Synthesis and characterization of (111)-oriented perovskite oxide heterostructures
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Thesis for the Degree of Philosophiae Doctor

Trondheim, January 2019

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Faculty of Information Technology and Electrical Engineering
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Summary

The limits of silicon in semiconductor devices are fast approaching, with feature sizes reaching the realm where quantum effects start to dominate. A promising approach is to include materials with new functionality such as ferromagnetism and ferroelectricity, creating more energy efficient and tailored electronic devices. Perovskite oxides are interesting for this purpose due to their wide range of available functional properties and strong coupling between structure and functionality, opening for property control through depositing these materials as thin films on suitably chosen substrates. Although a significant amount of research has been devoted to exploring this class of materials, the effect of growing on different substrate crystal orientations is not well understood. In this study we focus on films and substrates cut along the pseudocubic (111)-facet. While the more commonly used (001)-orientation has a square symmetry, the (111)-orientation has a hexagonal symmetry. Additionally, employing the (111)-orientation results in altered oxygen octahedra connectivity across interfaces and different geometrical boundary conditions compared to the (001)-orientation. These properties of the (111)-orientation can induce interesting topological properties, novel phases such as polar metals, and enhanced interfacial exchange coupling. In this work, we study how the symmetry, strain, and interface morphology of the pseudocubic (111)-orientation affects the properties of ferromagnetic and ferroelectric perovskite oxides.

Ferromagnetic La$_{0.7}$Sr$_{0.3}$MnO$_3$ and ferroelectric BaTiO$_3$ is chosen as model materials. Thin films are deposited on a variety of single crystal substrates using pulsed laser deposition. Both La$_{0.7}$Sr$_{0.3}$MnO$_3$ and BaTiO$_3$ are grown on SrTiO$_3$, while La$_{0.7}$Sr$_{0.3}$MnO$_3$ is additionally deposited on DyScO$_3$ and NdGaO$_3$ in order to study the effects of (111)-oriented strain on the magnetic properties. To achieve high quality thin film synthesis, control over the substrate surfaces is important. Treatments of SrTiO$_3$, DyScO$_3$, GdScO$_3$, and NdGaO$_3$ substrates are developed and optimized, resulting in atom-
ically flat step-and-terrace surfaces, providing for layer-by-layer growth of perovskite thin films. While the step heights of the SrTiO$_3$ surface correspond to one (111) interplanar distance due its cubic symmetry, the step heights of the orthorhombic substrates, DyScO$_3$, GdScO$_3$, and NdGaO$_3$, can be tailored to be either one or two (111) interplanar distances depending on the specific (111)-orientation used. Analysis of the film growth indicates that the surfaces are reconstructed due to the polar stacking along the [111]-orientation, which can result in an intermixed layer at the substrate and thin film interface.

The application of strain provides an avenue towards control of both structural and functional properties. A range of strain values are applied by employing DyScO$_3$, SrTiO$_3$, and NdGaO$_3$ as substrates for deposition of epitaxial La$_{0.7}$Sr$_{0.3}$MnO$_3$, enabling investigation into (111)-orientated strain. Moreover, the effects of different (111)-oriented in-plane symmetries are studied by exploiting the fact that SrTiO$_3$ possesses a different crystal structure than DyScO$_3$ and NdGaO$_3$. We use various experimental techniques to probe the magnetic properties of the La$_{0.7}$Sr$_{0.3}$MnO$_3$ films and find the respective easy and hard axes through the shape of the hysteresis curves. It is found through reciprocal space maps that La$_{0.7}$Sr$_{0.3}$MnO$_3$ can assume rhombohedral, monoclinic, or triclinic unit cells depending on the applied strain and substrate symmetry. We link the observed anisotropy and structure through theoretical models of magnetic anisotropy.

The step and terrace structure is shown to be important for the magnetic anisotropy of La$_{0.7}$Sr$_{0.3}$MnO$_3$ on SrTiO$_3$, where a uniaxial anisotropy is found at remanence. Through measuring the magnetic properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$, we find the direction of the anisotropy is dependent on the film thickness. The easy axis is aligned perpendicular to the step edges below a critical thickness while in thicker films the easy axis lies parallel to the step edges. The magnetic anisotropy is additionally sensitive to the structural phase transition of the SrTiO$_3$ substrate at 105 K, and a sharp increase of the anisotropy constant in the tetragonal phase is observed. For both the strain and step and terrace induced anisotropies we hypothesize that octahedral rotations along with the crystal structure are necessary to explain the results. By creating theoretical phase diagrams of the magnetic anisotropy as a function of octahedral tilt, it is shown that induced octahedral rotations can explain the observed results, indicating that the octahedral response to (111)-orientated strain and morphology is different from films in the (001)-orientation.

The growth of (111)-oriented BaTiO$_3$ is found to be dominated by defect
Films of 10 nm and thicker are completely relaxed in-plane, with indications of higher defect density with increasing film thickness. Signs of ferroelectricity are observed in films of thickness down to 5 nm. As in La$_{0.7}$Sr$_{0.3}$MnO$_3$, the properties of BaTiO$_3$ are found to be sensitive to the structural phase transition of the SrTiO$_3$ substrate, with a marked change in the measured pyroelectric current at 105 K.

Through material synthesis, experimental characterization, and theoretical models, we have gained further insight into (111)-orientated perovskite material systems. We are successful in preparing high quality (111)-oriented substrates facilitating the deposition of thin films. The crystal structure and magnetic anisotropy of the films are found to be highly susceptible to (111)-oriented strain, substrate symmetry, and interface morphology. Lastly, we explore the growth and properties of (111)-oriented BaTiO$_3$. The presented results demonstrate that utilization of the (111)-orientation is an interesting avenue in the development of functional material systems for use in future electronic devices.
Summary
Sammendrag (summary in Norwegian)

Grensene for silisium nærmer seg i høytt tempo, med komponentdimensjoner som når en størrelsesorden der kvanteeffekter dominerer. En lovende tilnærming er å inkludere materialer med ny funksjonalitet som ferromagnetisme og ferroelektrisitet og på den måten skape mer energieffektive og skreddersydde elektroniske komponenter. Perovskittoksider er interresante for dette formålet fordi de kan inneha både en stor rekke funksjonelle egenskaper og en sterk kopling mellom struktur og funksjonalitet, som åpner for kontroll av egenskaper gjennom deponering av disse materialene som tynne filmer på utvalgte substrat. I denne studien fokuserer vi på filmer og substrat med pseudokubiske (111)-orienterte overflater. Mens den mer brukte (001)-orienteringen har en kvadratisk symmetri så har (111)-orienteringen en heksagonal symmetri. I tillegg så vil bruk av (111)-orienteringen gi forskjellig kopling av oksygenoktahedraene på tvers av grensesjikt og annerledes geometriske grensebetingelser sammenliknet med (001)-orienteringen. Disse egenskapene ved (111)-orienteringen kan inducere interresante topologiske egenskaper og nye faser som polare metaller. I dette arbeidet studerer vi hvordan symmetri, deformasjon og grensesjikt morfologi påvirker de ferroelektriske og ferromagnetiske egenskapene til oksider.

Ferromagnetisk La$_{0.7}$Sr$_{0.3}$MnO$_3$ og ferroelektrisk BaTiO$_3$ er valgt som modellsystem. Tynne filmer er deponert på forskjellige enkrystallsubstrat ved hjelp av pulset laserdeponering. Både La$_{0.7}$Sr$_{0.3}$MnO$_3$ og BaTiO$_3$ er deponert på SrTiO$_3$, mens La$_{0.7}$Sr$_{0.3}$MnO$_3$ er i tillegg deponert på DyScO$_3$ og NdGaO$_3$ for å undersøke effekten av (111)-orientert deponering på de magnetiske egenskapene. Kontroll av substratoverflatene er viktig for å oppnå tynnfilmsyntese av høy kvalitet. Behandlingsprosedyrer av SrTiO$_3$, DyScO$_3$, GdScO$_4$ og NdGaO$_3$ er utviklet og optimert, som resulterer i
Sammendrag (summary in Norwegian)

atomisk flatte ste og terrasse-overflater. Dette muliggjør lag-for-lag-vekst av perovskitt-tynnfilmer. Mens steghøydene til SrTiO₃ korresponderer med avstanden mellom to (111)-plan på grunn av SrTiO₃ sin kubiske symmetri, så kan steghøyden til de ortorhombiske substratene, DyScO₃, GdScO₃ og NdGaO₃, bli skreddersydd til å tilsvarer høyden til enten ett eller to (111)-plan, avhengig av den spesifikk (111)-orienteringen brukt. Analyse av filmvekst indikerer at overflatene er rekonstruert på grunn av den polare stablingen av atomlagene langs [111]-retningen, som kan resultere i et blandet lag i grensesjiktet mellom substrat og tynnfilm.

Deformasjon av tynnfilm gir en metode for kontroll av både strukturelle og funksjonelle egenskaper. Ved bruk av SrTiO₃-, DyScO₃- og NdGaO₃-substrat er et utvalg av grader av deformasjon påført La₀.₇Sr₀.₃MnO₃ som muliggjør en studie av (111)-orientert deformasjon. I tillegg er effekten av (111)-symmetri undersøkt ved å utnytte at SrTiO₃ har en annen symmetri enn DyScO₃ og NdGaO₃. Vi bruker forskjellige eksperimentelle teknikker til å undersøke de magnetiske egenskapene til La₀.₇Sr₀.₃MnO₃-filmene og å finne de respektive lette og vanskelige aksene gjennom å vurdere formen på hysteresene. Gjennom reciproker rom-kart er det funnet at La₀.₇Sr₀.₃MnO₃ kan inneha forskjellige krystallsymmetrier som er sterkt koplet til den magnetiske anisotropien.

