6. Discussion

The scope of this work was to study ferroelectric phenomena at a local scale on different materials in view of their prospective use in non-volatile memories.

An analysis of the available techniques by which ferroelectricity can be probed at a level as small as possible revealed that the most suitable method is the so-called "piezoresponse-SFM", a scanning probe technique, which is based on the converse piezoelectric effect (present in all ferroelectric materials). The reason for this choice is that this technique allows both the *detection* and *modification* of the ferroelectric state using the same experimental setup, down to a resolution of 10 nm. Special attention has been paid to explore and to point out the methodology to extract as much information as possible about the local material properties from the physical quantities accessible with this method. The capabilities of the experimental system were tested using barium titanate single crystals, whose properties are well known in the literature, both from macroscopic and microscopic characterization.

Ferroelectricity was investigated by means of the electromechanical response to an AC excitation voltage on a series of samples, with ferroelectric structures of decreasing size:

1. Polycrystalline *continuous* films of PZT consisting of grains with random orientation and sizes in the 100 nm - 600 nm range. The thickness of the films was in the same range, 200 nm up to 600 nm. These films can be considered as a two-dimensional assembly of ferroelectric entities.
2. *Individual* non-*c*-oriented grains embedded in a *c*-oriented matrix of different epitaxial films of BLSF materials. The grain size was again in the mesoscopic range (hundreds of nanometers), comparable with the contact area between the SFM tip and the grain i.e. the area from which the electromechanical data are collected. These grains, embedded into a background with *c*-orientation, were not completely independent or stand-alone, since they were surrounded by a matrix of the same material. However, since they were switchable independently from each other, they may be considered as individual grains.
3. A set of fine-grained *individual* ferroelectric structures having finite lateral sizes ranging from 1 μm down to 100 nm. These sizes are close to the experimental resolution limit (which is the contact area between the SFM tip and the structure).

The ferroelectric behavior was studied by means of domain imaging and local electromechanical probing. Although each experimental result was shortly discussed already, some general discussion will now be provided.

6.1 The ferroelectric domain structure

The configuration of the ferroelectric domains is the most important factor that determines the macroscopic ferroelectric properties, controlled by the domain nucleation and the domain wall mobility. From piezoresponse images a large variety of domains could be observed, starting from the single domain state that was found in $BaTiO_3$ single crystals over large areas and

down to very small (100 nm) and isolated grains of SBT containing even multiple domains of 30 nm in lateral sizes (like Figure 31 in Sect. 5.3.3).

Unlike other methods, scanning microscopy methods, in particular piezoresponse SFM, permit to verify whether the conditions for stability of the domain structure still hold in the range of tens of nanometers. It was found, for instance, that the rules found for the macroscopic equilibrium of ferroelectric domains are still valid at this scale, at least under normal conditions (moderate contact force and electric fields applied). For example, 90° domain wall structures, typical for BaTiO$_3$ single crystals, where they have a domain width of 10µm - 20µm (as in Figure 18, Sect. 5.1.2), were found in PZT (30/70) grains of only 500 nm size with domains of less than 10 nm in width (see Figure 23, Sect. 5.2.2). The same holds for the 180° domain walls. It may happen, however, that extreme local conditions such as stress from neighboring grains or from the substrate, or an intense poling field from the SFM tip induce charged domain walls or metastable domain states that are not allowed within equilibrium thermodynamics.

A common belief for simple perovskites is that grain sizes below 150 nm should be stable monodomains [153], and therefore would exhibit bad switching properties due to the inhibition of reverse domain nucleation. In switching experiments we indeed found that grains of 500 nm usually take the single domain state when poled at saturation (Figure 27, Sect. 5.2.4), but also that they can assume a multidomain state for lower poling voltages. This case was shown, for instance, in Figure 28c (Sect. 5.2.4), where the small domain nucleated was stable at least for several hours. Also, it was found that the domains may extend into the adjacent grain but do not necessarily extend over the whole grain. In the case of SBT, grains of 200 nm in lateral size may still exhibit a domain structure, even after poling at saturation.

