Structural domains in thin films of ferroelectrics and multiferroics

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CHAPTER 6

Summary and Outlook

This chapter presents a summary of the experimentally based findings presented in this thesis and an outlook for future research work.

6.1. SUMMARY

The objective of this thesis work has been the investigation of the structure and domain formation in ferroelectric (PbTiO$_3$) and multiferroic (TbMnO$_3$) thin films. We explored these thin films using transmission electron microscopy for better understanding of the crystallographic domain structures and their orientation relationship with the substrates used.

PbTiO$_3$ thin films were chosen as model system for our investigations. PbTiO$_3$ thin films are well known ferroelectrics and well investigated systems since the early 90’s because of their simple perovskite structure, which forms an appropriate basis to understand functional and structural properties in other complex oxides. SrTiO$_3$ became the obvious substrate choice for growing PbTiO$_3$ thin film because it has a very low lattice mismatch with the PbTiO$_3$ thin films and it can be treated by a well established method to obtain a single type of termination at the substrate surface. We also used DyScO$_3$ substrates, which has almost identical pseudo-cubic lattice parameters with the PbTiO$_3$ thin film at its cubic structure just above $T_c = 490$°C.

Growth and characterization of thick mono-domain (only $c$-axis oriented) strained PbTiO$_3$ films on SrTiO$_3$ substrates were discussed in Chapter 3. This work demonstrates that instead of paraelectric PbTiO$_3$, completely $c$-oriented ferroelectric PbTiO$_3$ thin films were directly grown on (001)-SrTiO$_3$ substrates by pulsed-laser deposition with thickness up to 340 nm at a temperature well above the Curie temperature of bulk PbTiO$_3$. The influence of laser-pulse frequency, substrate-surface termination on growth and functional properties were studied using x-ray diffraction, transmission electron
microscopy, and piezoresponse force microscopy. At low growth rates (i.e. laser-pulse frequencies < 5 Hz) the films were always monodomain. However, at higher growth rates (i.e. frequencies ≥ 8 Hz) a-domains were formed for film thickness above 20–100 nm. Due to coherency strains the Curie temperature \( T_c \) of the monodomain films increased approximately 350 °C with respect to the \( T_c \) of bulk PbTiO\(_3\) even for 280nm thick films. Nonetheless, up to now this type of growth mode has been considered unlikely to occur since the Matthews-Blakeslee model already predicts strain relaxation for films having a thickness of only 10 nm. However, the present work disputes the applicability of the MB model. It clarifies the physical reasons for the large increase in \( T_c \) for thick films, and it is shown that the experimental results are in good agreement with the predictions based on the monodomain model of Pertsev et al. [See reference [7] of chapter 2].

In chapter 4, we investigate the shape of a-domains in PbTiO\(_3\) thin films grown on SrTiO\(_3\) and DyScO\(_3\) substrates. The development of a-domain in PbTiO\(_3\) thin films as a result of strain relaxation mechanism was known earlier. However, the influence of the substrate on the shape of a-domain has not studied before.

To summarize chapter 4, high-resolution transmission electron microscopy was used to investigate the 90° domain structure in the PbTiO\(_3\) thin films. The films were found to have a predominant fraction of c-domains along with a certain minor volume fraction of a-domains that is clearly higher in case of the DyScO\(_3\) substrates. In PbTiO\(_3\) on SrTiO\(_3\) the a-domains were found to have a wedge shape, whereas in PbTiO\(_3\) on SrRuO\(_3\)/DyScO\(_3\) they have a nearly uniform width. The presence of steps in the domain walls has been observed in the films on both substrates, but the steps are clearly more dominant in the case of SrTiO\(_3\) than of SrRuO\(_3\)/DyScO\(_3\) and are responsible for the observed wedge shape. The observed difference in the films induced by the two substrates is attributed to a higher stiffness of SrTiO\(_3\) than of SrRuO\(_3\)/DyScO\(_3\) as we corroborated with nano-indentation experiments.

Chapter 5 is about the control of domain structures in multiferroic thin films, which is of crucial importance in order to gain access to their functional responses. Here we report on the evolution of the nano-domain structures observed in epitaxial thin films of multiferroic TbMnO\(_3\) grown on SrTiO\(_3\) substrates. Thin films with thickness ranging from 2 to 140 nm were grown at 0.25 and 0.9 mbar oxygen partial pressures.
Transmission electron microscopy was employed to understand the domain evolution. A transition from a fully coherent, highly strained, tetragonal film to a partially coherent, distorted, orthorhombic structure occurs via a transformation twinning mechanism, giving rise to four different domain orientations. At higher thicknesses, a transition to the fully relaxed orthorhombic structure occurs via changes in the domain-substrate orientation relationships leading to only two domain variants. Differences have been observed in the strain relaxation behavior for films grown at different oxygen pressures. These observations improved the understanding of the evolution of the domain structures and to accurately explain the measured orthorhombic distortion. This mechanism can be generalized for (001)-oriented orthorhombic perovskites grown on cubic substrates with significant misfit values.