Steg-og-terrasse-strukturen er vist å være viktig for den magnetiske anisotropien til La₀.₇Sr₀.₃MnO₃ på SrTiO₃ hvor en uniaksiell anisotropi er funnet ved remanent felt. Gjennom å måle den magnetiske anisotropien til La₀.₇Sr₀.₃MnO₃ og å bruke teoretiske magnetiske modeller finner vi at anisotroplaget til den er avhengig av filmtykkelsen. Den lette aksen ligger perpendikulært til stegkantene under en kritisk tykkelse og parallel med stegkantene over den kritiske tykkelsen. Ved den strukturelle faseovergangen til SrTiO₃ ved 105 K introduseres en deformasjon i La₀.₇Sr₀.₃MnO₃ som fører til at anisotropikonstanten stiger kraftig. For både anisotropien indusert av deformasjon og anisotropien indusert av ste og terrasse oksideres en hypotese basert på oktahederrotasjoner og krystallstruktur som indikerer at oktahedrerrotasjoner til (111)-orientert deformasjon er forskjellig fra oktahedrerrotasjoner til (001)-orientert deformasjon.

Vekst av (111)-orientert BaTiO₃ er funnet å være dominer av formasjoner av defekter. Filmer 10 nm tykke og tykkere er fullstendig relakserte i planet med indikasjoner på økende defektetetthet med økende tykkelse. Tegn til ferroelektrisitet er observert i filmer med tykkelse ned til 5 nm.

Gjennom materialsyntese, eksperimentell karakterisering og teoretiske mod-
eller har vi fått større innsikt inn i (111)-orienterte perovskittmaterialesystemer. Vi forbereder substrat med høy kvalitet som muliggjør syntese av tynne filer. Krystallstrukturen og den magnetiske anisotropien til filmene er observert til å være sensitive til (111)-orientert deformasjon, substratsymmetri og grensesjiktmorfologi. Til sist utforsker vi veksten og egenskapene til (111)-orientert BaTiO$_3$. De presenterte resultatene demonstrerer at bruk av (111)-orienteringen er en interessant vei mot utvikling av nye funksjonelle materialsystem for bruk i fremtidige elektroniske komponenter.
Preface

This dissertation is submitted in partial fulfillment of the requirements for the degree of Philosophiae Doctor (PhD) at the Norwegian University of Science and Technology (NTNU). The work was mainly carried out at the Department of Electronic Systems (IES) with Professor Thomas Tybell as main supervisor. Professor Jostein Grepstad and Associate Professor Erik Folven have been co-supervisors.

Acknowledgements

First, I would like to thank my main thesis advisor, Thomas Tybell. For always seeing an opportunity in every experimental result and inspiring me with his passions for material physics and oxide electronics. Your boundless energy never ceases to amaze me. I especially appreciate your always open door and invaluable feedback on my article manuscripts.

Furthermore, numberless scientific problems have been solved with the help and support of other people the Oxide Electronics Group at IES: Ingrid Hallsteinsen, Magnus Moreau, Kristoffer Kjærnes, Ambjørn Dahl-Bang, Fredrik Kjemperud Olsen, Sam Sløetjes, Einar Digernes, Runar Dahl-Hansen, Erik Folven, and Jostein Grepstad. In particular, a large thank go to Ingrid and Erik for always knowing the solution to practical problems at the PLD-lab and always being ready to help take it apart and screw it together again afterwards. In that regard, Tore Landsem, Sverre Vegard Pettersen, Gaurav Sharma, and Tron Arne Nilsen is greatly acknowledged for all the help with practical issues related to the lab equipment. Magnus, thanks for taking the time to answer all my questions about octahedral rotations and sharing your theoretical knowledge. And to the rest of the group, thanks for the monday meetings, discussions, lunches, and lønnøl. With regards to the lunches and lønnøl I also have to thank my other colleagues: Hans Olaf

I would like to thank the collaborators I have had during my PhD. I have had three master students and one project student: Kristoffer Skogen Raa, Kristoffer Kjærnes, Einar Digernes, and Zuzana Čiperová who have all in different ways contributed to the my scientific work. Ryota Takahashi and Mikk Lippmaa have been tremendously helpful at the University of Tokyo with pyroelectric measurements. Elke Arenholz who at the Advanced Light Source have facilitated magnetic characterization of my samples with Ingrid Hallsteinsen. The work done by Erik Lysne and Ulf Österberg by setting up the MOKE equipment, enabling easy characterization of the magnetic anisotropy, was very valuable. Lastly, a thanks to Ingeborg-Helene Svenum for doing XPS characterization on my samples.

Finally, a big thanks is directed towards my family. For always being there with help, advice, and dinner I did not have much time to make myself. A special thanks goes to my girlfriend, Eline Hansen Næset, thank you for being there for me and being patient as I have slipped gradually into a PhD-induced coma the last year.

With regards to funding, I would like to acknowledge the Research Council of Norway for funding my PhD-position through Grant No. 231290. The lab work performed at the University of Tokyo was in part supported by the Norwegian PhD Network on Nanotechnology for Microsystems, which is sponsored by the Research Council of Norway, Division for Science, under contract no. 221860/F60. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Torstein Bolstad
Trondheim, Norway
July 2018
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Part I

Background
Chapter 1

Introduction

Ever since the invention of the semiconductor transistor in 1947 by Bardeen, Brattain, and Shockley [1, 2] and the integrated circuit in 1958 by Kilby [3] there has been a race to continually increase performance. This development was observed by Gordon Moore, who in 1965 coined what has been known as Moore’s law, that the number of transistors per unit area would double every two years [4, 5]. Meanwhile, Intel executive David House predicted that the performance would double every 18 months [6]. This would be accomplished through both increases in transistor speed and density, in addition to important advances in processor design and material technology. Important to this progress was the simultaneous development of fabrication techniques, enabling the study and utilization of materials in the nanometer range [7]. This law became a self-fulfilling prophecy, with Moore’s prediction proving accurate until recently by the efforts of the semiconductor industry. The industry’s long term planning has been guided by the desire to match Moore’s law, largely through the International Technology Roadmap for Semiconductors (ITRS) where the challenges and opportunities of semiconductor innovation have been laid out [7]. However, 2016 marked the year with the last roadmap, alongside the acknowledgement that the sun was setting on Moore’s law [8]. The size of the transistors has reached a fundamental limit, the quantum regime, where controlling the current flow becomes more difficult. Even without the size of atoms as a limit, the industry is fast approaching the limits of economics. Rock’s law, named after Arthur Rock, predicts the price of a semiconductor chip fabrication plan doubles every four years [9]. This increase has largely been offset by the economics of scale and other cost saving measures, thereby continuously lowering the
price per transistor. However, for gate sizes below 28 nm, the price per gate has increased, with the price per hundred million transistors being $1.30 and $1.58 for 28 nm technology and 7 nm technology, respectively [10]. Thus, a new approach incorporating new physics and functionality is needed, both due to physical and economic limits.

A promising avenue towards novel electronic devices is through the concept often referred to as "more than Moore"; the inclusion of functional properties in semiconductor devices, such as ferromagnetism, antiferromagnetism, and ferroelectricity among others. An interesting field is that of spintronics, where both the electron spin and charge are utilized [11]. Spintronics and magnetism in electronics have been the focus of extensive research, with the most significant application being the use of spin valves in magnetic hard drives. In spin valves, two metallic ferromagnetic layers are separated by a nonmagnetic material. In these structures, the magnetic anisotropy and switching characteristics of the ferromagnetic layers are important. The magnetic anisotropy is the directional dependence of the magnetic properties of a material. The magnetic spins can have a preferential orientation, a direction or plane where the material is easier to magnetize, called the easy axis or easy plane, respectively. Conversely, there can be a direction or plane where it is energetically unfavorable for the spins to orient along, called the hard axis or hard plane, respectively. Materials can exhibit anisotropy with regards to other properties, for example the electrical resistance can be higher or lower along certain directions.

This spin valve is the basis of the magnetic tunnel junction (MTJ), which is the building blocks of magnetic random access memory (MRAM). MRAM promises the speed and density comparable to dynamic random access memory (DRAM) in addition to non-volatility and low energy consumption [12]. In spite of this, MRAM has so far only been used in niche products, due to high prices and low density compared to DRAM. Many issues have been related to how information is written, namely how the ferromagnetic materials are switched. In the first commercially available MRAM devices, a current was sent through a wire inducing a field switching one of the ferromagnetic layers. However, due to the extent of the magnetic field, this method puts strict limits on the size of each memory cell in order to avoid writing adjacent cells, making it almost impossible to scale below 100 nm technology [13]. In more recent devices, switching occurs through spin transfer torque (STT) where a polarized spin current running through the ferromagnet can switch the magnetization [13, 14]. Though first introduced in the 70s and 80s [15, 16], STT has first recently been used in devices due to improvements
in fabrication techniques and material science [14], facilitating local switching of magnetic layers. Nonetheless, there are still issues; for example, joule heating from the SST current is a major limiting factor in MRAM performance. The magnetic anisotropy is also important for novel devices based on domain walls, such as the racetrack memory concept proposed by IBM [17, 18]. In racetrack memory, also called domain-wall memory, information is stored in small magnetic domains in nanowires which are moved along the wire by spin-polarized currents over a read/write section, thus enabling high memory density.

Alternatively, an approach based on ferroelectrics, where the direction of polarization is the information carrier, have been studied since the first proposal of ferroelectric materials in memory (FeRAM) in 1952 [19]. The inclusion of ferroelectrics is from a device design perspective initially easier compared to MRAM, as a possible FeRAM design involves replacing the dielectric in a DRAM cell with a ferroelectric layer. Another simple memory concept is the ferroelectric field effect transistor (FeFET), a single transistor memory device where the gate dielectric is a ferroelectric material, resulting in the current through the transistor being dependent on the ferroelectric polarization. However, as MRAM, FeRAM has until now primarily been used in niche products despite its potential, due to a low memory density and high price. Moreover, the ferroelectric thin films have issues concerning imprint (shift of the polarization curve) and fatigue (loss of polarization) [20]. Thus, a stronger insight into the nature of ferroelectric materials is needed.

In addition to memory applications, ferroelectric materials are important in devices such as capacitors, actuators, and MEMS devices due to the presence of large dielectric constants, piezoelectricity, pyroelectricity, and high non-linear optical activity [21, 22, 23, 24]. One of the most widely used and studied ferroelectric materials is lead zirconate titanate (PZT) [25]. However, as PZT contains lead, the use of PZT is associated with the toxicity concerns as other lead-based compounds, which has led to efforts to create lead free ferroelectrics with comparable properties.

