure (Fig. 2). Perovskite structure ABO$_3$-type oxides, where A = Ba, Pb, Na, K, etc, and B = Ti, Nb, Ta, Zr, etc., are generally called “ferroelectrics”. Such perovskites, however, can exhibit the low-temperature FE (e. g. PbTiO$_3$) or antiferroelectric (e. g. PbZrO$_3$) properties, and the high-temperature paraelectric behavior. Some of ABO$_3$-type FEs does not reach FE state on cooling. These are incipient FEs or quantum paraelectrics (SrTiO$_3$, KTaO$_3$, CaTiO$_3$). Besides single-phase ABO$_3$ FEs, a variety of their solid solutions has been synthesized, with the most known Pb(Zr,Ti)O$_3$, or PZT. Perovskite-structure materials with generic formula AB$^I$B$^II$O$_3$, where A = Pb, B$^I$ = Mg, Sc, Zn, Y, Lu, Ho, etc, and B$^II$ = Nb, Ta, Ni, etc. exhibit relaxor behavior. Among all materials, relaxors possess the highest ever obtained dielectric permittivity and the coefficient of electro-mechanical coupling.

**Fig. 2.** Perovskite-type lead zirconate titanate (PZT): (a) in the symmetric cubic state above the Curie temperature. (b) Tetragonal distorted unit cell below the Curie temperature.

Below the Curie temperature, perovskite-structure FEs usually have tetragonal or rhombohedral crystal unit cells. Due to their permanent electrical and mechanical asymmetry, these types of unit cells exhibit spontaneous polarization and deformation.
FEs possess large and switchable polarization, large piezoelectric coefficients, dielectric permittivity, electro-optical coefficients, etc., with a strong dependence of the properties on applied electric field and temperature. This enables variety of device applications of FEs. FE devices using bulk ceramics are numerous [4]. In the last years, additionally to the well established fields of FE applications, especial attention is paid to the possibility of energy harvesting using strong piezoelectric and pyroelectric effects in these materials. Modern demands for compact and environmentally friendly devices stimulates research of FE thin films, including ceramic-type thin and thick layers, and single-crystal quality epitaxial films.

1.2 Ferroelectric thin films

FE films are normally formed on substrates coated with the bottom electrode layers, and with the top electrode layers created on the top surface of the film. This is a so-called vertical capacitor structure. Direction normal to the surface of the film or substrate is often called out-of-plane direction, and that parallel to the substrate surface is called in-plane direction. Independently of film microstructure, the primary size effect in FE thin films is connected with presence of depolarizing field. In the films, depolarizing field created by the out-of-plane polarization is characterized by an electrostatic energy. In order to minimize the total energy, the depolarizing field must be screened by free charges coming from metallic or oxide electrodes, if any, or minimized by breaking into polarization domains. Domains are formed in FE film in any case, also without electrode layers.

Thus at small dimensions, the FE properties are influenced by the spatial confinement (film thickness) and the film-electrode interface [5]. In ultrathin films, the size limit of ferroelectricity can be understood using electrostatics approach: the depolarizing field intensity increases with decreasing thickness of the FE film, [6] thus increasing the electrostatic energy of the system.

1.3 Domains in heteroepitaxial films

In FE crystals and films, the total energy is minimized by creating instead of single-domain state, a poly-domain configuration, with many polarization domains separated by domain walls. In equilibrium, the energy associated with the appearing domain walls must offset the reduction in energy of the depolarizing field.
It should be noted that in epitaxial films, the terms “single-domain” and “polydomain” have also another meaning. For instance, in epitaxial films with tetragonal crystal structure, the state is “single-domain” if all unit cells have longer, polar axes in the out-of-plane direction (c-domains) or in the in-plane direction (a-domains). Presence of both c-type and a-type domains simultaneously is called “polydomain” state. FE domains with opposite direction of polarization – upward and down directed – can obviously exist in the c-oriented “single-domain” film. Epitaxial films which are structurally “single-domain” can contain many FE domains.

FE domains are largely responsible for such characteristics of FEs as total polarization, coercive fields, switching dynamics, piezoelectric response, nonlinear optical properties, etc. Knowledge of a domain configuration and a domain switching process is of key importance for developing many FE devices. This is valid for both bulk FEs and especially for thin-film FEs, where domain configuration can be strongly affected by film thickness and microstructure features.

In the classical Kittel’s approach [7], the width of 180° magnetic domains (w) is correlated to the thickness of a crystal in a well defined manner: the square of the domain width (w) is directly proportional to the thickness of the crystal (d) [8]. Kittel’s law was extended for FE materials by Mitsui and Furuichi (1953) [9], and by Roytburd (1972) for epitaxially clamped ferroelastic films [10]. The Kittel’s approach generally applies for small-sized FE crystals, as shown in the recent experimental studies on BaTiO₃ nanocrystals [11]. Domain width decreases with decreasing thickness. In epitaxial thin films, this is additionally influenced by misfit strain, which appears due to a mismatch between the in-plane lattice parameters of the film and substrate materials. This aspect has been analyzed in numerous works of Roytburd, Tagantsev, Pertsev, Levanyuk, and others [12]. Theoretical considerations, however, are often unable to account for microstructure of real films. For instance, in ceramic-type polycrystalline films, presence of grains of different shapes, sizes, and with different types of grain boundaries is difficult for theoretical description. The main qualitative result is that FE domain size can be restricted by the grain size. Polarization switching can also become nucleation-limited due to grain boundaries [13].

In contrast to ceramic-type films, single-crystal epitaxial films are free of grains, making the modeling easier. It is known, however, that growth of single-crystal heteroepitaxial films requires the substrates with the perfect match of crystal structure, lattice parameters, surface energy, and thermal expansion
coefficients to those of the film material. The choice of such substrates is very narrow for the perovskite-structure FE films. In practice, it is often limited to SrTiO$_3$. For FE films grown on substrates or electrode layers with a certain mismatch, elastic energy associated with misfit strain increases with increasing film thickness. To minimize this energy, strain relaxes [14]. Several mechanisms of strain relaxation are considered, including formation of misfit and other types of dislocations, three-dimensional defects, crystal domains, and others [15]. The main mechanism is believed to be via dislocation formation. This is valid, however, for the relatively small misfit, not exceeding $\sim$ 1%. It has been shown, that films of different materials with misfit of 10–12% still can epitaxially grow [16]. The mechanisms of such growth are under study. The main feature seems to be related to three-dimensional island-type growth mode. Considering FE thin films, growth and studies of heterostructures with a large lattice mismatch is very important. First, such heterostructures are able to replace polycrystalline films and would improve performance of many existing devices. Next, and more exciting, is potential development of completely novel devices, which are based on new functionality arising from combination of epitaxial FE films with films of other materials, for instance, of magnetic materials. In such heterostructures, a large mismatch is almost inevitable.

