Motivation and outline

The mechanisms of ferroelectricity are known since long ago. Nowadays, the interest in ferroelectricity from the fundamental and applied points of view, is in the behavior at the nanoscale. Ferroelectrics are already present in devices ranging from memory elements in your Playstation II or IR sensors to ultrasound generators or piezoelectric gas igniters. Within the light of miniaturization of many of these applications, there is a strong interest in learning how ferroelectricity works at the nanoscale and how ferroelectrics respond at reduced sizes. Questions like: “Down to which size does a ferroelectric remain ferroelectric?” have attracted much attention in recent years and the answer is not straightforward. One of the major breakthroughs in the field in recent years is the experimental evidence that a 3 unit cell thin film of the ferroelectric \( \text{PbTiO}_3 \) is still ferroelectric [1]; something that was at odds with the classical understanding of ferroelectricity.

In this thesis, we focus on ferroelectric thin layers and the effects and mechanisms that take place upon reducing the film thickness. In order to attain a large degree of crystal perfection, the layers are to be grown on crystalline substrates. One of the important questions we consider involves the critical thickness for the relaxation of the strain introduced by the substrate (misfit strain). Due to the increasing energy cost of lattice strain with increasing thickness, compared to the cost of domain wall formation (the most efficient mechanism for strain relaxation), a critical thickness for strain relaxation exists. Below this thickness, the concept of “strain engineering” is applicable: The crystal lattice of the thin film is deformed to elastically accommodate to the substrate. Above this thickness, \( 90^\circ \) ferroelastic domains
appear, to relax the misfit strain. The large thicknesses found for coherent $PbTiO_3$ films on $SrTiO_3$ substrates, of $\sim 300\,nm$, compared to those calculated by commonly used models ($\sim 10\,nm$), shows that the misfit strain is not always calculated or interpreted correctly. This discrepancy between model and experiment has remained long unexplained. This work resolves this issue and shows that a proper choice should be made between different strain relaxation models (Matthews-Blakeslee [2] and People-Bean [3]) to correctly predict the critical thickness.

While $PbTiO_3$ on $SrTiO_3$ has a large critical thickness for strain relaxation, this system is of little interest for “strain engineering” of the ferroelectric response, because the room temperature in-plane lattice parameters of film and substrate are nearly equal and the lattice is barely deformed. A more appropriate choice of substrate to modify the $PbTiO_3$ crystal symmetry is $DyScO_3$. We will also investigate the critical thickness for strain relaxation of this film/substrate system. In this case, the lattice parameters of the substrate are in between those of the tetragonal film, and 90° domains are expected to form. We show that the coincidence of film and substrate lattice parameters at the growth temperature minimizes the presence of defects and highly periodic domain patterns appear. We will use the presence of in-plane superlattice peaks in the X-ray diffractograms, due to periodic ferroelectric (180°) or ferroelastic (90°) domain formation to extract a maximum of information about the films. While this method has been used in recent years to monitor 180° domains for thin films of different thicknesses, we will use it here to detect low-symmetry phases in epitaxially strained $PbTiO_3$ and to monitor 90° domains as a function of film thickness. Since the domain width of these 90° domains scales with thickness, large domain wall densities and small domain sizes can be obtained for thin films with thicknesses just above the critical thickness for strain relaxation.

Both the observation of low symmetry phases and high domain wall densities are thought to be correlated with the enhanced ferroelectric response in solid solutions of $PbTiO_3$ with other lead compounds (as PZT, used in current applications) but the exact mechanisms are unknown. This makes these thin films of $PbTiO_3$ on $DyScO_3$ highly relevant to study the relationship between either of these two properties and the ferroelectric response. Functional ferroelectric measurements on such thin films are problematic due to
leakage and electrode effects and, therefore, most of our characterization is performed using indirect methods, such as X-ray diffraction, to obtain information about the ferroelectric state.

We have studied the coherence of the periodic 90° domain wall structures in thin films with thicknesses 10 < H < 100 nm, in much more detail. While the coherence of periodic 180° domains has been recently exploited to study ferroelectrics [1], 90° domains with large enough registry to produce coherent diffraction have not been previously reported. The large registry of these periodic 90° domain patterns, is especially interesting because it could be used to preferentially deposit materials on these periodic nanometer-sized polar templates. The observed dependence of the domains size (d) with thickness (H), is in agreement with a model proposed by Speck et al. [4], in which the twin formation and clamping to the substrate is attained by means of dislocations. The stress fields present in the films according to this model were calculated by Pertsev et al. [5]. These calculations show non-monotonic d − H scaling for very small thicknesses and a linear relationship between d and H for intermediate thicknesses, in agreement with our observations.

Finally, we present two examples of more advanced structures of ferroelectric $\text{PbTiO}_3$: $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices and chains of $\text{PbTiO}_3$ nanoparticles with $\sim 50$ nm diameter. We will describe the methods to fabricate these structures which allow to study the effects of interfaces and reduced dimensions on the ferroelectric properties.

A summary providing an overview of this thesis is presented in the previous chapter. In short, a general and more advanced introduction into the field of ferroelectrics can be found in chapters 1 and 2, respectively. While chapter 1 serves as an introduction to thin films and ferroelectrics for a more general readership, chapter 2 gives a more advanced overview of the understanding and theory of ferroelectrics in their bulk and thin film form. Chapter 3 describes the experimental techniques used in this work to fabricate and characterize ferroelectric thin films. In chapter 4 and 5, we investigate the critical thickness for domain formation and the resulting domain structures under different epitaxial conditions. Domains have a strong influence on the switching behavior of ferroelectrics and their role is not yet fully understood. By studying domains and their formation in more detail, we hope, first, to increase the understanding of the influence of domains on the ferroelectric
properties and, second, to improve our control of the domains, their orientations, density and periodicity. Related to this, in chapter 5, we investigate the influence of different mechanical and electrical boundary conditions on the domain structures. Finally, in chapter 6, we show how we have constructed artificial structures, like rods of ferroelectric nanodots and superlattices. This allows to study the influence of the size and shape of ferroelectrics on their properties. We will conclude with a publications list, appendices and the bibliography.