Domain imaging in small grains of SrBi$_2$Ta$_2$O$_9$ revealed a very fine and very stable domain structure, grains of different sizes usually exhibiting domains of less than 50 nm in width. Figure 31 (Sect. 5.3.3), for instance, shows a grain 250 nm in length divided into five stripe domains 50 nm in width each, and a smaller grain, about 150 nm in diameter, shows three similar domains. In contrast, there are two other small grains discernible in the flat background, each about 50 nm in lateral size, which are in the single domain state. The hypothesis could be put forward that, at least for this type of ferroelectric systems (*a*-oriented grains of SBT embedded into the *c*-oriented matrix), grains under 50 nm are single domains. This value is, however, very close to the lateral resolution of the experiment, estimated to 30 nm – 50 nm. Therefore, even finer domains could exist (also in grains that appear with gray contrast) without being visible due to the too large probing contact area. Assuming nevertheless that in SBT the smallest domain size is 50 nm, it is possible to compare the domain wall energy in different materials using the relation [5]:

$$\sigma = \frac{d^2 \varepsilon * P_0^2}{t} , \qquad\qquad Eq.\ 34$$

where *d* is the smallest stable domain size in a periodic domain structure having the thickness *t*, P_0 is the spontaneous polarization, $\varepsilon*$ is a constant related to the dielectric permittivities of the crystal, and σ is the domain wall energy density. Since the smallest stable domain observed in grains of similar sizes in BaBi$_4$Ti$_4$O$_{15}$ and Bi$_4$Ti$_3$O$_{12}$ was about 100 nm, it is

possible to predict that the domain wall energy density is at least four times bigger for the two materials than for SBT.

As a general feature, the bismuth layer-structured ferroelectric (BLSF) thin films studied in this work exhibit grains of non-*c*-orientation embedded into a flat *c*-oriented matrix. These grains, a few fractions of micrometer in lateral size, are either spherical (as seen in the SEM images) or rectangular with an aspect ratio higher for $Bi_4Ti_3O_{12}$ than SBT and $BaBi_4Ti_4O_{15}$. The formation of these structures is an effect of the high anisotropy of these materials, which leads to an anisotropic grain growth during deposition. The piezoelectric contrast is always zero in the *c*-oriented matrix, except for $Bi_4Ti_3O_{12}$ where domains can be induced by poling the samples. The non-*c*-oriented grains exhibit a well-defined piezoresponse, slightly stronger in spherical grains than in the rectangular-shaped grains. The magnitude of the signal from the grains will be discussed below (Sect. 6.3). The sign of the piezoresponse indicates that the polarization in the as grown state is usually oriented towards the bottom electrode, which consists of an epitaxial $LaNiO_3$ film or of a Nb-doped $SrTiO_3$ crystal. A possible reason for this initial orientation of the spontaneous polarization is the negative carrier concentration present in the bottom electrode. Negative charges in the bottom electrode, near the interface with the ferroelectric film, create an electric field that favors the top-to-bottom orientation of the polarization in the ferroelectric. However, this hypothesis has to be checked, for instance by depositing films on oxide electrodes with a *p*-type conduction. In this case the onset of polarization should be positive.

In all the BLSF films investigated, the domain walls in the rectangular grains were parallel to the c-axis of the grains, as revealed by a comparative analysis of piezoresponse measurements and HRTEM investigations of grains in the same area of the samples. The occurrence, under certain circumstances, of domain walls with other orientations was followed by the pinning of these atypical domain walls after less than ten switching cycles of the polarization (see Sect. 5.3.5).

Ferroelectric domains induced in isolated PZT nanostructures were stable at least on the experimental time scale (a few days). Writing and imaging of two domains within the same structure of 1 μm or 500 nm in lateral size was also achieved. The smallest domain we could write and further image in these very fine-grained nanostructures was about 200 nm in size, as shown in Figure 45, Sect. 5.4.1 (the positive domain in the upper right cell). We believe that these domains certainly extend through the entire thickness of the structure.