Theoretical studies of FE domains in heterostructures with a large mismatch are absent. Experimental studies of FE domains in heteroepitaxial FE films have been limited to systems with minor mismatch, for instance tetragonal PZT films grown on SrRuO$_3$ coated SrTiO$_3$ substrates. Studies of FE domains in heterostructures with a large mismatch are practically absent.

### 1.4 Misfit strain – temperature phase diagram of epitaxial films

Over a decade ago, the first theoretical prediction of novel crystal phases in perovskite-structure epitaxial FE films have been done [17]. Due to biaxial in-plane clamping of the films by the substrate surface, the film phase diagram dramatically changes compared to bulk FE. The temperature of the paraelectric-to-FE phase transition has been predicted to increase with increasing strain magnitude. Instead of one low-temperature FE phase, several new phases can appear depending on sign and magnitude of strain. An order of phase transition can change too. In strained films, polarization can be considerably enhanced compared to bulk.
Since the pioneering work [17], phase diagrams of numerous perovskite-structure epitaxial FE films have been theoretically analyzed using phenomenological and first-principles approaches [18]. The modeling has been further developed to account for effects of film thickness, presence of film surface, coupling to electrode material, non-uniform strain distribution, and finite lateral dimensions.

Systematic experimental studies of the phase diagrams of epitaxial FE films are absent. In part, this is due to the limited choice of substrates necessary to cover broad range of in-plane strains. Another difficulty is related to films thickness. To sustain the required strain without relaxation, the thickness of FE film should be smaller than a certain critical one. For instance, the critical thickness can be about 5–7 nm for misfit 2%. Experimental identification of FE state in such ultrathin films is very difficult.

In heterostructures with large mismatch, the misfit strain in FE films can be partially or fully relaxed, while epitaxial biaxial in-plane clamping remains present. In terms of Pertsev diagram [17], such films are located in the vicinity of the zero misfit strain. In this region, slight strain variation can lead to different FE phases. In such FE films, various defects generated during strain relaxation may also create non-uniform electric and elastic internal fields, additionally influencing the phase diagram. Theoretical prediction of phases in such films is very difficult if not impossible. Experimental studies of phases and FE phase transitions in films grown in heterostructures with large mismatch are practically absent.

1.5 Heteroepitaxial films for nanometer scaled device applications

Large and switchable polarization, excellent dielectric, piezoelectric, and other properties, and variety of effects in perovskite-structure FEs enable numerous device applications of bulk FE ceramics and crystals.

Studies of FE thin films have been greatly stimulated by development of memory devices [19]. Polarization and its switching in FE films are employed. Polycrystalline PZT and SrBi$_2$Ta$_2$O$_9$ (SBT) films are typically used. Storage density is mainly limited by minimum critical dimensions allowed by lithography process. Currently it is 15nm [20]. When this size further decreases, the grain size in the films must shrink to nanometer scale leading simultaneously to unwanted increase of density of grain boundaries. An alternative promising way to increase storage density is by using high-quality epitaxial FE films [21]. Another approach
involves development of high-density multistate memory devices using multiferroic epitaxial films. Such films exhibit FE and magnetic properties simultaneously. Currently, especial effort is paid to studies of epitaxial films of multiferroic BiFeO$_3$ [22]. However, multiferroic behavior can be achieved in heterostructures of FE and magnetic films too. As mentioned before, such heterostructures possess a large lattice mismatch. Studies of FE functionality in such heterostructures are important for realization of nanometer scaled memory devices.

FE thin films can be used as tunnel barriers in FE tunnel junctions (FTJs) [23]. Theoretical calculations of the tunnel current across a FTJ strongly support the idea that the polarization reversal in a FE barrier may result in a pronounced resistive switching [24]. Polarization-dependent resistive switching behavior was demonstrated at room temperature in ultrathin films of BaTiO$_3$ [25], PbTiO$_3$ [26] and Pb(Zr$_{0.5}$Ti$_{0.5}$)O$_3$ [27]. The tunneling electroresistance through a 3.6 nm PbTiO$_3$ film reaches values of 50000% [26]. For a 3-nm BTO film, the tunneling electroresistance can be as high as 75000% [28].

Numerous FE devices employ strong piezoelectric effect inherent to perovskite-structure FEs. The ability to convert mechanical energy to electrical energy and vice versa is used in variety of ultrasonic detectors, sensors, actuators, motors. Very compact micron-sized devices are desired for medical applications. They require high-quality FE films. Heteroepitaxial films may be candidates for such applications too. Harvesting of mechanical energy is another direction where FE films can find their niche. Studies of piezoelectric properties of epitaxial films are important for these applications.

In the high-temperature paraelectric state, the dielectric permittivity of FEs is a function of applied electric field. This ability is often called “tunability”. Tunable devices using FE thin films in the paraelectric state are attractive for high-frequency, or microwave, applications including voltage-controlled oscillators, delay lines, matching networks, phase-shifting devices, etc. [29] For nanometer scale thickness of the films, the tuning voltage can be considerably reduced compared to bulk. The largest tunability is achieved in the vicinity of the para-to-FE transition. Besides large enough tunability, the films should possess thermal stability of permittivity and be free of dielectric hysteresis. By controlling epitaxial strain, both the tunability can be enhanced and the temperature of the phase transition can be adjusted [30]. Studies of phase transitions and phase diagrams of epitaxial films are important for such applications.
Due to large dielectric permittivity, perovskite-structure FE thin films are excellent candidates for energy storage capacitors. In ceramic-type films, the presence of nanosized grains and grain boundaries is known to lead to reduction of permittivity. In contrast, single-crystal epitaxial films are free of grains and can have larger effective permittivity. Remarkably, in epitaxial films of relaxor PbMg$_{1/3}$Nb$_{2/3}$O$_3$, the permittivity larger than in bulk has been demonstrated [31]. Studies of low-frequency dielectric properties of epitaxial films are important for capacitor applications with nanoscale thickness of the FE films.

### 1.6 Objectives and outline of the thesis

The present work was aimed at experimental study of FE functionality scaling for nanometer-sized devices. Functionality of heteroepitaxial films of Pb(Zr,Ti)O$_3$, (Pb,Sr)TiO$_3$, BaTiO$_3$, PbMg$_{1/3}$Nb$_{2/3}$O$_3$, KTaO$_3$, and superlattices of NaNbO$_3$ – SrTiO$_3$ was studied. FE domains and local polarization switching were explored on the nanometer scale with the use of piezoresponse force microscopy. The macroscopic dielectric response was investigated as a function of frequency, temperature, and applied electric field. The local properties were related to the macroscopic response. The low-temperature state of the films, the temperature and nature of the phase transitions, domain configuration, and domain dynamics were analyzed with respect to microstructure of the films. It was shown that in heteroepitaxial films with a large lattice mismatch, strain relaxation can lead to such unexpected peculiarities as a random domain configuration, step-like switching, and strain enhanced relaxor state.
2 Methodology and experimental

In the work, functional characterization of epitaxial perovskite-structure films was performed both locally using piezoresponse force microscopy (PFM) and macroscopically using low-frequency impedance measurements. The films were grown by in situ pulsed laser deposition (PLD) and their crystal structure was analyzed prior to functional characterization.