An attractive feature of magnetic and ferroelectric memory is the non-volatility, i.e. the information in the form of magnetization or polarization persists in the absence of external stimuli. While the capacitor in conventional RAM needs to be recharged, the non-volatile RAM retains its polarization, thereby offering a vista to electronics with lower power consumption. In 2012, the energy consumption by consumer devices, communication networks, and data centers was 4.7 % of global energy usage [26]. As a worst
case scenario, the energy consumption can account for as much as 51% by 2030 [27]. In servers, the power consumed by memory accounts for 20% of energy usage, making the development of low power memory important.

With regards to the incorporation of functional materials in electronics, the class of materials known as perovskite oxides is interesting due to a wide range of functional properties and a strong structure-property coupling [28], facilitating the design of new device concepts. In addition to ferromagnetism, oxides can exhibit properties such as ferroelectricity, superconductivity, antiferromagnetism and colossal magnetoresistance. To facilitate the inclusion of this class of materials in electronics, an oxide electronics roadmap was created in 2016 [29]. It outlines the challenges associated with developing oxide electronic devices that can compliment traditional silicon devices. One of the possibilities and avenues of progress discussed is the use of different crystal facets and symmetries, such as the (111)-orientation, as a means to control functionality and induce novel functional properties. (In this work all crystal plane and direction notation refer to the pseudo-cubic symmetry if not stated otherwise with subscript.) The (111)-orientation is interesting as it has a hexagonal in-plane symmetry, opposed to the cubic symmetry of the most commonly used orientation in perovskite oxides, the (001)-orientation. In a Nature Materials commentary [30] geometric engineering through employing the (111)-orientation was identified as one of the most promising opportunities towards further development of the field of oxide electronics. However, synthesis of (111)-oriented films also presents considerable material challenges.

The aim of this work is to investigate how symmetry and geometric engineering affects the structural and functional properties of thin films. Specifically, we focus on how the symmetry, strain, and morphology of the (111)-orientation influence thin films of ferromagnetic and ferroelectric oxide perovskites. To enable the growth of high quality thin films, methods of substrate preparation and interface control for a range of different substrates need to be established. This is the first challenge addressed here. We chose ferromagnetic La$_{0.7}$Sr$_{0.3}$MnO$_3$ and ferroelectric BaTiO$_3$ as our model materials to be grown in the (111)-orientation. Both are materials that have been widely studied in the (001)-orientation, which facilitates comparisons. The magnetic properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ is known to be highly susceptible to strain, lattice distortions and octahedral rotations, which we use to control the magnetic anisotropy. Finally, the growth and properties of BaTiO$_3$ on (111)-oriented SrTiO$_3$ is investigated.

The thesis is structured as follows: Part I introduces background know-
ledge related to the thesis work and includes two chapters in addition to the current chapter. Chapter 2 serves as an introduction to the physics of perovskite oxides, existing knowledge, and recent development within the field. The material system is described in Chapter 3 along with the experimental techniques and theoretical framework used. Part 2 presents the results in the form of five papers. Finally, the conclusions and outlook are given in part 3.
Introduction
Chapter 2

Perovskite oxides

Perovskite oxides exhibit a wide range of functional properties which are strongly coupled to the structural properties. This strong coupling enables control through thin film synthesis and substrate engineering. This chapter offers a basic introduction to the structure and physics of perovskite oxides with a particular focus on the model thin film materials, La$_{0.7}$Sr$_{0.3}$MnO$_3$ and BaTiO$_3$. In addition, other intriguing material systems will be presented to highlight challenges and opportunities.

2.1 Atomic structure

Perovskite oxides have the general chemical formula ABO$_3$, where A is a transition metal cation and B is a transition or rare earth metal cation. The prototypical perovskite structure is shown in figure 2.1, a cubic unit cell with space group Pm-3m. The A ions are located at the corner sites, while B ions are located at the center of the unit cell, surrounded by six oxygen anions forming an octahedra. The octahedra are coupled to adjacent unit cells through the corners. In order to achieve charge neutrality, the sum of the cation charge needs to be +4 as the oxygen ions each have a charge of -2. The wide range of transition metals available and the ability to assume several oxidation states result in a broad spectrum of different perovskite compounds [31].

The unit cell of perovskite materials commonly deviates from the cubic structure, often due to geometric constraints from the differing radii of the A and B ions. This is expressed in the Goldschmidt tolerance factor [33]:
where \( r_A, r_B, \) and \( r_O \) are the radii of the A cation, B cation and oxygen anion, respectively. A tolerance factor of one results in a cubic unit cell (figure 2.2 (a)), while a deviation from one can result in a tetragonal, rhombohedral, hexagonal, orthorhombic, monoclinic, or triclinic unit cell. \( t > 1 \) usually leads to a movement of the center cation, creating a polar displacement (figure 2.2 (b)). On the other hand, \( t < 1 \) commonly results in rotations of the oxygen octahedra (figure 2.2 (c)).
2.1. Atomic structure

symmetry along with a displacement of the oxygen octahedra in the opposite direction, visualized in figure 2.2 (b), resulting in a dipolar moment in the direction of displacement.

As many interesting properties in perovskites, such as magnetism, are dependent on interactions between the B cations and the connecting oxygen, the tilt of the oxygen octahedra is important. A change in the octahedral rotations will alter both the B-O bond length and the B-O-B bond angle, potentially altering the functional properties [31]. Rotations are commonly categorized using the Glazer system [34], in which the rotations are characterized by the degree of rotation around each of the pseudo-cubic axes and whether the rotations are in-phase or out-of-phase. Moving along a direction of connected octahedra, the rotations around that direction can all rotate towards the same direction. This is called in-phase rotation. Conversely, for out-of-phase rotations, the octahedra rotate towards alternating directions. Glazer notation is written as \( a^\# b^\# c^\# \), where \( a, b, \) and \( c \) describe the degree of rotation around each of the axes, and the superscript, \( \# \), can either be +, -, or 0. + symbolizes an in-phase rotation along that pseudo-cubic direction, - symbolizes and out-of-phase rotation, and a lack of rotations are symbolized by 0.

2.1.1 Orbital structure

Important to the characteristics of perovskite oxides are the electrons located in the \( d \)-orbitals of the ions on the B-site [31]. There are five different \( d \)-orbitals, giving five energy levels \( d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, \) and \( d_{z^2} \), which in an isolated atom are degenerate. However, due to the perovskite crystal field, the energy levels of the orbitals split into two states, \( e_g \) and \( t_{2g} \) [35]. By engineering the surrounding crystal field, for example with applied strain, the degeneracies of the \( e_g \) and \( t_{2g} \) states can be lifted. Strain can bring the orbitals either closer together or further apart, thus raising or lowering the energy of the orbital, respectively. The exact splitting depends on the plane of applied strain [35]. The evolution of the energy levels moving from an isolated atom to a perovskite structure strain applied in the (001)- and (111)-plane can be seen in figure 2.3. Under (001)-oriented strain, the \( e_g \) states are split into two energy levels, while the same states remain degenerate under (111)-oriented strain. The difference between compressive and tensile strain is observed in the splitting of the \( t_{2g} \) state. The \( e'_g (d_{xy}) \) and \( a_{1g} (d_{xz} + d_{yz}) \) states switch relative positions depending on if compressive or tensile (111)-oriented ((001)-oriented) strain is applied.

Engineering of the orbital energy levels have been used to change the mag-
Figure 2.3: An illustration of the splitting of the d-orbital energy levels when subjected to a crystal field and (001)- and (111)-oriented strain. The figure is generated with VESTA [32].

2.2 Thin film engineering by substrate control

The strong coupling between structure and functionality in perovskite oxides opens the possibility of tuning existing properties and creating novel properties through structure manipulation [28]. A powerful and much employed method of property control and engineering is through deposition of thin films on a substrate. The choice of substrate can, through for example strain, interfacial coupling, and morphology, greatly influence the properties of the film [42]. Commonly used substrates are presented in figure 2.4 along with their pseudocubic lattice constants.

A film grown on a substrate with differing lattice spacing from the film material will experience strain from the underlying substrate. If the films are epitaxially strained, the film in-plane lattice spacing will be equal to that of the substrate, while the out-of-plane lattice spacing will be allowed to relax according to Poisson’s ratio [42]. In the case of a substrate with a lattice constant larger than the bulk values of the deposited material, the...
2.2. Thin film engineering by substrate control

Figure 2.4: The pseudocubic lattice parameters in Å of common perovskite substrates (blue) and the thin film material systems used in this work (orange). LSAT corresponds to (LaAlO$_3$)$_{0.3}$-(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.7}$ and LSMO corresponds to La$_{0.7}$Sr$_{0.3}$MnO$_3$. The values of the pseudocubic lattice parameters are taken from [42, 39].

film will be tensile strained. Conversely, if the substrate lattice spacing is smaller, the film will be compressively strained.

Epitaxial perovskite thin films accommodate the strain through several mechanisms: changes in bond length and angle, polar distortions, octahedral rotations, and the introduction of defects [43]. Mechanisms which in turn will be discussed in the following subsections. Typically, the relation between these mechanisms and the strain state are reciprocal, i.e. the presence of these structural distortions will also affect the strain state.

2.2.1 Bond elongation

As previously stated, the out-of-plane lattice parameter is distorted according to Poisson’s ratio. Poisson’s ratio is usually positive, meaning that a compression (expansion) in-plane leads to an expansion (compression) out-of-plane. The degree of out-of-plane distortion is affected by the thickness of the film. In the case of (001)-oriented La$_{0.7}$Sr$_{0.3}$MnO$_3$ on SrTiO$_3$, four deformation regimes have been identified, dependent on the film thickness, d: a ratio close to zero for the thinnest films ($d < 2.5$ nm), a ratio increasing with thickness for $2.5$ nm $< d < 10$ nm, a plateau with a relatively constant ratio for films of thickness between 10 nm and 25 nm, and a decreasing Poisson’s ratio for thicker films [44]. The magnetic properties are also observed to be affected by the thickness with decreasing Curie temperature and saturation moment with decreasing thickness. In SrRuO$_3$ films the Curie temperature and magnetization is found to increase for films epitaxially grown on (001)-oriented SrTiO$_3$ compared to bulk, due to the strain imposed on the film by the substrate [45].