Another disputable aspect in piezoresponse imaging of ferroelectric domains is the depth into the sample over which the detected domain extends. This aspect may be defined as the "z-sensitivity" of the method and is basically determined by the ferroelectric material investigated. Calculations with the simple model described in Appendix A indicate that 90% of the voltage applied between the SFM tip and the bottom electrode is applied to about 30% of the sample thickness (see Figure A 3b in Appendix A) for a permittivity of the ferroelectric material of $\varepsilon_r = 100$. Other simulations using the finite element method have estimated the "active" layer that piezoelectrically responds to be 30 nm out of 128 μm thickness of a $BaTiO_3$ single crystal [168] and a similar value is suggested for a 400 nm thick epitaxial PZT (20/80) film [169].

Rather contradictorily, Ahn et al. [40] have experimentally *demonstrated* the field effect in a PZT/SrRuO$_3$(110)/SrTiO$_3$(001) epitaxial heterostructure. Systematic and stable changes in the resistance of the SrRuO$_3$ layer were induced by poling the upper surface of the 400 nm thick PZT film with an SFM tip. In other words, the ferroelectric domains induced at the surface extended *throughout* the thickness down to the bottom electrode and reversibly modified its carrier concentration [40].

Our estimates (using the simple model described in Appendix A) regarding the penetration depth of the electric field have clearly established the following two aspects:

1. The permittivity is a very important parameter; higher values imply smaller fields inside the sample, as indicated by our simple model in Eq. A 4[*]. Therefore, the region which piezoelectrically responds will be very thin, and consequently the piezoresponse of high permittivity materials is concentrated to the near-surface region. For instance, in BaTiO$_3$ single crystals, one can estimate that the field penetrates 20 times deeper into the *c*-domains than into the *a*-domains ($\varepsilon_a / \varepsilon_c \approx 4000 / 200$).

2. The aspect ratio *contact area / film thickness* of the electrostatic system plays an important role, too. A large contact area (of blunt tips for example) or a small thickness of the ferroelectric film makes the geometry to get closer to that of a planar capacitor, therefore decreasing the degree of non-homogeneity of the electric field. As a consequence, the piezoresponse of thin films may reflect the contribution of a larger percent of the film depth than the piezoresponse of thick samples. The stray field, however, remains important in both cases and it may polarize the region parallel to the film plane.

Therefore, we may assume that the piezoresponse images of thick (more than about 1 µm) samples illustrate only the domain structure near the surface, whereas in thin films (less than 500 nm in thickness), the whole thickness of the film contributes to the measured piezoresponse. Nevertheless, these assumptions depend on the specific experimental circumstances, e.g. on the permittivity and the grain size of the sample.

6.2 Piezoelectric and ferroelectric hysteresis

The procedures for recording the hysteresis loops were explained in Sect. 4.3.3. It is obvious that these loops are not usual hysteresis loops, in a classical sense. While the in-field loops are similar in nature to the small-signal capacitance measurements, the remanent loops are of a more particular type. They reflect in fact the retention characteristics after the application of a particular voltage pulse and after the specific history of polarization states. In contrast, the in-field loop characterizes a domain state in the presence of the electric field applied, a ferroelectric state that may not remain after the suppression of the field. This is actually the case in many macroscopic measurements, where the polarization value read a few fractions of a second after the field removal is much lower than the zero field polarization of the

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[*] V_{M2} inside the ferroelectric is proportional to $(\varepsilon_2)^{-1}$.

(dynamical) in-field loop. Therefore, the hysteresis loop of the relaxed state (defined as *remanent hysteresis loop* by our group [73]) is much more suitable not only for local electromechanical measurements but also for ferroelectric characterization in general.

