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## Structure and domain formation in ferroelectric thin films

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## Abstract

Ferroelectric materials are both piezoelectric and pyroelectric. Piezoelectrics have been widely used for decades now: Sonar devices were their first application and electromechanical actuators and gas igniters are amongst their most frequently used applications in modern everyday life. As pyroelectrics, ferroelectrics are used in heat detectors. Ferroelectrics present a memory effect, since their electrical polarization remains after the removal of an electric switching field and can exist in two different states, allowing binary information to be stored. Still, only recently, ferroelectrics have found their way into memory applications like computer ferroelectric random access memory (FeRAM) and radio-frequency identification (RFID) tags. For these applications, the thin film geometry has shown to be very important, since it allows to achieve the high electric fields needed to switch the polarization between the “up” and “down” state (*coercive fields*) with moderate voltages. A promising advantage of thin films, which serves as the starting point for this research, is the possibility to use the lattice misfit between the film and the substrate onto which it is grown (epitaxial strain) to apply stress to a ferroelectric and modify its response to the electric field or temperature. Besides these advantages, the thin film geometry also poses several challenges, like the interface control to make devices operate reliably in applications or the leakage currents that are present at very small thickness. In addition, for device miniaturization of thin film memory applications, a controlled domain structure is required.

$PbTiO_3$  is a classical ferroelectric with a large remanent polarization. In many applications, chemical substitution to  $PbTiO_3$  is used, which has a similar effect to applying stress (most notably in  $PbZr_{1-x}Ti_xO_3$ , the material of

choice in many applications). A large enhancement of the physical properties has been obtained for these so-called “solid solutions”. One of the remaining open issues about these materials is the origin of the gigantic piezoresponse for solid solutions with compositions close to the so-called morphotropic phase boundary (MPB), between two crystallographic phases. Reproducing similar phase boundaries in thin films of  $PbTiO_3$  under epitaxial strain can contribute to clarify this issue. The large chemical and crystallographic order in the material simplifies the interpretation of the structural properties and how they determine the ferroelectric response. Unfortunately, thin films of  $PbTiO_3$  without intentional substitution and doping suffer from impurity and defect induced conduction, hindering functional measurements. We show that epitaxial strain can give rise to a very high domain wall density or to lowering of the crystal symmetry in thin films of  $PbTiO_3$ . Both are expected to lead to an improved ferroelectric and piezoelectric response.

In chapter 4, we show that the critical thickness for strain relaxation of  $PbTiO_3$  on (001)<sub>c</sub>-oriented  $SrTiO_3$  substrates is much larger than previously assumed. This is due to the small lattice misfit between  $SrTiO_3$  and tetragonal  $PbTiO_3$ , which implies that the critical thickness cannot be correctly calculated by the commonly used Matthews-Blakeslee model, which assumes a relatively large misfit at the growth temperature. Instead, the model by People and Bean is much more appropriate since it correctly assumes a very low amount of defects and dislocations at the growth temperature and predicts a critical thickness in line with our observations. We show that it is energetically favorable for cubic  $PbTiO_3$  on  $SrTiO_3$  at the growth temperature ( $T_{growth} > T_c^{bulk}$ ) to achieve coherency by transforming into the tetragonal “self-strained” state instead of accommodating the cubic state coherently with large internal stresses or creating dislocations. This gives a physical explanation for the  $T_c$ -shift predicted by Landau theory to occur under epitaxial strain. Furthermore, we show that as long as  $PbTiO_3$  is grown sufficiently slow, up to a thickness below the critical thickness for strain relaxation, high-quality, single (001)-oriented thin films are obtained with very good coherency. The substrate/film coherence is evidenced by the observation of “Umweganregung” or double diffraction peaks. Especially for closely lattice matched systems, the observation of “Umweganregung” peaks in thin film X-ray diffraction (XRD) is often not recognized but it can be a powerful

tool to determine the lattice relations.

In chapter 5, we expand our investigation of the effects of epitaxial strain on ferroelectric thin films and show that thin films of the same material,  $PbTiO_3$ , are epitaxially strained on  $DyScO_3(110)_o$  substrates only for thicknesses below 12 nm. These single oriented thin films form  $180^\circ$  domains whose periodicity ( $D$ ) scales with film thickness ( $H$ ) following a  $D \sim \sqrt{H}$  dependence, known as Kittel's law. The crystal symmetry of these thin films corresponds either to the so-called  $ac$ - or to the so-called  $r$ -phase. These phases do not exist in bulk and, although they have been predicted to exist under epitaxial strain, they had not been observed before. These "bridging" phases between the  $a$  and  $c$ -phase and the  $aa$  and  $c$ -phase, respectively, are associated with symmetries that lack a polar axis, similar to those found at the morphotropic phase boundary of PZT. Therefore, these phases are expected to display a large enhancement in dielectric constants, piezoelectric coefficients and electromechanical coupling constants.