In thin films, substrate phase transitions can be taken advantage of to induce marked changes in the film properties. For example, the magnetization and
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Resistivity of epitaxial SrRuO$_3$ on BaTiO$_3$ changes sharply, due to the abrupt change in strain, when the substrate undergoes first order phase transitions [46]. Strain can additionally affect the structural phase transitions of the film. While bulk SrRuO$_3$ have three phase transitions, strained SrRuO$_3$ on (001)-oriented SrTiO$_3$ has only one: from orthorhombic at low temperatures to strained cubic at 553 K [47].

The most commonly studied substrate is SrTiO$_3$ due to its cubic symmetry. However, there are several other substrates employed, such as the scandate (ASC$_3$O$_3$) and galate (AGaO$_3$) families of materials. They have a wide range of lattice parameters (figure 2.4), enabling tuning of film unit cell symmetry and properties. The multiferroic material BiFeO$_3$ can be caused to take on a tetragonal, monoclinic, rhombohedral, or orthorhombic unit cell, depending on substrate lattice parameters and symmetry [48]. As observed in thin films of La$_{0.67}$Sr$_{0.33}$MnO$_3$ and SrRuO$_3$, multiple unit cell parameters can change simultaneously to accommodate the strain: The evolution of the lattice parameters, monoclinic distortion, orthorhombicity, and unit cell volume of (001)-oriented epitaxial La$_{0.67}$Sr$_{0.33}$MnO$_3$ and SrRuO$_3$ thin films as a function of strain is shown in figure 2.5 [49].

For La$_{0.7}$Sr$_{0.3}$MnO$_3$, the Curie temperature is distinctly affected by a change of strain, with a difference of ~100 K between films deposited on (LaAlO$_3$)$_{0.3}$-(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.7}$ and NdScO$_3$. The change is partly ascribed to changing crystal field splitting. As the scandates and galates are orthorhombic, the strain applied to the film is biaxial which can lead to increased Jahn-Teller distortions [155, 161], thereby lowering the Curie temperature [39]. In La$_{0.7}$Sr$_{0.3}$MnO$_3$ film orthorhombic substrates has been used to control of the anisotropy direction, with the easy axis generally aligning along the least strained direction [50, 51, 52].

### 2.2.2 Polar distortions

Strain relief through polar distortions is relevant for the manipulation of ferroelectric properties. For (001)-oriented films, out-of-plane displacement of the ion on the B site will be enhanced under compressive strain, while in-plane displacement will be enhanced under tensile strain. This was first shown theoretically by Pertsev et al. [53]. The effects of the increased displacement has been measured experimentally for (001)-oriented BaTiO$_3$ through an enhancement of the ferroelectric polarization [54, 55]. At -1.7% strain, the remanent polarization increased 250% and the ferroelectric transition temperature was found 500 °C higher as compared to bulk [56]. For BTO thin films it is predicted from first principles calculations that the
2.2. Thin film engineering by substrate control

Figure 2.5: The evolution of some of the structural parameters of La$_{0.67}$Sr$_{0.33}$MnO$_3$ (red) and SrRuO$_3$ (blue) as a function of strain: (a) The free unit cell parameters, $a$ and $b$, and the angle $\gamma$ between them, (b) the orthorhombicity ($a/b$), and (c) the unit cell volume. Figure adapted from [49].

A depolarization field in the thin film will destabilize the ferroelectric state [57]. Theoretically, it has been found that thin films as thin as seven unit cells can exhibit a polarized ground state [58], matching experimental results [59].

SrTiO$_3$ is in bulk an incipient ferroelectric, which entails that it approaches a ferroelectric transition at low temperatures, though never transitions due to quantum fluctuations [60]. However, through epitaxial strain, a ferroelectric phase can be induced with the polarization out-of-plane for compressive strain and in-plane for tensile strain [61, 62]. In EuTiO$_3$, a phase of simultaneous ferroelectricity and ferromagnetism was induced through tensile strain [63], showing that strain as a tuning parameter can be important in...
the realization of multiferroics. Similarly, in SrMnO$_3$, first principles calculations have predicted that a polar mode can be induced through strain, thereby producing a multiferroic state [64].

2.2.3 Octahedral rotations

As stated earlier, the tilt of the oxygen octahedra is important for many functional properties in perovskites. As octahedral rotations change the overlap between the B cation $e_g$ and $t_{2g}$ states and O 2$p$ states, the degree of rotation can affect both the transport and magnetic properties [65]. Suppression of the octahedral rotations near the La$_{0.7}$Sr$_{0.3}$MnO$_3$ / SrTiO$_3$ interface has been observed to coincide with a magnetic deterioration in the same region, linked to the magnetic "dead-layer" observed in La$_{0.7}$Sr$_{0.3}$MnO$_3$ / SrTiO$_3$ interfaces [66]. The octahedral tilt is also interesting for ferroelectric functionality as it has been shown that octahedral rotations can induce improper ferroelectricity in materials which are not ferroelectric in bulk [67, 68].

An relevant method of octahedral manipulation is through applying strain. For (001)-oriented films compressive strain increases the octahedral rotations around the out-of-plane axis, while in the tensile regime the rotations around the in-plane axes increase. This has been seen experimentally in LaNiO$_3$ and LaAlO$_3$ systems [70, 71]. Manipulation of the octahedral rotations through strain have been linked to the direction of uniaxial anisotropy of La$_{0.7}$Sr$_{0.3}$MnO$_3$ on (LaAlO$_3$)$_{0.3}$-(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.7}$. Similar results have been reported in EuTiO$_3$ by first principles calculations, where the magnetic anisotropy is strongly correlated to the octahedral tilt and ferroelectric polarization [72]. In SrRuO$_3$ the effects of strain on octahedral rotations results in an out-of-plane anisotropy for compressive strain and an in-plane anisotropy for tensile strain [73].

The effects of the strain on octahedral rotations can be modulated through interface engineering. In the case of ultrathin films of La$_{0.66}$Sr$_{0.33}$MnO$_3$ on NdGaO$_3$, the direction of the uniaxial anisotropy is changed by the insertion of a SrTiO$_3$ layer between the substrate and the film. This suppresses the octahedral rotation in the film (figure 2.6) [69]. Another route to octahedral control is through superlattices. In La$_{0.7}$Sr$_{0.3}$MnO$_3$/Eu$_{0.7}$Sr$_{0.3}$MnO$_3$ the ferromagnetism and electric bandwidth is spatially modulated through modulations of octahedral rotations, commensurate with the super lattice period [74].

A constraint in strain engineering is that the limited number of available
2.2. Thin film engineering by substrate control

Figure 2.6: Inversed annular bright-field scanning tunneling electron microscopy images of La$_{0.7}$Sr$_{0.3}$MnO$_3$ on NdGaO$_3$ substrates. From left to right: La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) on NdGaO$_3$ (NGO), La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) on NdGaO$_3$ (NGO) with a 9 unit cell spacer buffer layer of SrTiO$_3$, La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) on NdGaO$_3$ (NGO) with a 1 unit cell spacer buffer layer of SrTiO$_3$. The red dots and yellow lines indicate the oxygen positions and oxygen octahedra, respectively. Underneath the respective magnetic hysteresis curves along the in-plane a and b directions are shown. Figure adapted from [69].

substrates results in discrete values of imposed strain, removing the possibility of continuous tuning of the functional properties. To overcome this limit, a possible route is He implantation. Through He implantation, the structure of SrRuO$_3$ on SrTiO$_3$ changes from orthorhombic to tetragonal accompanied by an increased out-of-plane strain and a shift the oxygen octahedral rotation pattern [75]. Another proposed route is through using a buffer layer. By depositing a Ba$_{1-x}$Sr$_x$MnO$_3$ / BaTiO$_3$ buffer bilayer on SrTiO$_3$ followed by high temperature annealing, a cubic defect free surface
can be created with a tunable in-plane lattice constant in the range 3.905 Å to 4.02 Å controlled by the Ba / Sr ratio [76].

2.2.4 Defects

As seen in the last section, with implantation of He, defects affect the strain state. However, applying strain can also introduce defects. Oxygen vacancies are expected to be introduced through tensile strain, while compressive strain favours cation vacancies. This has been shown by density functional theory calculation [77, 78] and later confirmed experimentally for oxygen vacancies under tensile strain [79]. The vacancies are found to order spatially depending on the amount of strain, which can manifest in anisotropy of functional properties. Oxygen vacancies have been seen to order in the brownmillerite structure in (001)-oriented La$_{0.7}$Sr$_{0.3}$MnO$_3$ on SrTiO$_3$ [80, 81, 82]. Tuning of the vacancy ordering in La$_{0.7}$Sr$_{0.3}$MnO$_3$ allows for the creation and control of the coupling of magnetic substructures [83] and the switching between resistance states [84]. In PbTiO$_3$, a combination of strain and polarization near the interface to SrTiO$_3$ is hypothesized to generate cation defects as a mechanism to screen strain, explaining the preference for downward polarization of as-grown PbTiO$_3$ films [85].

Lastly, multiple strain relief mechanisms can appear simultaneously. Ferroelectricity is induced by applied strain in SrMnO$_3$ along with an increase in the oxygen vacancy concentration. The ferroelectric domain walls couple with the vacancies, establishing a barrier to electron migration resulting in polar, conducting domains limited by insulating domain walls [86].

2.2.5 Surface morphology

In addition to strain, the choice of substrate morphology can affect the film structure and properties. Vicinal surfaces, i.e. surfaces cut at an slight angle relative to a low-index plane resulting in step and terrace surfaces, are important for thin film growth as they facilitate step flow growth [87]. Moreover, the steps can play a key role determining the structural domain formation during synthesis. Due to the rhombohedral structure of La$_{0.7}$Sr$_{0.3}$MnO$_3$, the unit cell can align four different ways on SrTiO$_3$. On exact substrates, all four variants are observed, while depositing on a stepped surface results in a two-variant film [88]. A vicinal interface between SrTiO$_3$ and La$_{0.7}$Sr$_{0.3}$MnO$_3$ is seen to induce a uniaxial magnetic anisotropy, the strength of which increases with the step density, i.e. the miscut angle [89]. The strength relative to the magnetocrystalline biaxial anisotropy, is seen to decrease with increasing thickness and decreasing temperature.
As the magnitude of the anisotropy constant is thickness dependent, it is suggested to be an interface effect, such as shape anisotropy or an anisotropy arising from a uniaxial roughening of the terraces [92, 93].