Interpretation of the hysteresis loop shape

Whereas the physical meaning of the saturation parts on the hysteresis loops is clear, the meaning of the intermediate points of the loops, near the coercive voltage, is not trivial. In the ideal case, for the 180° switching of a single grain, the loop should be perfectly rectangular-shaped, similar to that of grain No.1 in Figure 32 (Sect. 5.3.3). This would indicate that once the local threshold field has been reached, nucleation and growth of an opposite domain take place in the whole volume probed within some nanoseconds, giving rise to an ideal square-shaped hysteresis loop. The experiments have shown, however, that abrupt switching from one state to another only rarely occurs, depending on the material, grain size or grain orientation. Nucleation and growth of the domains actually take place over a set of pulses applied with amplitudes around the coercive voltage, suggesting intermediate *stable* states of the domain configuration. Compared with macroscopic switching it appears very unusual that switching - a highly non-equilibrium process - occurs by passing through (at least) metastable states. However, the different conditions imposed on the system in the case of the local piezoresponse and macroscopic ferroelectric polarization hysteresis make them difficult to compare. In the SFM measurements only one nucleation center is activated, whose evolution depends on the local environment, whereas in macroscopic measurements a well-defined electric field is applied to a statistical system of domains (each with its own parameters) that evolve together, with a strong mechanical and electrostatic coupling [170,171].

The interpretation of the transition regions between the two saturated states of polarization on a hysteresis loop needs a special treatment. As mentioned above they characterize intermediate switching states as "seen" by the tip through the small piezoelectric oscillations induced in a certain volume underneath the contact region. During polarization reversal, in this volume, mainly nucleation and growth of opposite domains occurs, at least for those domains having the polarization oriented perpendicular to the film plane. Nevertheless, in order to minimize the total energy of the system, either ferroelastic switching or motion of an existing domain wall from a previous position to a more stable one may also take place, as imposed by the field and by the specific boundary conditions. The first hysteresis loop of grain No. 2 in Figure 32 (Sect. 5.3.3) certainly resulted from a ferroelastic switching, and as consequence, a strange loop was recorded during this 90° switching. Simultaneous recording of both out-of-plane and in-plane hysteresis loops will help the elucidation of these processes, specific to *local* probing experiments.

Since the system evolves according to the local boundary conditions, the hysteresis loops recorded at different places should, at least in principle, be different. Local strains and electric fields produced by nearby grains should influence the local behavior. Indeed, this is a general trend that was observed during this work, where differences in hysteresis parameters were found not only between grains, but also within the same *individual* grain, less than 300 nm in lateral size [58,60]. The hysteresis loops in Figure 44 (Sect. 5.4.1) are another example where the presence of the edges of the structure (1μm in the lateral size) shifts the onset of polarization downwards.

Considerations on numerical values

The values obtained for the piezoelectric coefficients are calculated as described in Sect. 4.2. Those of the *local* saturation piezoelectric coefficients are typically 2 – 4 times smaller than the ones measured from macroscopic measurements on films, and about 10 – 20 times smaller than the bulk values. However, similar values have been reported in the literature from other piezoresponse SFM measurements [66,90,111]. The clamping of the film to the substrate (Appendix C) is not sufficient to explain the low experimental values of the effective piezoelectric coefficient even in macroscopic measurements on thin films [172]. Since piezoelectricity implies strain, which exists mainly at each 90° domain walls[*], it is believed that the reduced number of non-180° domain walls in thin films (compared to the bulk) is responsible for the further decrease of the piezoelectric response [173]. In the case of the piezoresponse measurements, even more factors may cause the reduction of the effective piezoelectric coefficient. A few possible reasons for the very small values of the local piezoelectric coefficient measured (for example, 3 to 6 pm/V in $BaTiO_3$, compared to the bulk value of 86 pm/V) are:

1. The high permittivity of ferroelectrics

Due to the high permittivity (usually several hundreds), and also to the large thickness of the sample, the electric field is confined to a thin region near the surface, in the vicinity of the contact place (see Figure 9 in Sect. 3.2.4). This implies that only a small region of the sample will respond piezoelectrically to the AC testing voltage [168]. The region is clamped by the *immobile* surroundings not only in the film plane (as shown in Appendix C) but also perpendicular to it, and therefore the effective piezoelectric coefficient appears smaller than that of the film.

2. The very high electric field under the tip

Because the electric field is similar to that given by a point charge, therefore extremely inhomogeneous, the testing voltage (in the range of 2 V_{rms}) may be high enough to switch the polarization in a very small region under the contact area, where the field exceeds the *local* coercive field. Occurrence of switching under the influence of the AC testing voltage, with the same frequency as the excitation, will lead to a decrease of the first harmonic response and to an increase of the second harmonic oscillation.