In the course of the work, the PLD set-up, the low-frequency measurement set-up, and the PFM experiment were modified or adjusted to satisfy specific requirements put forward by thin and ultrathin films.

2.1 Pulsed laser deposition

The films were prepared by pulsed laser deposition (PLD). The PLD method allows film to grow at relatively high pressure of ambient oxygen, making the method especially attractive for fabrication of oxide films. In PLD, different films and multilayers can be deposited in situ in the same deposition chamber.

In the PLD set-up, shown schematically in Fig. 3, a pulsed laser beam from the high-energy excimer laser ablates a small amount of the target material to be deposited. The ablated material in the form of plasma plume reaches the substrate surface and deposits there.

Fig. 3. Scheme of the PLD setup.
The PLD setup consists of a vacuum chamber with a gas-mixing facility, an ultraviolet excimer laser and an optical system for beam focusing and scanning. The substrate is mounted on a heated holder. For the growth of epitaxial oxide thin films, sufficient ion mobility is needed. It is provided by heating the substrate during deposition to high temperature, typically exceeding 550 °C.

Ceramic target is mounted on a motorized rotating holder. Target rotation or scanning of laser beam over the target surface reduces the inhomogeneity of the ablation, the target surface roughening, and hence droplets formation. Laser scanning over different targets allows growing of superlattices and films with adjustable or graded composition. The beam scanning is realized by utilizing two motorized mirror mounts with a programmable motion controller.

After evacuation of the ablation chamber, the computer-controlled gas-mixing system prepares the ambient atmosphere for deposition. Deposition atmosphere can be composed of an argon, nitrogen, or oxygen. Accurate control of chemical composition and pressure of the ambient gas is especially important for deposition of multicomponent materials, including perovskite-structure FEs. The ambient gas influences dynamics of the plasma plume, and hence kinetics of the film growth. In oxygen ambience, chemical reactions in the plume can additionally affect oxide film growth.

To sustain the required ambient gas pressure, vacuum pumping is combined with introducing gas by means of mass-flow controllers. A mass flow controller (MFC) is a device comprised of a mass flow sensor and a proportional control valve and is used to measure and control the flow of gases. The MFC is fitted with a closed loop control system that compares set-point to the value from the mass flow sensor and adjusts the proportional valve accordingly to achieve the required flow. Three MFCs are used to allow independent supply and mixing of oxygen, nitrogen and argon. The MFCs are connected to the MKS 247D four-channel MFC power supply/readout and set point source. The MKS 247D is connected to the computer via NI-6008 (National Instruments) ADC/DAC modules. Pressure gauge signal is also digitized by NI-6008. The software for gas flow control (Fig. 5) was developed to allow automatic gas mixing at a desired pressure during deposition, post-deposition annealing and cooling.
Fig. 4. Scheme of the PLD gas flow control system.

Fig. 5. Screenshot of the PLD control program.
2.2 Low-frequency impedance measurements

In FEs, studies of the dielectric permittivity as a function of frequency, temperature, applied dc electric field and amplitude of ac electric field can provide knowledge of both the fundamental physical phenomena and of the performance required for device applications.

The low-frequency permittivity is normally determined from the measured capacitance of vertical or lateral capacitor structures. Thin-film capacitors were formed by depositing a bottom and a top electrodes (vertical capacitor) or by depositing and patterning top electrodes separated by a gap (lateral capacitor).

The capacitance was extracted from the impedance measured using sinusoidal ac electric field with small amplitude. The impedance was measured with an HP 4284A LCR-bridge. The equipment used allowed the variation of the frequency (100 Hz–1 MHz), of the amplitude of an ac voltage (5 mV to 20 V), and of the superimposed dc voltage (−20–+20 V). The temperature variation during measurements was realized using a Linkam LTSE350 MultiProbe stage controlled by a Linkam TMS94 programmer with remote control capability. Setup for dielectric measurements is schematically shown on Fig. 6.

![Fig. 6. Scheme of the setup for dielectric measurements.](image-url)
To perform accurate measurements with statistically sufficient amount of data points in a broad range of conditions and in different regimes, special measurement software was developed for the simultaneous control of the Linkam programmer and LCR-bridge. Several measurement regimes were implemented, with the most important being:

- impedance as a function of frequency and temperature;
- impedance as a function of frequency and AC drive at a number of fixed temperatures;
- impedance as a function of frequency and DC bias at a number of fixed temperatures.

The stand-alone software program was developed for the post-processing of the acquired data. It allows the conversion between impedance and capacitance representations using different model approximations for each frequency of a dataset independently.

In contrast to bulk FE samples, in the vertical FE thin-film capacitors, small thickness of the FE layer, small thickness of electrode layers, and finite conductance of probes affect the measured impedance. The relatively small resistance of FE, the relatively large resistance of electrode layers and probes, and also the presence of near-electrode interfacial layers with their own capacitance and resistance should be taken into account for the accurate estimation of the FE capacitance from the measured impedance. Since mentioned parameters are not exactly known, the capacitance estimation remains approximate. However, two basic models of an ideal capacitor and of a leaky capacitor are often satisfactory. The accuracy can be improved by analyzing the frequency dispersion of the extracted capacitance and loss factor as described in Ref. 32 and 33.

2.3 Piezoresponse Force Microscopy (PFM)

2.3.1 Principles of the method

In bulk samples, size, shape, and growth kinetics of FE domains are studied using variety of methods. The most widely applied are optical microscopy observations in polarized light, using selective chemical etching or decoration and orientation of liquid crystals on the surface of FEs [1, 34, 35]. The spatial resolution of optical methods is on the micrometer scale. To study FE domains or polar regions
with dimensions at nanometer scale, methods of electron microscopy are employed. These methods require special sample preparation and are destructive. Today the non-destructive methods allowing studies of nanometer-sized FE domains are based on atomic force microscopy. The most efficient one is piezoresponse force microscopy, or PFM. In thin FE films, width of FE domains decreases with decreasing of film thickness and is at the nanometer scale. PFM technique is able to resolve such domains.

In the original PFM scheme [36, 37], an AC voltage is applied to an AFM conductive probe acting as a movable top electrode to the FE surface as illustrated in Fig. 7. Another electrode is the bottom electrode of the sample. Due to coupling between polarization and deformation via the converse piezoelectric effect, FE domains respond to the applied ac electric field with a deformation (strain) having a characteristic direction and magnitude. As the sample deforms, the deflection of the cantilever of the AFM probe is monitored by means of a lock-in amplifier. The amplitude and the relative phase shift of surface oscillations are registered at a fixed frequency of the driving ac voltage. They are recorded simultaneously with surface topography.