Vicinal SrTiO$_3$ is also used to engineer the structural domains of BiFeO$_3$, where, as La$_{0.7}$Sr$_{0.3}$MnO$_3$, four different ways of orienting the unit cell are possible. Through the degree of miscut angle chosen, BiFeO$_3$ can be synthesised as one-variant, two-variant, or four-variant [94]. Through domain engineering of BiFeO$_3$, the ferroelectric properties can be enhanced with lower leakage currents [95], and nucleation sites can be created at the step edges, thus lowering the coercive field [96]. The structural properties of Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ grown on MgO is likewise affected by the step and terrace structure, resulting in structural antiphase boundaries [97]. In the double perovskite LaBaCo$_2$O$_{5.5+\delta}$ grown on SrTiO$_3$, anisotropy is induced in the transport properties due to the vicinal interface [98]. This is also observed in La$_{1-x}$Ca$_x$MnO$_3$ grown on SrTiO$_3$ and MgO where, additionally, anisotropies is the thermoelectric properties are found [99, 100].

### 2.3 (111)-oriented interfaces

Until recently, most perovskite related research has been focused on (001)-oriented films. However, altering the substrate orientation has been identified as an avenue towards novel functionality and property control, important for emerging oxide devices [30]. In this regard, the (111)-orientation is especially interesting due to the hexagonal symmetry, the octahedral coupling, and the stacking sequence of the (111)-facet, illustrated in figure 2.7.

The interest in the hexagonal symmetry of (111)-oriented SrTiO$_3$ was elevated with the theoretical prediction that the cubic perovskite phase of SrIrO$_3$ would exhibit non-trivial band topologies when in an (111)-oriented SrTiO$_3$ / SrIrO$_3$ / SrTiO$_3$ stack [101, 102]. Due to the honeycomb lattice and strong spin-orbit coupling, a two-dimensional topological insulator was predicted. However, experimentally it has been difficult to synthesize SrIrO$_3$ thin films in the perovskite phase, with growth on (111)-oriented SrTiO$_3$ producing (001) monoclinic SrIrO$_3$ [103, 104]. (111)-oriented SrIrO$_3$ in the perovskite state can be synthesised in a metastable phase through depositing ultra-thin films [105]. However, the SrTiO$_3$ capping layer is necessary to avoid degradation in air [106].

Interesting phases, such as Dirac semimetal, Chern insulator, and multiferroicity are also predicted to appear in (111)-oriented material systems such as superlattices of (LaXO$_3$)$_N$ / (LaAlO$_3$)$_M$ (X = transition metal),
Figure 2.7: (a) Top view of a (111)-oriented surface. (b) Angled view of a (111)-oriented interface. The interface is marked as a blue layer. (c) Side view of a (111)-oriented material with the layers marked along with atomic composition and nominal charge (x) of each layer.

due to the hexagonal symmetry of the (111)-orientation [107, 108]. However, as with the topologies in SrIrO$_3$, this has been difficult to observe experimentally [109, 110, 111, 112]. Recently, predictions of a Goldstone-like mode have been made in compressively strained LaAlO$_3$ and SrMnO$_3$; the hexagonal symmetry along with (111)-oriented strain result in degenerate phases with different octahedral rotation patterns [113, 114].

In contrast to (001)-oriented interfaces where the oxygen octahedra are connected through one apex atom, the octahedra are connected through three oxygen atoms in an (111)-oriented interface. Therefore, the octahedral coupling is expected to be different across (111) as compared to (001)-oriented interfaces. This has theoretically been shown to be the case in the La$_{0.7}$Sr$_{0.3}$MnO$_3$ / SrTiO$_3$ interface [115]. Moreover, octahedral coupling across an (111)-oriented interface has been shown to be able to induce a ferrimagnetic moment in an antiferromagnet without charge transfer [116].
Employing the (111)-orientation, magnetic exchange interactions can be induced in material systems which does not exhibit the same properties in the (001)-orientation. In (111)-oriented superlattices of paramagnetic LaNiO$_3$ and ferromagnetic LaMnO$_3$ positive and negative exchange bias, as well as antiferromagnetic interlayer coupling are observed [117, 118]. In figure 2.8, the different regimes can be seen. The blue and orange curves are obtained after field cooling in +0.2 T and -0.2 T magnetic fields, respectively. At 2 K negative exchange bias is observed (figure 2.8 (a)), while at 18.5 K a slight positive exchange bias is seen (figure 2.8 (b)). The positive exchange bias is more easily observed in figure 2.8 (c) where the evolution of the exchange bias field $H_{EB}$ is shown. Lastly, the rounding at 50 K indicates antiferromagnetic coupling (figure 2.8 (d)).
Interfacial coupling can also occur at interfaces between ferromagnetic and ferroelectric materials. Ab initio calculations suggest that the magneto-electric coupling between ferromagnetic La$_{1-x}$Sr$_x$MnO$_3$ and ferroelectric BaTiO$_3$ will be stronger in (111)-oriented interfaces [119].

The geometric constraints of the (111)-orientation has opened up the possibility of novel phases such as polar metals [120]. Through geometric engineering, Kim et al., found thin films of NdNiO$_3$ could be made a polar metal on (111)-oriented LaAlO$_3$ by stabilizing an $\alpha^-\alpha^-c^{0+\delta}$ rotation pattern at the interface. By depositing NdNiO$_3$ on NdGaO$_3$, the temperature of which the metal to insulator transition and the antiferromagnetic transition occurs at is altered. While both the metal-to-insulator transition and the antiferromagnetic transition appears at 200 K in (001)-oriented NdNiO$_3$, in (111)-oriented films the transitions occur at different temperatures. In (111)-oriented NdNiO$_3$ the metal-to-insulator transition occurs at 335 K and the antiferromagnetic transition occurs at 230 K. This change is ascribed to the octahedral rotations induced in the film [121].

With regards to ferromagnetism in (111)-oriented films, there are several reports of La$_{0.7}$Sr$_{0.3}$MnO$_3$ on (111)-oriented SrTiO$_3$ [116, 122, 123, 124, 125, 126, 127]. While (111)-oriented La$_{0.7}$Sr$_{0.3}$MnO$_3$ is macroscopically magnetically isotropic at high fields, the magnetic switching happens through microscopic domains with a six-fold anisotropy [122]. Compared to (001)-oriented films, the magnetic properties of (111)-orientation is found to be more bulk-like, with earlier saturation as a function of thickness [123], and a stronger angular dependence on the out-of-plane magnetic anisotropy [127]. Compared to the (110)-orientation, both the (001) and (111)-orientation have larger interfacial magnetism due to charge discontinuities across the substrate film interfaces [126]. While thoroughly investigated in the (001)-orientation, few reports on the effects of strain or vicinal surfaces have been found for the (111)-orientation.

Concerning ferroelectric properties, the polarization of BaTiO$_3$ is predicted to decrease with applied (111)-oriented compressive strain, contrary to what is found to (001)-oriented ferroelectric films where the polarization is observed to increase in compressively strained films. However, the out-of-plane parameter is predicted to increase in both cases [128]. Comparing the transport properties of (001) and (111)-oriented BaTiO$_3$ on SrTiO$_3$, a lower leakage current density and a higher dielectric constant have been reported for (111)-oriented films [129, 130]. A ferroelectric polarization of 1.35 $\mu$C/cm$^2$ has been reported in (111)-oriented BaTiO$_3$/SrTiO$_3$ superlattices on SrTiO$_3$ [131], a magnitude lower than observed in similar (001)-oriented
superlattices [55]. The synthesis of (111)-oriented BiFeO$_3$ is interesting as the ferroelectric polarization is largest for bulk rhombohedral BiFeO$_3$ in the (111)-plane. (111)-oriented BiFeO$_3$ does assume a rhombohedral unit cell on SrTiO$_3$ [94], with a higher polarization than (001) and (110)-oriented films. However, the (111)-oriented film also experiences fatigue earlier due to domain wall pinning during switching [132].

Important to the realization of novel properties and functional coupling in (111)-oriented heterostructures is the preparation of atomically sharp interfaces. Atomically sharp, stable, and single-terminated surfaces have been prepared for a wide range of substrate materials in the (001)-orientation [133, 134, 135, 136]. However, preparation of (111)-oriented substrates is still a challenge, and high-quality surfaces have been difficult to achieve [137, 138], with only reports of preparation of (111)-oriented SrTiO$_3$ being found. The preparation of (111)-oriented SrTiO$_3$ has been studied since the 70s, initially by hydrogen reduction and annealing, resulting in Ti rich surfaces [139, 140]. Later, it was found that etching in a solution of HCl and HNO$_3$ followed by annealing in oxygen at 850 °C resulted in a step and terrace structure with step heights corresponding to integer multiples of half unit cells, an indication of a mixed termination [141]. Several groups have reported step and terrace surfaces with Ti-rich termination by selective etching of Sr with buffered hydrogen fluoride or deionized water, followed by annealing in an oxygen atmosphere [142, 143, 144].

A relevant difference between the (001)- and (111)-orientation is the stacking along the surface normals. The stacking sequence in the [001]-direction is AO + BO$_2$ + AO + BO$_2$ + ··· while in the [111]-direction the stacking sequence is [111]-direction is AO$_3$ + B + AO$_3$ + B + ···, resulting different nominal charges along the [001]- and [111]-directions (figure 2.7 (c)). As an illustration, SrTiO$_3$ have charge neutral layers along the [001]-direction and layers with nominal charges of ±4 along the [111]-direction. Importantly, polar stacking along the surface normal has been observed to lead to surface reconstructions in a variety of materials: (111)-oriented SrTiO$_3$ [145], (110)-oriented SrTiO$_3$ [146], (001)-oriented DyScO$_3$ [147], (001)-oriented LaAlO$_3$ [148], and (110)-oriented LaAlO$_3$ [149, 150]. Tailoring of the interfacial charge can lead to novel emergent phenomena at the interface, such as the appearance of low temperature sheet conductance at the SrTiO$_3$ / LaAlO$_3$ interface [151]. Thus, it is important to understand the effect of the polar stacking order along the [111]-direction on the surfaces of substrates and interfaces of heterostructures.
2.4 Opportunities and challenges

In summary, the last decades have seen large improvements in the understanding of the control and synthesis of perovskite material systems. There are, however, still many opportunities and challenges to be examined. While atomically flat (111)-oriented SrTiO$_3$ surfaces have been reported, little is known about preparation of other (111)-oriented substrates and the effect of the [111]-stacking sequence on subsequent film growth. Secondly, the effect of vicinal surfaces and strain on thin films, while thoroughly investigated in the (001)-orientation, has so far not been explored extensively in the (111)-orientation.