3. The adsorbed (water) layer at the surface

Any adsorbed surface layer with a relatively low dielectric constant will further decrease the field in the ferroelectric sample, due to the large permittivity of ferroelectric materials.

4. The contact force between tip and surface

A simple estimate of the stress applied to the sample for a contact force of 5 μN and a contact area of $\pi \cdot 40^2 \ nm^2$ (as usual in the present measurements) leads to a value of 1 GPa. Such a huge pressure may considerably clamp the mechanical response of the sample.

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[*] The contribution of the domain wall movements to the dielectric permittivities and piezoelectric coefficients is known in the literature as "extrinsic contribution", which has to be added to those of the lattice (single crystal), called "intrinsic contribution".

To obtain reasonable numerical values from local piezoresponse measurements, some scientists simply scale the average signal over a poled area with respect to the piezoelectric coefficient measured macroscopically. Other works use a standard sample, for instance quartz, to calibrate the signal. Despite these calibrations, the piezoresponse SFM measurements are not comparable with macroscopic piezoelectric measurements and are not really comparable among the different types of samples investigated each of them reflecting specific measurement conditions. Therefore, in this work, the values resulting from the direct calculations were given. In contrast, estimates of the electrostriction coefficient are of the same order of magnitude as those from macroscopic measurements on SBT polycrystalline films [73], and even showed a better match for PZT and $BaTiO_3$ (single crystal).

6.3 Dependence of the local ferroelectric properties on the local crystallographic orientation

As already established, piezoresponse SFM allows to obtain information on the *existence* of polarization, and whether or not the material is *switchable*, in other words, to test for ferroelectricity. In our epitaxial films, the exact crystallographic orientation has been established by other means (XRD and HRTEM). The piezoresponse measurements have not only shown the absence of polarization along the *c*-direction for BLSF materials with even Aurivillius parameter, but also the impossibility to pole or to create domains in these regions. In other terms, *the complete absence of ferroelectricity along the c-direction* has been demonstrated.

It should be emphasized that in piezoresponse imaging it is not the polarization which is being sensed, but an induced *piezoelectric oscillation*. It was proven in Sect. 4.1 that the movement of the SFM tip reflects the induced vibration of the sample surface underneath. This piezoelectric oscillation should now be analyzed more in detail. At first, if we consider only the out-of-plane imaging, we can say that the physical quantity probed is certainly the piezoelectric coefficient perpendicular to the film plane. Therefore, the piezoresponse images represent, exactly speaking, *piezoelectric* and not ferroelectric domains. Although they are strongly correlated, as already explained in Sect. 5.2.3 and as it is shown more precisely in Appendix B, the piezoelectric oscillation detected is not strictly proportional to the out-of-plane component of the polarization even in the simple ferroelectric system PZT. If we look to $BaTiO_3$ (Appendix B, Figure A 4b) we immediately notice that the maximum in d_{zz} (the piezoelectric coefficient "seen" by the tip; see notations in Appendix B) appears along a direction making a large angle (about 52° [174]) with the direction of the spontaneous polarization. This implies that out-of-plane piezoresponse imaging in $BaTiO_3$ does not describe simply the out-of-plane polarization, and that additional information is needed to deduce the actual ferroelectric domains. Such knowledge may be, for example, either the film orientation or the in-plane piezoresponse image. In the case of polycrystalline films, it may be difficult to extract information about the polarization. In fact the piezoelectric coefficient and the spontaneous polarization are still related, but this correlation depends on the specific orientation of each grain. The reason for this specific shape of the d_{zz}-surface of $BaTiO_3$ is the large value of its d_{15} piezoelectric coefficient (see Appendix B), which in turn is related (*via* Eq. 10c, Sect. 2.2) to the permittivity ε_{11} that is about 20 times larger than ε_{33}. Since no other

material studied in this work showed such large differences in the magnitude of the permittivities, we assume that the d_{zz}-surfaces of the materials with tetragonal symmetry approximate in shape the one of tetragonal PZT, given in Figure A 4a.