![Fig. 7. Scheme of a classic PFM setup.](image)

For a homogeneously polarized (in $z$ direction), stress-free FE, the vertical displacement ($\Delta z$) is determined by the converse piezoelectric effect and electrostriction:

$$\Delta z = d_{33} V + \frac{M_{333}}{t} V^2,$$
where $V$ is the applied voltage, $t$ is the sample thickness, $d_{33}$ and $M_{333}$ are the piezoelectric and electrostrictive constants, respectively.

The electrostrictive deformation is typically much smaller than the piezoelectric one in a polarized state [38]. Under the external voltage

$$V = V_{dc} + V_{ac}\cos(\omega t)$$

the surface displacements registered by lock-in at first and second harmonics of ac drive are:

$$\Delta z_0 = d_{33} V_{ac} + M_{333} \frac{V_{dc}}{t} V_{ac}$$

$$\Delta z_{2\omega} = \frac{1}{2} M_{333} \frac{V_{dc}^2}{t}$$

The sign of the converse piezoelectric signal depends on the relative orientation of the polarization and applied electric field. The polarization and the PFM tip movement are schematically shown in Fig. 8. By acquiring all three components of the PFM signal it is possible to perform a reconstruction of polarization orientation of the domains.

The amplitude of the PFM signal is a measure for the local piezoelectric constant and the phase carries information about its relative orientation. For polarization components parallel to the applied electric field, the resulting oscillating movement will be entirely in-phase with the modulated electric field. For an anti-parallel alignment, the motion will be 180° out-of-phase. The PFM scheme with the out-of-plane surface oscillations is often called vertical PFM, or VPFM.

In case that there are domains with a lateral (in-plane) polarization direction, shear deformations are induced by the electric field (Fig. 8 b). They are transferred via the frictional force into the torsion of the cantilever and can be detected by lock-in amplifier.
Fig. 8. PFM contrast formation: (a) electric field aligned parallel to the spontaneous polarization leads to a vertical contraction or expansion of the ferroelectric due to the $d_{33}$ effect (out-of-plane signal), (b) electric field applied orthogonally to the polarization results in a shear movement due to the $d_{15}$ coefficient (in-plane signal).

The corresponding PFM mode is called lateral PFM (LPFM) [39, 40]. LPFM has been applied to a number of materials systems including films, crystals, nanostructures and capacitors [41, 42, 43, 44, 45, 46]. By using second lock-in amplifier, the LPFM signal can be recorded simultaneously with the VPFM. Both signals can be combined to reconstruct a map of the local polarization orientation [46].

In PFM, additionally to classical scheme with conducting tip acting as a top electrode, FE domains can be imaged using a thin-film top electrode (Fig. 9). In this case, the field is applied across the FE using the bottom and the top electrodes of the capacitor structure.
In the classical PFM, lateral resolution is mainly limited by the tip–sample contact area (nominally determined by the radius of the tip apex). Besides, additional mechanisms such as electrostatic interactions and the formation of a liquid neck in the tip–surface junction can deteriorate imaging. In the case of PFM through a metal electrode, the resolution is limited by the thicknesses of the top electrode and FE layer [47].

One more PFM configuration employs measurements of piezoresponse in the gap of a lateral, or planar, capacitor (Fig. 10). In the present work, this scheme was demonstrated for lateral capacitor with the gap width of 3 μm.
Fig. 10. PFM contrast formation: in-plane electric field aligned parallel to the spontaneous polarization results in a shear movement due to the $d_{33}$ coefficient (in-plane signal).

The classical configuration is the most difficult to realize in ambient conditions with thin-film samples. The tip–sample interaction is complicated, and many parameters can influence PFM signal. In air, the tip is contacted with surfaces with adsorbed water layers resulting from exposure to an ambient environment. The proximity of the tip results in the condensation of liquid at the tip–surface junction due to capillary and electrocapillary effects [48, 49]. Importantly, the electrochemical reactions are possible at the tip–surface junction. Water layers are known to be responsible for phenomena such as anodic oxidation by AFM [50] and strongly affect SPM tip–surface adhesion forces [51], electrostatic tip–surface interactions [52, 53], tip-induced electrochemical reactions [54], etc. For most perovskites, the surfaces are highly reactive [55, 56]. Furthermore, dissociative water adsorption is one of the favored mechanisms for the screening of FE surfaces [57, 58, 59, 60, 61]. The screening can affect the PFM contrast [62, 63] and polarization switching [64].

The PFM configuration with the top electrode alleviates most problems with tip-surface contact, since it relaxes strict requirements for a conductive tip and strong indentation to obtain good electrical contact. Importantly, with this configuration, a homogeneous electric field is generated throughout the piezoelectric layer and the electrostatic tip-sample interaction is suppressed [65]. It should be noted that in classical PFM scheme, the electric field generated by the PFM tip is highly inhomogeneous. This makes quantitative measurements of the field dependent parameters difficult. Moreover, studies of strongly nonlinear materials become uncertain.

The development of PFM technique was greatly stimulated by applications of FE films in memory devices. In these devices, one of important issues is
polarization switching. Switching kinetics and homogeneity are extensively studied by PFM. Often the experiments involve applying a switching voltage pulse and recording the PFM image afterwards. Switching in FE capacitors has been studied by Gruverman [66, 67], Stolichnov [68, 69, 70] and Noh [71] in the context of applications to FE random access memories (FeRAM). PFM can be employed to study capacitor switching in the stroboscopic mode, in which domain pattern changes as a function of voltage pulse length [72, 73]. This step-by-step switching approach [74, 75, 76] can be used to measure the domain kinetics (nucleation and growth) during polarization reversal and the results can be compared with experimental macroscopic results and with theory [77,78,79,80]. This approach was extensively used to study imprint and flexoelectric effects in capacitors [66], variability of switching behavior in capacitor structures [81, 82], interplay between nucleation and domain wall motion [83] and nucleation probability distribution in capacitors [71].

2.3.2 Optimization of measurement conditions

Top contact

In the PFM scheme with the thin-film top electrode, electric field can be applied using conducting AFM tip. Such a scheme was realized and tested in the present work (Fig. 9). Veeco Dimension III scanning probe microscope with Nanoscope IV controller and external SR-844 digital lock-in amplifier were used. As a top electrode, a 50 nm thick Pt film was used. Minimum possible thickness of the top electrode was chosen to satisfy the requirement of a good electrical conductivity without sacrificing the high resolution of the PFM imaging.