In this work, we study how these control parameters can be employed to manipulate the synthesis, functional and structural properties of (111)-oriented thin films. The effects of epitaxial strain, substrate imposed symmetry, and interface morphology on the structural and magnetic properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ is reported and discussed. Lastly, we report on the synthesis of (111)-oriented BaTiO$_3$ thin films with a focus on defect formation, structural and ferroelectric properties.
Chapter 3

Experimental

This chapter gives first an introduction to the material systems used in this work, organized into two categories: thin film systems and substrate systems. In order to study these material systems, a range of experimental techniques have been used, and they are presented in the following section. Lastly, theoretical models of magnetic anisotropy used in the analysis of the experimental data is presented.

3.1 Material systems

3.1.1 Thin film systems

In this work, two thin film material systems, ferromagnetic La$_{0.7}$Sr$_{0.3}$MnO$_3$ and ferroelectric BaTiO$_3$, have been used. They have been chosen due to their technologically interesting properties and coupling between structure and functionality.

La$_{0.7}$Sr$_{0.3}$MnO$_3$

La$_{0.7}$Sr$_{0.3}$MnO$_3$ is a material that has been extensively studied due to its robust room temperature ferromagnetism, colossal magnetoresistance, and a high degree of spin-polarization, making it relevant for application in spintronic devices [152, 153, 154]. The parent compounds of La$_{0.7}$Sr$_{0.3}$MnO$_3$, LaMnO$_3$ and SrMnO$_3$, are both antiferromagnetic. However, the mix of La and Sr in La$_{0.7}$Sr$_{0.3}$MnO$_3$ results in a ferromagnetic material due to the mixed Mn valence of 3+ and 4+, culminating in ferromagnetism through double exchange [155]. The manganites in general are characterized by a strong interplay between electronic structure, transport, functional proper-
Figure 3.1: (a) The MR as a function of temperature for a 10 nm La$_{0.7}$Sr$_{0.3}$MnO$_3$ film on SrTiO$_3$. (b) The MR as a function of magnetic field for a set of temperatures in the range 320 K to 380 K.

...ties, and crystal lattice structure [156, 157]. The energy landscape is defined by competing energy minima due to high electron correlations and strong electron-phonon interactions, making the material a good model system for investigating the effect of strain and symmetry changes on functional properties [155]. Bulk La$_{0.7}$Sr$_{0.3}$MnO$_3$ has a ferromagnetic transition temperature of 370 °C [158]. Close to the Curie temperature, La$_{0.7}$Sr$_{0.3}$MnO$_3$ undergoes a metal-to-insulator transition, with La$_{0.7}$Sr$_{0.3}$MnO$_3$ being a half-metal at low temperatures [159]. Near this transition, the electronic phase is very susceptible to the influence of a magnetic field, lowering the resistance dramatically, known as colossal magnetoresistance.

In bulk, La$_{0.7}$Sr$_{0.3}$MnO$_3$ has a rhombohedral unit cell (R$\bar{3}$m) with an $a^-a^-a^-$ rotation pattern and a pseudo-cubic lattice parameter of $a_{pc} = 3.88$ Å. (The
3.1. Material systems

subscripts pc, rh, c, and o refer to the pseudo-cubic, rhombohedral, cubic, and orthorhombic symmetries, respectively.) The rhombohedral parameters are \( a_{\text{rh}} = 5.471 \, \text{Å} \) and \( \alpha = 60.43^\circ \) [160]. Due to the mixed valence of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) the \( e_g \) orbitals are partly occupied by an electron. To lower the energy level of the occupied state, the oxygen octahedra distorts, commonly referred to as the Jahn-Teller effect [155, 161]. Magnetically, bulk \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) has either an easy (111)-plane [162, 163] or an easy [111]-axis [164]. The structure of epitaxial \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) thin films is dependent on the substrate orientation and lattice parameter. For (001)_{pc}-oriented films, tensile strain results in tetragonal or monoclinic unit cell, while compressively strained films are found to be monoclinic [165, 166, 50].

There has been limited reports discussing the magnetic properties of (111)-oriented \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) [116, 122, 123, 124, 125, 126, 127]. However, few reports of the transport properties have been found [123]. The magnetoresistance (MR) as a function of temperature is plotted in figure 3.1 (a) based on the difference in resistance under 0 T and 2 T applied magnetic field with a response typical for magnetoresistance in manganites. The peak magnetoresistance is observed at approximately 320 K. At 3 T applied field at 320 K, the maximum magnetoresistance is 45 % (figure 3.1 (b)), higher than previously reported for (001)-oriented and (111)-oriented films (between 15 % and 35 % at 5 T) [123, 167, 168]. More details regarding the transport measurements can be found in reference [169].

\( \text{BaTiO}_3 \)

Barium titanate, \( \text{BaTiO}_3 \), has been one of the most extensively studied ferroelectric ceramics since its discovery in 1945 [170]. It is a good candidate for a variety of applications due to its excellent ferroelectric, piezoelectric, and dielectric properties, without the lead associated problems of \( \text{PbZr}_{x}\text{Ti}_{1-x}\text{O}_3 \) [171]. \( \text{BaTiO}_3 \) is an archetypical ferroelectric with a soft mode freezing in at the Brillouin zone center at the curie temperature (T\( _C \)), displacing the Ti atom relative to the oxygen atoms and thereby creating dipoles, which gives rise to the ferroelectric polarization [172].

\( \text{BaTiO}_3 \) is a perovskite with its structure closely linked to its ferroelectric properties. Below 183 K \( \text{BaTiO}_3 \) is rhombohedral (R\(^3\)m), between 183 K and 278 K it has orthorhombic symmetry (Amn2), from 278 K to 393 K tetragonal (P4mm), and above 393 K it is cubic (Pm\(^3\)m). The measured polarization from polarization reversal current measurements for the rhombohedral, orthorhombic, tetragonal phases are 33 μC/cm\(^2\), 36 μC/cm\(^2\), and 27 μC/cm\(^2\) respectively [173].
3.1.2 Substrate systems

As discussed in the previous chapter, the choice of substrate is important for high quality synthesis and engineering of thin films. We have chosen four substrate materials with differing lattice parameters and symmetry in order to be able to study the effects of both strain and symmetry on the deposited thin films.

**SrTiO$_3$**

SrTiO$_3$ is a widely used material for substrates in perovskite oxide thin film research due to its low lattice mismatch and chemical compatibility with many other materials, along with well-developed methods of achieving atomically smooth single termination surfaces [142]. At room temperature SrTiO$_3$ has a cubic unit cell (Pm$\overline{3}$m) with a lattice parameter of 3.905 Å (table 3.1) and no rotations of the oxygen octahedra ($a^0a^0c^0$) [174], while at 105 K it undergoes a second order structural phase transition. Under 105 K it assumes a tetragonal unit cell with octahedral rotations around the c-axis ($a^0a^0c^-$) [175]. In this work substrates cut in the (111)$_c$-orientation have been used. Due to the cubic unit cell, the surface has a hexagonal in-plane symmetry and stacking along the [111]$_c$-direction as seen in figure 3.2 (a) and (b), respectively. The low-index in-plane directions are the \{1-10\}$_c$ and \{11-2\}$_c$ families of directions.

Table 3.1: The lattice parameters of SrTiO$_3$, DyScO$_3$, GdScO$_3$, and NdGaO$_3$, along with the crystal symmetries.

<table>
<thead>
<tr>
<th></th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>Crystal symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$ [174]</td>
<td>3.905</td>
<td></td>
<td></td>
<td>cubic (tetragonal under 105 K)</td>
</tr>
<tr>
<td>DyScO$_3$ [176]</td>
<td>5.44</td>
<td>5.71</td>
<td>7.89</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>GdScO$_3$ [177]</td>
<td>5.481</td>
<td>5.745</td>
<td>7.929</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>NdGaO$_3$ [178]</td>
<td>5.427</td>
<td>5.500</td>
<td>7.705</td>
<td>orthorhombic</td>
</tr>
</tbody>
</table>

The substrates are prepared by wet etching in a buffered hydrofluoric acid solution, followed by annealing at 1050 °C in oxygen, producing atomically flat step and terrace surface [142, 143].

**DyScO$_3$ and GdScO$_3$**

DyScO$_3$ and GdScO$_3$ are both orthorhombic (Pnma) perovskite rare-earth scandates with an $a^−a^−c^+$ octahedral rotation pattern, commonly used to study the effects of strain on thin films, as they have a higher pseudo-cubic lattice parameter than SrTiO$_3$ (3.944 Å and 3.973 Å for DyScO$_3$ and
GdScO₃, respectively) and can be grown without twinning [39, 179]. Both materials are paramagnetic, making surface sensitive magnetic measurement techniques necessary to measure the magnetic properties of deposited thin films.

Here, (101)₀-oriented scandate substrates have been used, corresponding to the (111)₀ört_hex-orientation. Due to the orthorhombic unit cell the (101)₀-orientation results in a compressed hexagon as seen in figure 3.2 (c) where also the low-index in-plane directions can be seen. The directions are not six-fold degenerate as with a (111)₀-oriented cubic substrate. The octahedral stacking along [111]₀ also differ due to the octahedral rotation pattern (figure 3.2 (d)). The orthorhombic lattice parameters are shown in table 3.1.

The DyScO₃ and GdScO₃ substrates used in this work are prepared by a set of different methods. All substrates are first annealed in an oxygen atmosphere at 1000 °C, which then can be followed by etching in 12 M solution of NaOH and dionized water for one hour.

