Strain and composition effects in epitaxial ferroelectrics

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Summary

A ferroelectric is a material that displays an spontaneous electrical polarization that is switchable. Moreover, all ferroelectric materials are also piezoelectric, which means that they show a (strong) coupling between mechanical stress and polarization. The properties of ferroelectrics are widely used in devices such as capacitors, memory elements, ultrasound generators, accelerometers and sensors, to name some. The growth of thin films of ferroelectric materials on substrates with similar crystal structure opens the possibility to modify (improve) the properties of a ferroelectric by using the epitaxial strain, which is induced by the difference of lattice parameters between the film and the substrate. Theory predicts that the transition temperature between the ferroelectric phase and the nonpolar high-temperature (paraelectric) phase is increased when the magnitude of the strain increases. For this it does not matter whether the strain is compressive or tensile. Epitaxial strain can also stabilize (low symmetry) ferroelectric phases that are not stable in bulk. Phase boundaries between ferroelectric phases with different symmetries are expected to show large piezoelectric and dielectric responses, as observed at the so called "morphotropic phase boundary" of the $PbTi_xZr_{1-x}O_3$ solid solution (PZT), and thus are very interesting for applications. Theory has provided phase diagrams as a function of strain for various ferroelectric materials, in order to help choosing the desired properties. Tuning the properties of materials using the epitaxial misfit strain as adjustable parameter is often called "strain tuning".

The aim of this thesis is to explore the possibilities of strain tuning in ferroelectric thin films. The main idea is to pursue a more precise control of the strain state by combining composition and substrate effects. For this purpose thin films of $Pb_xSr_{1-x}TiO_3$ have been grown both on (001) $SrTiO_3$ and (110) $DyScO_3$ substrates using Molecular Beam Epitaxy (MBE). X-ray diffraction techniques have been used as the main tool to study the ferroelectric properties.

In chapter 2, the MBE growth of $Pb_xSr_{1-x}TiO_3$ thin films is described. There are no previous reports on $Pb_xSr_{1-x}TiO_3$ films grown by MBE. The MBE growth of $PbTiO_3$ has only been reported by few groups. The MBE process can be summarized as a growth process where molecular or atomic beams of the reactants arrive at the heated substrate surface and react to form the desired material. However, the formation of molecular beams, rather than clouds from an evaporation source, sets strict limits on the background pressure in the (vacuum) growth chamber. This vacuum requirement combined with the desire to produce thin films with low oxygen vacancies leads to the use of a stronger oxidizing gas (oxygen plasma). Moreover, incorporation of oxygen is also promoted by using PbO as a lead source rather than metallic lead. The high volatility of both Pb and PbO makes MBE growth of $PbTiO_3$ difficult as it easily re-evaporates from the substrate into vacuum at the used substrate temperatures. This complication is used to our advantage by applying an adsorption controlled growth mechanism, where an large excess of PbO is supplied, but the adsorption is controlled by the presence of Ti, leading to $PbTiO_3$ films with good stoichiometry. The direct control over the molecular beams by shuttering, makes the substitution Sr relatively easy, compared to more common, target based, growth techniques.

In chapter 3 the characterization of ferroelectrics using x-ray diffraction (XRD) techniques is discussed. The basics of XRD and measurement geometries are introduced. XRD is used to probe the crystal structure, and as in ferroelectrics in general and in $PbTiO_3$ specifically, the polarization is strongly coupled to the structure, it is a very suitable technique to probe the ferroelectric properties in thin films, where measuring functional properties can be difficult. The relation between the c/a ratio (tetragonality) and the polarization allows to learn about the ferroelectric properties from purely structural measurements. In combination with temperature dependence, the c/a ratio can give valuable information about both the polarization and the phase transition. Moreover, interference effects at the interfaces of a polar material give rise to subtle changes in the finite thickness fringes around the Bragg peaks of thin films. Careful simulation of these patterns gives information about the orientation of the polarization and the fractions of domains. In addition, if domains are periodic, they can give rise to satellite peaks around certain Bragg peaks, where the spacing of the satellites indicates the periodicity of the domains. Moreover, the directions along which these satellites appear and their presence or absence around certain Bragg peaks tells about the direction of the polarization and the domain walls. Although these effects are well-described in the recent literature, here we illustrate the potential of this methods applied to Pb-containing ferroelectrics, compared to a regular x-ray scatterer such as $BaTiO_3$, to determine the polarization direction, the substrate/film termination or

the presence of dead layers.

The transition temperature, T_C, of $PbTiO_3$ is already relatively high. When it is further increased by compressive strain, the transition temperature becomes higher than the growth temperature and the material grows in the ferroelectric phase. In chapter 4 we show that growing directly in the ferroelectric phase has an important influence on the properties. Only after heating a film to the paraelectric phase, the temperature dependence of the tetragonality becomes reproducible. When Sr substitution is used to decrease T_C below the growth temperature, and thus we grow in the paraelectric phase, the temperature dependence is reproducible. Using Landau-Ginzburg models we show that an increase in depolarization field after visiting the paraelectric phase can explain this behavior. The films grown in the ferroelectric phase show a non-equilibrium domain structure and higher leakage in the as-grown state.

In general, the experimental verification of the theoretical strain-phase diagrams proves difficult due to the limited amount of suitable substrate materials. In chapter 5 we propose to use cation substitution to modify the lattice parameters of the film. This allows continuous tuning of the strain. This concept is applied by growing $Pb_xSr_{1-x}TiO_3$ films on both $SrTiO_3$ and $DyScO_3$ substrates. As cation substitution is expected to have more influence than just changing the lattice parameters, Landau-Ginzburg theory is used to predict the expected phase diagrams. Although compressively strain $Pb_xSr_{1-x}TiO_3$ on $SrTiO_3$ seems not a very exciting system system from the theoretical point of view, the growth of these films shows that the Landau-Ginzburg approach works, as well as the concept of strain and composition tuning. $Pb_xSr_{1-x}TiO_3$ on $DyScO_3$, which is under tensile strain, shows a more interesting phase diagram with phase boundaries and low symmetry phases where high responses are expected. A phase boundary has been observed at the predicted compositions and a novel ferroelectric phase with in-plane polarization is obtained, in agreement with the calculations. However, it has been observed that the thickness of the grown films (20nm) does not allow to fully maintain the strain in the whole composition range and, for the Pb-richer compositions relaxation through domain formation has taken place.

In conclusion, epitaxial strain can be used to modify the properties of ferroelectrics and stabilize new ferroelectric phases. Increasing the transition temperature over the growth temperature leads to non-equilibrium behavior, that has an impact on the properties. Combining strain and composition effects allows continuous tuning through the phase diagram and thus the stabilization of phases that are neither accessible in bulk, nor in films of pure materials.