To study electrical contact between conductive tip and top electrode, the LCR bridge was connected to the bottom electrode of the sample and to the AFM probe. The indentation force was gradually raised until it was possible to measure the impedance of the capacitor. After initial contact, the force can be lowered slightly. The contact could be characterized as noisy or intermittent due to scanning. The required force was arbitrarily high. Scanning would wear the tip in several passes, and also the extreme indentation would suppress piezoresponse. To get rid of these drawbacks, a separate contact lead to the top electrode was realized. Instead of conducting tip, an electrically passive tip was used. This approach allowed us to employ more durable and sharp uncoated tips. (The coated sharp tips are
vulnerable to damaging effect of high current density in the coating near the contact point.) In the scheme with a separate top electric lead, the contact area between tip and surface is small due to small radius of curvature of a tip and weak indentation. This enables high-resolution domain imaging, limited mainly by thickness of the top electrode. Low exerted pressure in the point of mechanical contact guarantees measurements undisturbed by such unwanted effects as pressure-induced polarization suppression or switching.

**AC drive**

To obtain PFM images with high contrast and good lateral resolution, the measurement conditions should be optimized. For instance, in order to maximize piezoelectric strain, large ac electric field applied to FE is desired. The amplitude of ac drive, however, should remain small enough to avoid unintentional switching of polarization. It should be mentioned that in experiments with superimposed dc and ac electric field, the relatively large amplitude of ac drive can lead to such artifacts as an apparent decrease of coercive field or even disappearance of switching. Optimization of the measurements frequency is also important. Like many other mechanical systems, the cantilever of the probe has resonant frequency. This mechanical resonance should be avoided, although it gives strong signal at the reference frequency. Steep dependence of resonant frequency from cantilever strain will result in cross-talk of piezoresponse signal with deflection signal.

**Probe for LPFM**

For studies of $a$-domains with the in-plane direction of polarization, the measurement conditions of the lateral PFM, or LPFM should be optimized. In the work, it was demonstrated that proper selection of AFM probes can considerably improve LPFM. In polydomain epitaxial film of Pb$_{0.5}$Sr$_{0.5}$TiO$_3$, the volume fraction of $a$-domains was about 35% (from x-ray diffraction analysis). LPFM measurements were performed using the Pt top electrodes as described above.

The influence of cantilever stiffness can be seen in Fig. 11 and Fig. 12. Short and stiff cantilever of NSC15 probe resists to the torsion from shear deformations, and lateral signal is rather weak. Using long and soft cantilever of NSC18 probe allows improving the contrast and the lateral resolution considerably (Fig. 12 and Fig. 13).
Fig. 11. (a) Topography, (b) LPFM amplitude and (c) phase of Pb$_{0.5}$Sr$_{0.5}$TiO$_3$ film, NSC15 probe. Scan size 5 × 5 μm.

Fig. 12. (a) Topography, LPFM (b) amplitude and (c) phase of Pb$_{0.5}$Sr$_{0.5}$TiO$_3$ film, NSC18 probe. Scan size 2 × 2 μm.

Fig. 13. (a, d) Topography, (b, e) LPFM amplitude and (c, f) phase of Pb$_{0.5}$Sr$_{0.5}$TiO$_3$ film, NSC18. Scan size is (a, b, c) 2 × 2 μm and (d, e, f) 500 × 500 nm.
To obtain PFM signal, the signal from the photodetector of an AFM must be passed through a lock-in amplifier. In the present work, an external SR844 lock-in amplifier was used. The lock-in amplifier is synchronized with signal from LCR bridge, and gives as outputs the amplitude and relative phase of detected response signal. This amplitude and phase are recorded by the AFM software as corresponding images simultaneously with topography. For high-resolution imaging, the low-pass filter after the phase-sensitive detector of lock-in amplifier is set to minimum 6 dB/octave roll-off and a low time constant is selected to attenuate noise without limiting the bandwidth of piezoresponse. By increasing the time constant, the output becomes more steady and easier to measure reliably. The trade off comes when real changes in the input signal take many time constants to be reflected at the output. This is because a single $RC$ filter requires about 5 time constants to settle to its final value. The time constant reflects how slowly the output responds, and thus the degree of output smoothing.

**Local switching**

To investigate polarization switching locally, the tip is placed over different sites of the film and the local electromechanical response is measured by applying a triangular-shaped bias signal with period of up to several minutes. In that case the lock-in time constant must be correspondingly high. The low frequency of bias voltage is favorable for better signal to noise ratio. Due to the digital nature of SR844 lock-in amplifier, it can operate with 100 dB of dynamic reserve without any output offset or zero drift. But the microscope scanner may be the source of tip creep, possibly leading to artifacts in hysteresis loop, thus the lowest frequency of bias must be limited.

The measurement procedure is performed with specially developed software. The software controls the LCR bridge and lock-in amplifier. The PFM signal is recorded simultaneously with the impedance of capacitor during the DC bias sweep. Therefore the local switching hysteresis loop can be directly compared with macroscopic switching hysteresis loop.
3 Domain configuration, switching, and dynamics in epitaxial ferroelectric PbZr$_{0.65}$Ti$_{0.35}$O$_3$ films

FE domains, their local switching, and their integrated dynamics were experimentally studied in 500 nm thick epitaxial films of rhombohedral PbZr$_{0.65}$Ti$_{0.35}$O$_3$ (PZT). PZT films grown on MgO (001) and LaAlO$_3$ (001) single-crystal substrates using an oxide La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) bottom electrode layer [84, 85, 86] possessed tetragonal perovskite crystal structure with the cube-on-cube-type epitaxial relationship [100](001) PZT || [100] (001) LSCO || [100] (001) substrate. The PZT in-plane lattice parameter 4.070 Å was considerably larger than in LSCO suggesting profound strain relaxation and possible three-dimensional island growth mode. The larger out-of-plane PZT lattice parameter 4.125 Å evidenced that PZT films were structurally single-domain c-oriented [Paper I]. The dielectric permittivity, determined in PZT films as a function of temperature, was smoothly increasing with increasing temperature to 620 K (maximum available during measurements), indicating that the temperature of the phase transition was above 620 K. The room-temperature state of PZT films was expected to be FE.

At room temperature, FE domains were imaged using PFM measurements in two different schemes: (1) using conducting tip and (2) using the 50 nm thick Pt top electrode and a non-conducting tip.

PFM studies of the bare surface of as-deposited PZT (Fig. 14 a,b) showed the presence of piezoresponse in the out-of-plane direction. A strong contrast in the phase image (Fig. 14 b) revealed domains with opposite direction of the out-of-plane component of polarization: up- and down-domains. No correlation between the phase image (Fig. 14 b) and surface topography (Fig. 14 a) can be found.

Switching of polarization direction was demonstrated by applying biasing dc voltage during PFM scanning: after the scanning, a change of contrast was clearly observed in the switched area (Fig. 14 c).
Fig. 14. PFM images of the bare PZT surface before (b) and after (c) local poling. (a) Topography and (b-c) phase of PFM signal. MikroMasch NSC18/Ti-Pt AFM probe. Scan size 5 × 5 μm.