**NdGaO₃**

NdGaO₃ is as DyScO₃ and GdScO₃ an orthorhombic (Pmna) perovskite with an $a^-a^-c^+$ octahedral rotations pattern, commonly used as a substrate
for epitaxial thin films, though with a lower pseudocubic lattice parameter than the previously mentioned substrates (a$_{pc}$ = 2.863 Å, the orthorhombic lattice parameters are presented in table 3.1). It is the only material of the lanthanide gallates that can be synthesised twin free. There are no known structural phase transitions below $\sim$900 °C [180]. As with the scandates, NdGaO$_3$ is paramagnetic, which makes surface sensitive magnetic measurements valuable for magnetic characterization of thin films [181].

The substrates used in this work are cut along the (011)$_o$ and (101)$_o$ plane, both corresponding to (111)$_{pc}$. The (011)$_o$-orientation, as (101)$_o$, results in a compressed hexagonal in-plane surface symmetry. However, it is compressed along the direction perpendicular to the direction of compression in (101)$_o$-oriented surfaces. A sketch of the (011)$_o$ surface along with the low-index in-plane directions is shown in figure 3.2 (e) and the stacking along [011]$_o$ is presented in figure 3.2 (f). Similar to DyScO$_3$ and GdScO$_3$, NdGaO$_3$ has alternating nominal charges of 3+ and 3- along [111]$_{pc}$.

The NdGaO$_3$ surfaces are prepared annealing in oxygen flow at 1000 °C which can be preceded by etching in buffered HF for 45 s - 120 s.

**Polar stacking**

As mentioned in section 2.3, the nominal charges of each layer differ along the surface normal is dependent on the orientation and material. While the commonly used (001)$_c$-orientation has charge neutral layers for SrTiO$_3$, (111)$_c$ SrTiO$_3$ is polar along the surface normal with alternating SrO$_3^{4-}$ and Ti$^{4+}$ layers (figure 2.7). DyScO$_3$, GdScO$_3$, and NdGaO$_3$ have in the (001)-orientation layers with alternating charges of 1+ and 1-. In the (111)-orientation DyScO$_3$, GdScO$_3$, and NdGaO$_3$ have alternating layers of DyO$_3^{3-}$ / Sc$^{3+}$, GdO$_3^{3-}$ / Sc$^{3+}$, and NdO$_3^{3-}$ / Ga$^{3+}$, respectively.

### 3.2 Experimental techniques

#### 3.2.1 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is the growth technique utilized in this study, a method widely used in the study of perovskite oxide thin films as it results in high quality, epitaxial and stoichiometric thin films with a relatively simple setup [182, 183]. PLD is a technique that employs a non-equilibrium laser-matter interaction for material transfer from a target to a substrate. In 1980, it gained momentum as it was found suitable for growth of epitaxial high-temperature superconductors [184, 185], demonstrating the possibility of growing high quality complex oxide thin film by PLD. In addition, PLD
allows for independent control of the deposition parameters, thus making it well suited for research.

PLD works by focusing a high intensity laser on a bulk target, transferring the energy to a small volume of material that is sublimated, creating a plasma plume of high-energy ad-atoms and ions as illustrated in figure 3.3. The ablated atoms interact with the ambient atmosphere, reducing the momentum, resulting in thermalization of the particles. When reaching the surface, the ablated atoms can absorb to the surface of the heated substrate. A too high momentum of the incoming ad-atoms can result in unwanted respattering and low quality films [186]. The ambient pressure and laser fluence along with the target to substrate distance are therefore central parameters. The thermal energy can cause the atoms to desorb, diffuse across the surface and nucleate. The rate at which this happens is dependent on the activation energy of the process, i.e. the relation of the binding energy of the ad-atoms to the surface and the binding energy to each other. Thus, the substrate temperature is an important parameter as it provides energy for the ad-atoms move around on the surface. Lastly, the repetition rate of the laser is relevant as it dictates the time given to surface diffusion before a new deposition of ad-atoms.

At thermal equilibrium, three growth modes can be identified [187]: Volmer-Weber (island growth), Frank-van der Merwe (layer-by-layer growth), and Stranski-Krastanov (layer-by-layer growth followed by island growth). When it is more energetically favorable for the ad-atoms to bond to each other instead of the surface, the result is island growth. On the other hand, layer-by-layer growth occurs when the ad-atoms binds more strongly to the surface. Stranski-Krastanov growth occurs when the surface energy for the first layers is favorable for layer-by-layer growth, then with increasing thickness, the surface energy changes, creating a preference for island growth. This change can come from, for example, strain and relaxation, creating preferable nucleation sites.

Here, substrates with a miscut angle are used, which results in a step and terrace surface. Providing that the diffusion length is longer than the terraces, most ad-atoms will nucleate at the step edge. This, along with layer-by-layer growth, can give step-flow growth, where the new layer grows out from the steps of the underlying layer, which is desired for high quality thin film growth. While (001)$_{pc}$ films are commonly deposited at high temperatures to ensure high ad-atom energy and thereby step-flow growth, (111)$_{pc}$-oriented films needs to be deposited at lower temperatures in order to achieve high quality 2D surfaces [188].
An illustration of the commercially available PLD system (TSST) is shown in figure 3.3. A KrF excimer laser (Lambda Physik, LPX Pro 210) with a wavelength of 248 nm, operating at 1 Hz was used. A set of mirrors change the orientation of the beam from horizontal to vertical and the most energetic part of the beam is selected using an aperture. The beam is focused on the target using a lens with a focal distance of 50 mm. Each pulse is 25 ns in duration with a fluence of approximately 2 J cm$^{-2}$. The substrate has been placed 45 mm from the target, and heated to typically 540 °C for the material deposition. The targets are stoichiometric sintered powder pallets. Prior to deposition the targets are pre-ablated for 5 minutes with a repetition rate of 5 Hz. Oxygen pressures of 0.35 mbar (La$_{0.7}$Sr$_{0.3}$MnO$_3$) and 0.05 mbar (BaTiO$_3$) are used during deposition. Post deposition, the samples are cooled in a 100 mbar O$_2$ atmosphere.

![Figure 3.3: A schematic of the experimental PLD setup with the main components.](image)

### 3.2.2 RHEED

In situ reflection high-energy electron diffraction (RHEED) was used for monitoring film thickness, growth mode, surface quality, and dynamics during deposition [183, 189]. An electron canon, situated in a differentially pumped part of the chamber, accelerates electrons with an electric field of 25 kV towards the substrate at a grazing angle, which is partly diffracted and reflected by the crystal. The diffracted beam hits a phosphor screen filmed by a CCD camera. The angle of the incoming electron beam relative to the substrate is optimized to obtain a high intensity, and the sample is rotated to achieve a symmetrical RHEED pattern. Figure 3.4 (b) shows a
3.2. Experimental techniques

A typical RHEED pattern indicating a high crystalline surface. A change in diffraction spot position during deposition can indicate a relaxation, while a change to a square pattern indicates a move from two-dimensional to three-dimensional growth. As a material is deposited, the intensity of the RHEED spots can change due to increased surface roughness during the formation of a new layer. This resulting in an oscillation of the intensity where each oscillation corresponds to the deposition of one layer. A plot of a typical RHEED intensity evolution is seen in figure 3.4 (b).

![Figure 3.4:](a) A typical RHEED diffraction pattern before deposition. (b) The RHEED diffraction spot intensity as a function of time during deposition of La$_{0.7}$Sr$_{0.3}$MnO$_3$. The arrow indicates the starting time of the deposition.

3.2.3 Scanning force microscopy

Scanning force microscopy is a surface imaging technique utilizing a scanning probe across a surface, able to discern sub nanometer differences in the surface structure. A cantilever with a sharp tip is scanned across the surface, measuring the interaction between the tip and surface (figure 3.5). Differences in structure are detected by deflection of the cantilever. Depending on the scanning mode and choice of tip, various surface properties can be imaged, such as topography, friction, charge, magnetization, or ferroelectricity. In this work, the topography has been imaged using atomic force microscopy (AFM) in tapping mode with Bruker RTESP-300 tips, the surface friction using force friction microscopy (FFM) in contact mode with Bruker ESPA-V2 tips, and the piezoelectric response using piezo-response force microscopy (PFM) in contact mode with Vecco MESP tips.

In tapping mode, the cantilever oscillates above the surface in resonance. The surface atoms exert force on the cantilever, and the changes in height relative to the cantilever are measured as changes in the resonance frequency,
thus giving information on the surface topography. For friction force measurements, the tip is in contact with the surface, the cantilever deflection changing depending on the relative surface friction and topography, enabling imaging of both simultaneously. Friction force measurements can give information on the homogeneity of the surface termination. A tip scanning over two differently terminated areas will experience differences in friction force. This shows up as a contrast in the friction force micrograph given that the domains are larger than the resolution. The tip is also in contact with the surface during the PFM measurement. The principle behind PFM is that the ferroelectric polarization can be indirectly imaged through the piezoelectric response of the film. An AC voltage is applied to the tip, which is scanned across the surface and the piezo-response is measured through deflection of the tip. Details regarding PFM measurements can be found in [190].

![Detector Laser Cantilever](image_url)

**Figure 3.5:** An illustration of the scanning force microscopy measurement technique.

### 3.2.4 X-ray diffraction

XRD is an analytic technique that utilizes the coherent scattering of x-rays from the electrons in a crystalline solid to gain structural information on the crystal. For certain directions of the incoming x-rays relative to the crystal yield constructive interference, where the direction is related to the distance between the scattering atoms [191]. In this work, x-ray diffraction (XRD) was used to determine the film thickness, lattice parameters, unit cells,
symmetry, and mosaic spread of the deposited films. A four circle Bruker D8 Discover x-ray diffractometer was used, with incident monochromatic CuK$_{\alpha 1}$ radiation, with a wavelength of 1.5406 Å. The theory presented in the following section has been to refine the structure parameters of the investigated material systems.