Therefore, for all materials having a tetragonal symmetry, the differences in the maximum induced piezoelectric coefficient could be expressed on the basis of the crystal orientation dependence of the piezoelectric coefficients. This was possible, because $d_{zz}(\theta)$ and $P_z(\theta)$ have the same trend, namely they are both at maximum for $\theta=0°$, at minimum for $\theta=180°$ and zero for $\theta=90°$. In PZT polycrystalline films the difference in the behavior of the grains could be explained on the basis of different orientations of the grains (Figure 26 in Sect. 5.2.3). Although the symmetry of the BLSF is not exactly tetragonal, it is usually assumed that a small orthorhombic or monoclinic distortion does not significantly change the piezoelectric tensor. In fact, knowing the crystallographic orientation, our results demonstrate that a similar correlation between the longitudinal piezoelectric coefficient and polarization is indeed valid for all the even-n members of the BLSF materials.

Let us have a closer look on bismuth titanate. $Bi_4Ti_3O_{12}$ has a monoclinic symmetry and therefore 10 independent components of the piezoelectric tensor. Neto and Cross [159] have measured the longitudinal coefficients d_{11}, d_{22} and d_{33} for single crystals, and separately calculated the other coefficients from previously published data. Using these values[*] the d_{zz} surface was calculated as a function of the direction as described in Appendix B for the tetragonal symmetry.

The result of this calculation is shown in Figure 49. Although there may be some other variants of the surface, this is the most probable dependency, in agreement with the measured coefficients. As can be immediately noticed in the figure, a maximum in the piezoelectric response can be reached in a direction parallel to [100], but also a small piezoelectric activity exists along the [001] direction. The ratio d_{11}/d_{33} is approximately equal to 4.
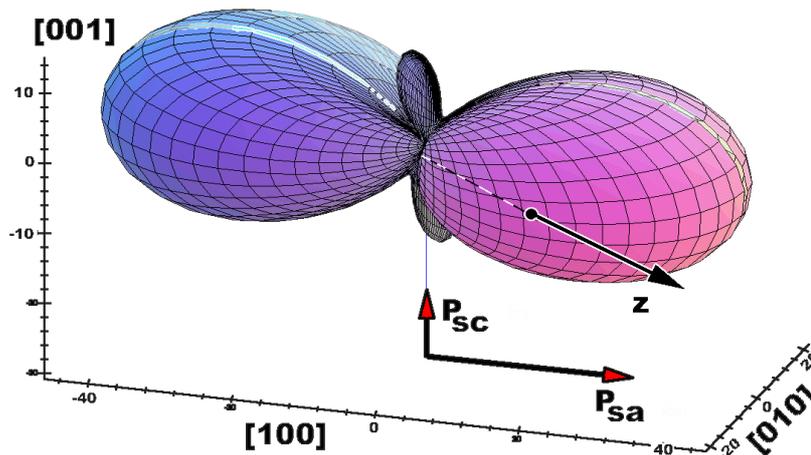

Figure 49 Expected dependence of the longitudinal piezoelectric coefficient on the measurement direction "*z*" in bismuth titanate. For the physical meaning of the surface plot see Appendix B.

Although about five times smaller than the bulk values, the piezoelectric coefficients in our measurements on $Bi_4Ti_3O_{12}$ epitaxial thin films (about 500 nm thick) revealed the same ratio

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[*] They found a discrepancy between the calculated and measured d_{33}, so the *experimental* value was used for the piezoelectric coefficient along the c-axis.

for the piezoelectric coefficient of non-*c*-oriented grains and of the *c*-oriented matrix (see the zero-field piezoelectric coefficients in Figure 41b, Sect. 5.3.5).

6.4   Size effect studies in ferroelectrics

Studies of size effects in ferroelectric materials historically developed in the following directions:

- Three-dimensional approach at macroscopic level: The size of the sample is kept constant, but the size of the single crystalline constituents is decreased. More exactly, the bulk properties are studied as a function of the grain size. The conclusion is that ferroelectric properties deteriorate with decreasing grain size.