A remarkably good lateral resolution in the PFM scheme with the top electrode allowed us to study FE domains in more detail. For as-deposited Pt/PZT, a random spatial arrangement of FE domains with arbitrary shapes was found (Fig. 15 d-f). The phase difference in the up- and down-domains was 180°, that in the c-oriented film can indicate {100} domain boundaries. Well-defined facet-type domain boundaries were detected. They had no preferential orientation with respect to crystal directions of the film, electrode, or substrate. The lateral sizes of domains with similar phase were from ~100 nm to > 1 μm, larger than the islands related surface features. This indicated that one domain can contain from several to tens of islands.
Prior to inspecting local polarization switching, the macroscopic response of the Pt/PZT/LSCO capacitor was investigated. The macroscopic dielectric hysteresis loop (Fig. 16) confirming FE behavior appeared to be asymmetric, with different negative and positive coercive fields. The offset field of about 0.3 MV/m was found. In part, it can be ascribed to a difference in work functions of the electrode materials. Presence of internal fields connected with strain relaxation and formation of defects in the vicinity of the bottom LSCO electrode can also contribute to the observed asymmetry.
To inspect homogeneity of switching, the piezoresponse of the capacitor was recorded after applying poling dc fields with the field magnitude slightly smaller than the macroscopic coercive field of the corresponding polarit. From the phase images, the areas, where direction of polarization remained unchanged, were detected (Fig. 17). These regions presented large domains including several islands. The tip was placed over such domains, and the local PFM response was registered during sweeps of dc electric field superimposed on the probing ac field. In all regions, the switching was realized.

The local phase – electric field loops and the local strain – electric field loops were recorded (Fig. 18). They are shifted in different directions along the field axis. The magnitudes of local negative and positive coercive fields and the loop width vary.
Fig. 17. (a) PZT capacitor topography, (b) PFM amplitude and (c) phase at zero DC bias. Probe NSC18. Scan area is 2 μm x 2 μm. In (b), sites for studies of local switching are marked by rectangles.

Fig. 18. Local (a-c) amplitude and (d-f) phase of PFM signal recorded at different studied sites during several sweeps of dc field $E$.

The inhomogeneity of the switching field might be explained by an inhomogeneous internal electric field. Such field may be produced, for instance, by dislocations creating also strain fields. The detected asymmetry in the amplitude – electric field loops evidenced the presence of such local strain fields, too. The inhomogeneous switching can be hardly explained by clamping at the island boundaries since such boundaries were equally found inside all domains.

To further study FE domains in PZT/LSCO heterostructures, sub-coercive domain dynamics was investigated.
The dielectric response of the capacitor heterostructures was measured along the [001] axis of the PZT film, normal to the substrate surface in the frequency range of $f = 10^2$–$10^6$ Hz. Temperature $T$ was varied from 80 to 675 K.

The real parts of the relative dielectric permittivity $\varepsilon_\text{DC}$ and $\varepsilon_\text{AC}$ were determined as a function of amplitude $E_\text{AC}$ of the sinusoidal ac electric field and as a function of magnitude $E_\text{DC}$ of the biasing dc electric field, respectively. The small-signal permittivity $\varepsilon(0)$ was defined at $E_\text{DC} = 0$ and smallest $E_\text{AC} = 14$ kV/m. To check repeatability of the response, the amplitude $E_\text{AC}$ or the field $E_\text{DC}$ was swept several times at a different rate and in different ranges. The nonlinear dynamic dielectric permittivity $\Delta \varepsilon_\text{AC}$ was determined as $\Delta \varepsilon_\text{AC} = \varepsilon_\text{AC} - \varepsilon(0)$.

It was found that dynamics of FE nanodomains differed from that of FE microdomains in bulk samples. For instance, in thick layers of tetragonal PZT, a linear dependence of the permittivity $\varepsilon_\text{AC}$ on amplitude $E_\text{AC}$ of ac field has been experimentally demonstrated [87] for the fields smaller than the coercive field. This has been modelled as resulting from the Rayleigh-type domain pinning [87]. In contrast, in heteroepitaxial PZT films, the linear $\varepsilon_\text{AC}(E_\text{AC})$ dependence could not be detected even at small amplitudes $E_\text{AC}$ (Fig. 19). Moreover, the sweeps clearly exhibited hysteresis that became better pronounced with increasing maximum drive.

**Fig. 19.** The normalized permittivity $\varepsilon_\text{AC}/\varepsilon(0)$ as a function of amplitude $E_\text{AC}$ of ac electric field at $f = 1$ kHz and $T = 363$ K.

In the drive sweeps, the observed deviation from the Rayleigh law, presence of hysteresis, and non-monotonic behaviour were temperature dependent (Fig. 20). Hysteresis-free curves were obtained at very low T. With increasing T, non-monotonic and hysteretic ac-loops appeared. The shape of the loops depended on frequency too. More detailed analysis of the temperature and frequency evolution of the dynamic dielectric nonlinearity revealed an increase of nonlinearity on cooling to about 200 K, followed by a decrease on further cooling. Interestingly,
the dynamic hysteresis appeared to be also sensitive to a rate at which drive amplitude was changed. Such behaviour was suggested to originate from at least two different processes contributing to the dynamic nonlinearity, in contrast to one Rayleigh-type mechanism in bulk.

The observed peculiarities were explained by fast (with characteristic times shorter than $10^{-5}$ s) change of the nanodomain configuration even at small sub-switching fields. In bulk at such fields, the electric field induces vibration of the domain walls and de-pinning of the walls, without nucleation or growth of new domains. In heteroepitaxial PZT films, local switching of nanodomains was found by PFM at the fields smaller than the apparent coercive field. In addition, the switching time can be as short as $10^{-7}$ s [88]. Thus both the vibrations of the domain walls and partial switching took place in thin-film PZT during the low-frequency cycling of ac field. Different kinetics of these two processes leads to the peculiar dynamic nonlinearity.

![Fig. 20. The permittivity $\varepsilon_{AC}$ as a function of amplitude $E_{AC}$ determined at $f = 1$ kHz and at different temperatures $T$ in the range of 103–453 K.](image)

In summary to this Chapter, FE domains were experimentally studied in epitaxial heterostructures PbZr$_{0.65}$Ti$_{0.35}$O$_3$ / La$_{0.5}$Sr$_{0.5}$CoO$_3$ / MgO (001) with a large lattice mismatch. In the c-oriented tetragonal PbZr$_{0.65}$Ti$_{0.35}$O$_3$ films, random arrays of FE domains with 180° facet-type {100} boundaries were found and explained by the island growth mode. In addition, laterally inhomogeneous switching fields and field induced strains were detected and ascribed to electric and strain fields associated with defects. Dynamics of the nanodomains was experimentally studied using low-frequency dielectric spectroscopy. The specific features of the dynamic nonlinearity were revealed including: the deviation from the Rayleigh law, hysteresis, and dependence on temperature, frequency, and time. They were
explained by contribution from the local switching at sub-coercive fields, in agreement with the PFM studies.
4 Effect of misfit strain and strain relaxation on ferroelectric domains in epitaxial Pb$_{0.5}$Sr$_{0.5}$TiO$_3$ films

In the study, epitaxial Pb$_{0.5}$Sr$_{0.5}$TiO$_3$ (PST) films were used. In bulk form, PST possesses a perovskite-type crystal structure and exhibits cubic paraelectric to tetragonal FE transition around 430 K. In PST ceramics, deviation from stoichiometry can lead to a shift of the transition temperature.