6.2 OUTLOOK

Today, ferroelectrics, multiferroics and oxide interfaces are among the key areas of research in condensed matter physics. Some of the topics of current scientific interest in the functional oxide materials in thin film form are discussed below.

**Strain Engineering & Interfaces**

The concept of strain engineering is based on utilizing the epitaxial misfit strain of the substrate–film to enhance the functionalities of the thin film. Recent reports show that SrTiO$_3$ and BaTiO$_3$ thin films having a thickness below 50 nm exhibit a huge increase in ferroelectric $T_c$ and remanent polarization. These increases occur through the use of substrate controlled coherent in-plane bi-axial strain. The new Scandate family of oxide substrates such as DyScO$_3$, GdScO$_3$, and (LaAlO$_3$)$_{0.29}$(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.71}$ (LSAT) with varying lattice parameters are used in order to tune the strain to the desired level and correspondingly tune their functionalities. Superlattices / multilayers / heterostructures are the interesting approach to create strained lattices. The properties of these structures can be tailored by stacking different functional materials like antiferromagnetic, ferromagnetic, ferroelectrics and induce the coupling between them at the interfaces.

In these structures, transmission electron microscopy is an essential tool to examine the exact mechanisms occurring at the interfaces. As discussed in the chapter 2 interfaces
play a very crucial role in determining properties. The role of TEM in studying these structures is not only limited to conventional microscopy, but also to understand the stoichiometry, analyzing the electronic structures, intermixing of atoms near the interfaces at nanoscale by analytical tools like Electron Energy Loss Spectroscopy (EELS), energy imaging filtering (Gatan Imaging Filter, GIF), Energy Dispersive Analysis by X-rays (EDAX) because of its high spatial resolution compared to the other techniques. With new technological advancements in the field of TEM, now it is possible to image even lighter elements, and the image resolution approaching 0.1 Å. Oxide interfaces are one of the research fields highly benefiting from the advances in electron microscopy techniques. The best example is the discovery of superconductivity at the interface between two insulating perovskites of LaAlO$_3$ and SrTiO$_3$. Such a localized interfaces can be viewed with the help HR-TEM and their electronic structures can be obtained by high resolution EELS.

It is interesting from a scientific point view to understand the interface between mono-domain PbTiO$_3$ thin films and SrTiO$_3$ substrates. However in chapter 3, figure 3.2, we observed a mixed trend for the formation of $a$-domains in thick films, particularly when films are grown at the rate of 2 to 3 Å/s. The substrate treatment determines the formation of $a$-domains at this growth rate. The results on in-situ heating X-ray diffraction of PbTiO$_3$ thin films described in chapter 3 show a hysteresis behavior for thick films. The exact origin of this behavior, e.g. the formation of misfit dislocations at the interface for strain relaxation and how this relaxation is influenced by the substrate treatment can be studied in more detail for each heating – cooling cycle of the thin films using TEM.

Functionalities at domain walls

Recent results on BiFeO$_3$ multiferroic thin films show that the physical properties at the domain wall are very different than those in the interior of the domains. The conduction has been observed in 109° and 180° domain walls of BiFeO$_3$ thin films [1]. It is observed that the magnitude of the exchange bias scales with the length of 109° domain walls in BiFeO$_3$ thin films [2]. The density of domain walls can be tuned with the thickness of the thin films and also by depositing thin films on substrates with different miscuts. This allows more freedom in tuning the properties of thin films. The idea of
domain wall magnetism, conduction, and presence of other physical entities is just gaining momentum among researchers. In chapter 5, our structural studies on TbMnO$_3$ thin films in combination with the work of Daumont et al [3], where ferromagnetic interaction in thin films of TbMnO$_3$ was observed, suggest that the ferromagnetic behaviour arises from the domain walls. Future work in this direction to prove this ferromagnetic behavior of domain walls in an antiferromagnetic thin film will be of scientific interest. In order to control and tune the domain structures of TbMnO$_3$ thin films, it is worthy and rewarding to investigate these films on different substrates to study their physical responses.

I would like to conclude my thesis by quoting the famous title of Feynman’s lecture i.e., “There is plenty of room at the bottom”. Certainly there is plenty of room at the interfaces of oxides that can be explored with the help of transmission electron microscopy.
References