For  $PbTiO_3$  films with thicknesses above 12 nm on  $DyScO_3$ ,  $90^\circ$  twinned domains form, by means of which the misfit strain is (partially) relaxed. A very well defined domain period and a large registry of these twinned domains is observed by atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and piezoresponse-AFM. However, we have found that their periodicity ( $D$ ) does not scale with the crystal thickness according to a  $\sqrt{H}$  law, as usually observed for  $90^\circ$  domains in free-standing crystals and for  $180^\circ$  domains in epitaxial thin films. Instead, we observe a linear dependence for thicknesses from 30 to at least 100 nm and an unusual upturn for thicknesses between 12 and 30 nm. Qualitatively, this behavior is reproduced properly by a model in which the stress fields in the thin film are described by that of fictitious dislocations. Our experimental data are the first experimental confirmation of this model. We reproduce the calculations and fit the model to our data to obtain a  $90^\circ$  domain wall formation energy density of  $27\text{mJ}/\text{m}^2$ . This value is in very good agreement with that obtained by first-principles calculations and shows that the domain walls are mobile even at room temperature.

However, this model does not provide a complete description of the problem. We show that the domain orientation in partially relaxed thin films with  $90^\circ$  domains, is sensitive to the electrical boundary conditions, which are not

taken into account in the model. When there is no depolarization field (short-circuited thin films), we have observed that the periodic  $90^\circ$  domains order only along the pseudocubic in-plane direction with the largest misfit. This suggests that the thin films are strained along the in-plane direction with the smaller misfit. Finally, when the depolarizing field does play a role (open-circuit), the domains order along both in-plane pseudocubic directions.

In addition, a gradient of lattice parameters is observed by XRD, showing that the crystal lattice in thin films with  $90^\circ$  domains is inhomogeneously strained. For tetragonal ferroelectrics, in which strain (tetragonality) and polarization are thought to be strongly coupled, a lattice spacing gradient will give rise to a polarization gradient. Out-of-plane lattice deformation maps, obtained from TEM, show that the strain gradients are caused by an increased compression in the acute angle of every domain wall and an increased tension in the obtuse angle.

The presence of nanometer-sized periodic polar domains with the polarization alternating in-plane and out-of-the-plane, raises the question of how size effects influence the properties of ferroelectrics. Therefore, in chapter 6, we have proposed two methods to fabricate structures by which the size and shape dependence of  $PbTiO_3$  can be studied. We have fabricated chains of  $PbTiO_3$  nanodots by using self-organized block-copolymer nanorods on  $SrTiO_3$ . Remarkably, the morphology of the nanorods can be transferred to the  $PbTiO_3$  by room temperature PLD and subsequent annealing. We believe that this is due to preferential crystallization of the  $PbTiO_3$  at the surface areas which are not covered by block-copolymer. We have shown that the nanodots are ferroelectric and that the chains are separated from each other.

Finally, we have fabricated  $PbTiO_3/SrTiO_3$  superlattices with periodicities of approximately 10 unit cells, to study the coupling between the ferroelectric  $PbTiO_3$  and the dielectric  $SrTiO_3$  and the role of their interfaces. We show impedance spectroscopy measurements that indicate that the  $SrTiO_3$  effectively diminishes the leakage mechanisms of the  $PbTiO_3$ . Besides, these measurements show that the dielectric constant of these superlattices is in close agreement to what is expected for a stoichiometric mixture of the two materials. This is in conflict with previous reports on similar superlattices grown by sputtering, which were shown to display a very large frequency-independent dielectric permittivity. This leads to the conclusion that the im-

portant role that the interfaces play in the ferroelectric response of these materials is not intrinsic but, rather, dependent on the deposition technique.

The main achievements and original results of this thesis work are

1. the growth of coherent ferroelectric films as thick as 300nm and the explanation of this phenomenon;
2. the synthesis of periodic twinned domains with very small periodicities and large coherence;
3. the observation for the first time, of a linear dependence and non-monotonic behavior of  $90^\circ$  domain periodicity with thickness;
4. the synthesis of novel ferroelectric structures with reduced dimensionality compared to that of the films, such as nanoparticles aligned in chains.