Epitaxial PST films with thickness 130 nm grown on La$_{0.5}$Sr$_{0.5}$CoO$_3$ / MgO (001) and SrRuO$_3$ / SrTiO$_3$ (001) were studied. The cube-on-cube-type epitaxial relationships were found by x-ray diffraction. In PST/LSCO, two out-of-plane and two in-plane lattice parameters were found, suggesting full relaxation of misfit strain and formation of $c$-oriented and $a$-oriented domains. The volume fractions of $a$- and $c$- domains estimated from the integrated diffraction intensity were 30–35% and 65–70%, correspondingly. From x-ray diffraction it was found that $a$-domains grow vertically from the bottom to the top of the film. In PST/SRO, the in-plane lattice parameters were 3.905 Å (SRO), and 3.918 Å (PST), revealing partial relaxation of misfit strain in PST film. In the $c$-oriented tetragonal PST/SRO, the estimated strain was compressive $-0.45\%$.

FE domains were imaged by PFM using the relatively large Pt top electrodes, and a non-conducting tip. Both the out-of-plane and in-plane responses were studied. In the PFM experiment using the top electrode, no correlation between surface topography and PFM images were found. In PST/LSCO, the out-of-plane (in-plane) response was mainly connected with the out-of-plane (in-plane) polarization in $c$-domains ($a$-domains).

In the relaxed polydomain PST/LSCO film, islands and $\sim0.1–0.5$ μm sized domains embracing several islands were detected. The $a$- and $c$-type regions were identified by comparing amplitudes of the out-of-plane (Fig. 21 a) and in-plane (Fig. 21 c) responses. For instance, the $c$-type of the region A was evidenced by simultaneously large out-of-plane and small in-plane responses. The region B was of $a$-type. The C and D regions may be of different types. Although a complete correct interpretation of the images would be difficult, they showed the formation of randomly distributed relatively large $a$- and $c$-domains. The configuration was influenced by island growth and differed from the striped $a/c$ patterns in strained epitaxial films [89].
In PST on SRO/STO, PFM amplitude (Fig. 21 a) and phase (Fig. 21 b) evidenced FE domains with an out-of-plane direction of polarization. Such $c$-domains agreed with structural analysis. In the amplitude image, remarkably sharp dark boundaries could be seen between domains with opposite polarization direction. Interestingly, the detected domain configuration was not regular. Rather, FE domains were distributed randomly, resembling the configurations in the previously studied PZT/LSCO and PST/LSCO films. This showed that in the strained epitaxial films, even partial strain relaxation could result in the change of the layer-by-layer growth mode to the island growth mode.

![Fig. 21. The (a, b) out-of-plane and (c, d) in-plane PFM images of (a, c) amplitude and (b, d) phase taken from the Pt coated PST surface. The shown scan area is 1.3 $\mu$m x 1.3 $\mu$m.](image)

In the relaxed polydomain PST on LSCO/MgO and in the strained PST on SRO/STO, the difference in domain configurations determined also the difference in the out-of-plane macroscopic polarization (Fig. 22). In the $c$-oriented strained PST on SRO/STO, large spontaneous polarization at the relatively small coercive voltage was obtained. The polarization is larger than in PST ceramics (20 $\mu$C/cm²). In the polydomain PST on LSCO/MgO, presence of $a$-domains with the in-plane direction of polarization determined smaller macroscopic out-of-plane
polarization measured even at large applied voltage. Remarkably, the polarization and coercive field abruptly increased with increasing voltage above 8 V (outer loop in Fig. 23b). In the film with two domain types, the observed two families of the loops can be understood as corresponding to switching of one type of domains at lower voltage and to complete switching of all domains at larger voltage. Switching of one domain fraction independent from switching of another one may be specific for epitaxial films with island-type random arrays of the relatively large domains of different kinds.

Fig. 22. (a) Amplitude and (b) phase of the out-of-plane PFM response in PST/SRO/STO. Scan area is 1.2 μm × 1.2 μm.

Fig. 23. Polarization – voltage FE hysteresis loops as a function of maximum applied voltage in (a) PST/SRO/STO and (b) PST/LSCO/MgO.
In summary, FE domains were experimentally studied in epitaxial heterostructures of PST/LSCO/MgO and PST/SRO/STO. In the polydomain tetragonal PST films on LSCO/MgO, random arrays of ~0.1–0.5 μm sized \( a \)- and \( c \)-domains were found and explained by the island growth mode. In the \( c \)-oriented tetragonal PST films on SRO/STO, random arrays of 180° domains were found and explained by the island growth mode too. In PST on LSCO/MgO, the step-like switching was observed and suggested to result from the island-type configuration of domains with different switching mechanisms.
5 Effects of microstructure on ferroelectric domains in BaTiO$_3$ films

For the PFM studies of the microstructure controlled FE domains in BaTiO$_3$ (BTO) films, the BTO films prepared by different techniques were selected [Paper IV]. Epitaxial (001) oriented pseudo-cubic BTO films (lattice parameter 4.007 Å) were grown by pulsed laser deposition on La$_{0.5}$Sr$_{0.5}$CoO$_3$ /MgO (001) (LSCO/MgO) and on SrRuO$_3$/SrTiO$_3$ (001) (SRO/STO). Polycrystalline randomly oriented tetragonal BTO films (lattice parameters 4.017 Å and 4.001 Å) with granular microstructure were obtained by solution deposition method on polished alumina substrates. Thickness of epitaxial films was 200–250 nm, and thickness of polycrystalline film was 600 nm.

For PFM imaging of the epitaxial films, the probing ac voltage was applied between the bottom electrode and a conducting tip. For studies of the sol-films, lateral capacitors with Cr/Au electrodes separated by gap ~ 3 μm were used. The voltage was applied across the gap, and a non-conducting tip was in contact with the film surface in the gap area. The out-of-plane and in-plane PFM responses were recorded.

In the polycrystalline BTO films with nanosized equiaxed grains, the amplitude and the phase of PFM response (Fig. 24 b,c) evidence the presence of spontaneous polarization. In the topography image, the grains with sizes 20–150 nm are seen, in agreement with the cross-sectional electron microscopy imaging. FE domains with different directions of polarization and hence, different phase of the in-plane component of piezoresponse are seen in the phase image as dark and bright areas. From comparison of topography, amplitude, and phase images, it is found that a nanosized grain can contain one domain. Due to random crystal orientation of the film, polarization in different grains is also randomly oriented.