- One-dimensional approach: Two dimensions of the ferroelectric sample are kept constant and the film thickness is decreased. In simple perovskites (BaTiO$_3$, PZT) the grain size is strongly related to the film thickness (due to the isotropic grain growth) and their effects on the ferroelectric properties could be estimated separately only recently [153]. Experiments have shown that the grain size is the main factor involved in the deterioration of ferroelectric properties when decreasing the film thickness. The same was found for SBT films. Due to the anisotropic grain growth in SBT, the same grain size and consequently the same ferroelectric behavior was reported for films with thickness from 50 nm up to 500 nm [151].

- True three-dimensional approach, achievable by *decreasing all three dimensions of the sample*.

During this work the size effects on the ferroelectric behavior have been experimentally studied using the third approach, which from a physics point of view is the proper one. Our results clearly prove that the ferroelectric behavior *does not depend on the size at least down to 100 nm lateral size* of the ferroelectric "sample". The one micron "samples" behaved as thin films when probed in the middle. Domains up to 500 nm lateral size were written and read as usual in very fine-grained thin films. Also, a multiple domain structure could be formed even in the 500 nm lateral size cells.

However, an increase of the vertical offset of the hysteresis loops was found with decreasing the structure size, an effect that may prevent the functionality of small memory cells. The vertical bias of the loops is certainly not related to the ferroelectric phenomenon, but most probably to the electrode asymmetry. Drawing the reciprocal of the relative offset (from Figure 47) versus the cell area it was noticed that the dependence can be fairly well fitted with a linear relation as shown in Figure 50. From the fitting parameters, the following empirical law was derived:

$$\Omega^{-1} = -\alpha A - \beta ,\qquad\qquad\qquad Eq.\ 35$$

where Ω is the relative shift of the hysteresis loop (as defined in Eq. 33, Sect. 5.4.2), A is the area of the cell, $\alpha = (28 \pm 3)\mu m^{-2}$ and $\beta = 1.9 \pm 0.2$. This dependence is difficult to interpret in the frame of the present imprint theories proposed in the literature. In the following, we will

try to relate our results to the two main attempts to explain the imprint of polarization in ferroelectric thin films.
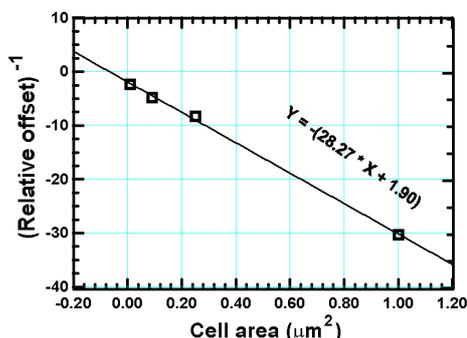

Figure 50 Size dependence of the reciprocal of the vertical hysteresis shift (imprint) in mesoscopic cells.

There are several reports in the literature on the effect of a layer with a fixed polarization on the leakage current [160] and on the vertical shift of the piezoelectric hysteresis loop in the case of *epitaxial* films [175]. According to the above studies, a lattice mismatch between the film and the substrate causes strong elastic in-plane strains in the film that build up a region with fixed polarization at the interface. The orientation of this strain-induced polarization depends on the lattice mismatch. If the lattice constant of the film is larger than that of the substrate, the polarization is directed towards the ferroelectric film. The size effect (in this case "thickness-effect") comes from the fact that the influence of this non-switchable layer (which is supposed to have a constant thickness for a given ferroelectric-substrate interface) becomes more important as the overall thickness of the ferroelectric film decreases. In our case, however, the existence of a layer with non-switchable polarization cannot be caused by a lattice mismatch, since the PZT structures are not epitaxial, but polycrystalline with an average grain size of about 20 nm. Moreover, since all the cells have the same thickness of 110 nm, a non-switchable layer with a fixed thickness cannot explain the effect of the lateral size on the relative offset.

Another approach to explain the imprint is based on the assumption that an internal bias field is present inside the ferroelectric or at least in the vicinity of its interfaces with the electrodes. The association of this internal field with the voltage shift of the macroscopic hysteresis loop of the polarization is supported by the linear dependence of the hysteresis shift on the value of the polarization remaining after a sustained (long time) poling [176,164].