In the epitaxial BTO film on SRO/STO, the presence of spontaneous polarization is detected too. However unexpectedly, the out-of-plane component of piezoresponse is below detection limit or absent. For the BTO film grown on the top of SRO/STO, the in-plane misfit strain is compressive. It means that the BTO unit cell is theoretically predicted to be elongated in the out-of-plane direction. This suggests the out-of-plane polarization component, even if the misfit strain is partially relaxed. Surprisingly, the out-of-plane polarization is absent. The observed in-plane response (Fig. 25 b,c) suggests the in-plane direction of polarization.
The surface topography includes rectangular brick-like features. Such features are often observed in $a$-oriented FE films grown on SRO/STO. The strained SRO layer mainly determines them. In pulsed laser deposition, the strained SRO is formed on STO via a step-flow mechanism [90]. The resulting step edges on SRO/STO are known to control strain relaxation that is non-uniform in the in-plane directions. This stimulates stabilization of FE domains with the in-plane orientation of polarization [91, 92]. The topography and PFM images agree with the step-controlled stabilization of FE $a$-domains in BTO films on SRO/STO.

Another unexpected observation is made in the epitaxial BTO film on LSCO/MgO. In this heterostructure, due to the compressive misfit strain, the out-of-plane polarization should also exist in the BTO film. However, the out-of-plane piezoresponse is absent. Moreover, the in-plane piezoresponse is also absent. This indicates absence of FE domains in BTO/LSCO/MgO. Together with other peculiarities such as absence of the high-temperature and low-temperature
Curie-Weiss behavior, and strong frequency dispersion of the temperature of the dielectric peak, this evidences the short-range relaxorlike polar order instead of the theoretically expected long-range FE order.

Thus, the microstructure of the BTO films can substantially influence FE domains. The shape, size, and polarization orientation of FE domains, and even domain existence as such are functions of microstructure. Interestingly, smaller domains are detected in polycrystalline film with thickness 600 nm, while somewhat larger domains are observed in thinner epitaxial BTO film on SRO/STO with thickness 250 nm. This shows that scaling of FE domain width in perovskite-structure films cannot be directly described using the Kittel’s principle. In the epitaxial BTO films grown on the compressive substrates, observations of $a$-domains and relaxor state cannot be explained in the frame of the existing theories. Both the Pertsev diagram and the relaxor concepts require further development.

In summary to this chapter, FE domains were investigated in perovskite BTO thin films with different types of microstructure. It is shown that the shape, size, and polarization orientation of FE domains and even domain existence as such are functions of microstructure. These observations cannot be explained by existing theory and ask for its further development.
6 Conclusions

Ferroelectric performance in heteroepitaxial thin and ultrathin films, and superlattices of ABO₃-type perovskite structure FEs was experimentally studied. Epitaxial heterostructures grown by pulsed laser deposition included BaTiO₃, (Pb,Sr)TiO₃, Pb(Zr,Ti)O₃, NaNbO₃, SrTiO₃, and KTaO₃ films with minimum thickness as small as 2–5 nm.

FE domains and local polarization switching were explored on the nanometer scale using PFM. The PFM experiment was modified. Additionally to the widely used classical scheme using ac voltage applied to the movable conducting AFM tip, a scheme using voltage applied to the thin Pt top electrode was realized. For the scheme with the top electrode, the measurements conditions were optimized. The thickness of the top electrode, the type of the AFM probe, the amplitude and the frequency of ac drive, and the settings of the external lock-in amplifier were optimized. The lateral resolution of piezoresponse imaging as good as 2–3 nm was achieved. A special scheme was realized and optimized for domain imaging in the lateral capacitor, which was formed by the top electrodes separated with a narrow gap. For studies of local polarization switching, the settings of the external lock-in amplifier and LCR bridge were optimized, and special software was developed. Local properties were related to macroscopic response. For this, a method of simultaneous on-wafer low-frequency impedance measurements was optimized allowing studies of thin and ultrathin (to 5 nm) films in a broad range of conditions and regimes. The PFM studies were accompanied by extensive studies of the low-frequency dielectric response of the films.

FE domain configuration, switching, and dynamics were studied in epitaxial heterostructures PbZr₀.₆₅Ti₀.₃₅O₃ / La₀.₅Sr₀.₅CoO₃ / MgO (001) with a large lattice mismatch. In the c-oriented tetragonal PbZr₀.₆₅Ti₀.₃₅O₃ films, random arrays of FE domains with 180° facet-type \{100\} boundaries were found and explained by the island growth mode. Laterally inhomogeneous switching fields and field induced strains were detected and ascribed to electric and strain fields associated with defects. The revealed specific features of the dynamic nonlinearity were due to contribution from the local switching at sub-coercive fields, in agreement with the PFM studies.

Effects of misfit strain and strain relaxation were analyzed in epitaxial heterostructures of Pb₀.₅Sr₀.₅TiO₃ films on La₀.₅Sr₀.₅CoO₃ / MgO (001) and on SrRuO₃/SrTiO₃ (001). In the polydomain tetragonal Pb₀.₅Sr₀.₅TiO₃ films on La₀.₅Sr₀.₅CoO₃ / MgO (001), random arrays of 0.1–0.5 \( \mu \)m sized a- and c-
domains were found and explained by the island growth mode. In the \( e \)-oriented tetragonal \( \text{Pb}_{0.5}\text{Sr}_{0.5}\text{TiO}_3 \) films on \( \text{SrRuO}_3/\text{SrTiO}_3 \) (001), random arrays of 180° domains were found and explained by the island growth mode too. In \( \text{Pb}_{0.5}\text{Sr}_{0.5}\text{TiO}_3 \) on \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 / \text{MgO} \) (001), the steplike switching was observed and suggested to result from the island-type configuration of domains with different switching mechanisms.

Microstructure effects were investigated in perovskite \( \text{BaTiO}_3 \) thin films. Epitaxial films on \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 / \text{MgO} \) (001) and on \( \text{SrRuO}_3/\text{SrTiO}_3 \) (001), and polycrystalline films with granular microstructure were studied. The shape, size, and polarization orientation of FE domains were found to be strongly influenced by grain size and strain relaxation route. The long-range FE order appeared to be unstable in some of the films.

In the studied heteroepitaxial films with a large lattice mismatch, experiments have revealed theoretically unexpected phenomena such as formation of random arrays of large domains, step-like switching, peculiar domain dynamics, and onset of the short-range polar order. The results cannot be explained in the frame of the existing theories and ask for their further development. The observed phenomena are important for applications such as multistate memory devices, storage capacitors, and ferroelectric tunnel junction devices.
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