We think that this is actually happening in our case, too, with the built-in electric field arising from the asymmetry of the ferroelectric-bottom electrode interface. In order to use the substrate as a bottom electrode, the mesoscopic devices were patterned directly onto Nb-doped STO substrates. Doping with niobium turns the perovskite strontium titanate into an *n*-type semiconductor [177]. This may provoke a region depleted from charge carriers near the interface, since ferroelectric materials can be considered as semiconductors with low mobility charge carriers. The region depleted from charge carriers generates an electric field at the ferroelectric-electrode interface [178], which in this case would be oriented top-to-bottom. This orientation of the bias field is in complete agreement with the sign of the offset found in our samples, for which the non-switchable layer also appears to have a spontaneous polarization

oriented top-to-bottom, therefore negative according to the convention used throughout this work (positive z-axis oriented bottom to top).

Next, we will try to explain the dependence of the offset *on the cell area* observed in our structures. The empirical relation expressed in Eq. 35 above, shows that the relative shift of the piezoelectric hysteresis loops of the cells depends on the reciprocal of a linear expression of the cell area. Using the linear dependence between the *effective* piezoelectric coefficient measured by the tip and the *effective* polarization underneath (Eq. 10a[*], Sect. 2.2) we may deduce from Eq. 33 (Sect. 5.4.2) and Eq. 35 the ratio between the zero-field polarizations for the two oppositely polarized states:

$$\frac{P^+}{|P^-|} = \frac{\alpha A + \beta - 2}{\alpha A + \beta + 2} \qquad\qquad Eq.\ 36$$

It should be mentioned that the exact physical processes occurring in ferroelectric films are presently not yet well understood, and finding the cause for the vertical shift of the loops remains an open question. For instance, the processing conditions, especially during the crystallization of the ferroelectric phase, have a very strong impact on the ferroelectric properties [161,179]. Following Pike et al. [180], and also Warren et al. [176], we may suppose that the imprint (internal bias field) is given by a component of the polarization, further referred to as P_D, determined by the dipolar defects present in the ferroelectric materials. In our case, P_D is oriented top to bottom. We may also suppose that the net polarization in the ferroelectric structure is given by the sum of the ferroelectric polarization and the defect-dipole component. For the two zero-field states we therefore may write, assuming that the pure ferroelectric polarization is symmetric:

$$\begin{cases} P^+ = P_{ferro} - P_D \\ \left|P^-\right| = P_{ferro} + P_D \end{cases} \qquad\qquad Eq.\ 37$$

Substituting Eq. 37 into Eq. 36, we find the dependence of the dipolar-defects component on the ferroelectric cell area (the sign is not included):

$$P_D = P_{ferro}\, \frac{2}{\alpha A + \beta} \qquad\qquad Eq.\ 38$$

Eq. 38 can be explained if we assume that the defects are mainly located at the surface of the ferroelectric structure over a certain thickness δ. It follows that the effect of the dipoles becomes important when the ratio between the volume and the surface of the structure (viz. the lateral size of the cell) decreases. This assumption seems to be supported by the experiment presented in Figure 44 (Sect. 5.4.1): The hysteresis loop recorded at the corner of the cell having 1 μm in lateral size exhibits a significantly larger imprint compared to the hysteresis loop recorded at the center of the same cell. The proximity of the cell edges has therefore shifted the hysteresis loop in the negative direction. Eq. 38 gives for $P_D / P_{ferro} = 0.87$ in the case of cells having 100 nm size. This ratio decreases to only 0.033 for cells of 1 μm

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[*] Although deduced for single crystals in the monodomain state, Eq. 10a still remains valid in the case of polycrystalline ferroelectrics (ceramics and films) if the values of the physical quantities involved are replaced with their effective values.

lateral size. It can also be found that the upper limit, $P_D = P_{ferro}$, is reached when the size of the structure decreases to zero.

In the case of PZT-based materials, the existence of these dipolar defects at the interfaces has been confirmed in different investigations, and therefore our explanation appears to be intuitively correct. However, further experiments, specifically on structures patterned on various p-type semiconductor substrates should confirm the opposite orientation of the dipolar defects compared to the present studies.