![Figure 3.6](image_url)

**Figure 3.6:** A simple illustration of the reflection of x-ray radiation from scattering centers in a crystal.

The process of scattering of x-rays from scattering centers is illustrated in figure 3.6, where incoming x-rays are reflected through coherent scattering by atoms in a crystal lattice. The difference in phase of the scattered radiation from two scattering centers is given by

$$\Phi = 2\pi \mathbf{x} \cdot \mathbf{S}$$  \hspace{1cm} (3.1)

where $\mathbf{S} = (\mathbf{S}_1 - \mathbf{S}_0)/\lambda$, $\mathbf{S}_0$ and $\mathbf{S}_1$ are the unit vectors of the incoming and scattered x-rays, respectively, $\lambda$ is the wavelength, and $\mathbf{x}$ is the distance vector between the centers. The intensity of the reflection is dependent on the scattering atom, i.e. the number of electrons and their positions. This is expressed by the atomic scattering factor

$$f = \int \rho(r) \exp(i\Phi) dr$$  \hspace{1cm} (3.2)
where \( \rho(r) \) is the electron density at position \( r \) and the integration is over all space. For a crystal, it is convenient to regard the unit cell and the translation symmetry. In other words view the crystal as a unit cell repeated in space. Suppose a unit cell has \( n \) atoms at positions \( r_j \) \((j = 1, 2, 3, \ldots, n)\) with respect to the origin and individual scattering factors \( f_j \), then the structure factor for the unit cell is

\[
F(S) = \sum_{j=1}^{n} f_j \exp(i\Phi_j)
\]

(3.3)

A crystal contains a large number of unit cells, constructed by the translation vectors of the crystal, \( \mathbf{a}, \mathbf{b}, \text{and} \mathbf{c} \). The numbers of unit cells along the translation directions are \( n_1, n_2, \text{and} n_3 \), respectively. A unit cell will have its origin at position \( t\mathbf{a} + u\mathbf{b} + v\mathbf{c} \), with \( t, u, \text{and} v \) being integers between 1 and \( n_1, n_2, \text{and} n_3 \), respectively. Thus, to obtain the total scattered ray from the crystal, \( K(S) \), the contributions by all unit cells have to be added.

\[
K(S) = F(S) \times \sum_{t=1}^{n_1} \exp(i2\pi t\mathbf{a} \cdot \mathbf{S}) \times \sum_{u=1}^{n_2} \exp(i2\pi u\mathbf{b} \cdot \mathbf{S}) \times \sum_{v=1}^{n_3} \exp(i2\pi v\mathbf{c} \cdot \mathbf{S})
\]

(3.4)

Because the number of unit cells is large, \( K(S) \) will always be close to zero, unless \( (\mathbf{a} \cdot \mathbf{S}) \) equals an integer \( h \), \( (\mathbf{b} \cdot \mathbf{S}) \) equals an integer \( k \), and \( (\mathbf{a} \cdot \mathbf{S}) \) equals an integer \( l \), which is known as the Laue conditions. \( (hkl) \) are the Miller indexes corresponding to crystal planes, thus enabling the determination of the crystal lattice by x-ray diffraction.

In an infinite crystal the resulting diffraction lines will be delta functions. For a real finite crystal the lines will be broadened. An epitaxial thin film will usually be very thin compared to the substrate, and thus the film diffraction peak will be significantly broader than the substrate diffraction peak.

From considerations of the phase \( (\mathbf{x} \cdot \mathbf{S}) \) along with the Laue condition it is possible to derive Bragg’s law

\[
2d_{hkl} \sin \theta = n\lambda
\]

(3.5)
where $d_{hkl}$ is the distance between two adjacent $(hkl)$ planes, $\theta$ is the angle of the incoming beam with regards to the reflecting plane, and $n$ is an integer.

$\mathbf{S}$ can be expressed as $\mathbf{S} = na^* + kb^* + lc^*$, where $a^*$, $b^*$, and $c^*$ are the reciprocal lattice vectors. Each reflecting plane $(hkl)$ is thus represented as a point in reciprocal space. For a thin film, the reflected planes are represented as truncated crystal rods.

In practice a typical measurement is done with a setup similar to the one shown in figure 3.7 where the crystal can be rotated relative to the incoming radiation through the angles $\theta$, $\omega$, $\phi$, and $\chi$. In addition, the detector can be rotated at an angle $2\theta$ relative to source. In this study linear $\omega/2\theta$ scans, where the crystal is rotated an angle $\omega = \theta$ and the detector an angle $2\theta$, has been used to determine the out-of-plane film parameter with Bragg’s law. Linear scans are also used to determine the film thickness using the framework presented in [192]. Rocking curves, where $2\theta$ is kept constant, while the crystal is rotated around $\theta(\omega = \theta \pm \delta)$, is used to determine the width of the linear $(111)_{pc}$ peaks. The width gives an indication of the mosaic spread of the film. Reflections are denoted in this work with brackets to facilitate the inclusion of the symmetry used.

By scanning the reciprocal space around asymmetrical peaks, reciprocal space maps (RSM) can be constructed, illustrated in figure 3.8. Each points represents, as mentioned earlier, a set of reflecting crystal planes, either in the substrate or thin film. Here the reciprocal space maps are expressed in reciprocal lattice vectors related to the in-plane and out-of-plane directions of the film, $Q_\parallel$ and $Q_\perp$, respectively.

![Figure 3.7](image_url): A schematic of the measurement setup with the rotation axes and radiation angles indicated.
Experimental

Figure 3.8: The position of reflection peaks from an epitaxial film on a substrate in the reciprocal space. In this case the out-of-plane direction is [111]pc and the in-plane direction is [1-10]pc.

\[
Q_\parallel = 2\sin(\theta)\cos(\theta - \omega)/\lambda = 2\pi/d_\parallel
\]
\[
Q_\perp = 2\sin(\theta)\sin(\theta - \omega)/\lambda = 2\pi/d_\perp
\]

(3.6)

where \(2\pi/d_\parallel\) and \(2\pi/d_\perp\) are the in-plane and out-of-plane components of the crystal plane spacing corresponding to the measured reflection. With a situation such as depicted in figure 3.8 the film in-plane position is equal to that of the substrate, indicating an epitaxially strained film. This information along with out-of-plane position allows us to determine the film lattice parameters and unit cell structure.

3.2.5 Vibrating sample magnetometer

Vibrating sample magnetometer (VSM) was used to measure the macroscopic magnetic moment of the samples. Invented by Foner [193] in 1955, a sample is magnetized by a uniform magnetic field and sinusoidally vibrated. The stray fields from magnetized sample will, according to Faraday’s law of induction, induce a voltage proportional to the sample magnetization, which is measured. The induced voltage will have the same frequency as the vibration of the sample; a pick-up amplifier is therefore commonly used to filter out the voltage contribution from other sources. Sweeping the applied magnetic field enables hysteresis measurements.

As the VSM measures the entire sample, the volume of the film and the volume of the sample along with its magnetic properties have to be known
3.2. Experimental techniques

In this work, the VSM used is a Quantum Design Versalab with the ability to vary the chamber temperature between 50 K and 400 K and apply a magnetic field in the range ±3 T. Magnetic data is gathered through hysteresis curves at set temperatures. The extrema of applied field is set to saturate the magnetization in the sample, though not significantly higher to minimize effects of persistent currents in the superconducting magnets. The field required to saturate the samples is dependent on both the strain state of the sample and on its temperature. The hysteresis curves are then analyzed to gather relevant data: high, low field, and remanent magnetization, coercive field, and hysteresis shape. Before measurements, the samples are heated above the Curie temperature and field cooled in a 2 T field.

3.2.6 Magneto-optical Kerr effect

In addition to the VSM, a magneto-optical Kerr effect (MOKE) setup has been used for magnetic measurements. Unlike the macroscopic nature of the VSM measurements, the MOKE technique is surface sensitive, probing only a limited number of nanometers beneath the surface, typically 10 nm to 20 nm in metallic films [194]. It is based on the principle of polarization change when linearly polarized light is reflected on a plane interface between an ambient and magnetic medium [195]. MOKE can be divided into three different categories, depending on the direction of the magnetic field relative to the plane of incidence and the interface. In this study, longitudinal MOKE (L-MOKE) has been chosen, where the magnetic field is parallel to both, as sketched in figure 3.9. To do measurements as a function of in-plane

![Figure 3.9: A sketch of the MOKE measurement setup.](image-url)
direction, the sample stage is rotated in-plane with the magnetic field fixed. The amplitude of the fields is, as with the VSM measurements, chosen to saturate the magnetization of the La$_{0.7}$Sr$_{0.3}$MnO$_3$ film, which is dependent on the nature of the samples. The field frequency is set to 10 Hz and averaged over 1000 repetitions.

3.2.7 X-ray magnetic circular dichroism

X-ray magnetic circular dichroism (XMCD) uses circularly polarized x-rays to probe the magnetic order of a material, for example to gain information on the magnetization. If there is an anisotropy in the electron orbitals of a material, the x-ray absorption will be polarization dependent (dichroism). In a magnetic material the existence of magnetic moments along with spin orbit interactions is needed to create magnetic dichroism. Absorption of x-rays results in electron emission proportional to the degree of absorption. The difference in emission between the right hand and left hand circularly polarized light is dependent on the magnetic moment. Applying an external magnetic field enables hysteresis measurements [196]. The element specificity of XMCD allows the determination of a material specific magnetization. In this work the L2 and L3 edges of Mn have been used. The measurements were done at beamline 4.0.2 at Advanced Light Source (ALS).

3.2.8 Pyroelectric measurements

The dynamic pyroelectric method, first developed by Chynoweth [197], is a measurement technique for probing the ferroelectric properties of a sample. This is especially relevant for samples with high leakage currents, in which the polarization can be masked when measured by a conventional ferroelectric tester. The polarization of a ferroelectric material is temperature dependent, thus a heating of the ferroelectric capacitor will result in a current which can be measured. The pyroelectric properties can be measured independently of externally applied fields, making it possible to probe the initial polarization of a ferroelectric material.

In this work, a pulsed (33 Hz) diode laser with wavelength 1080 nm and rise time of $\sim$3 $\mu$s was used. The laser focused down to a spot with a diameter of approximately 50 $\mu$m in order to locally heat the ferroelectric material and generate a photoelectric current. The laser spot is positioned on a top electrode of Pd with a diameter of 1 mm and a thickness of 100 nm in order not to photoexcite carriers in the ferroelectric. The pyroelectric response of heating from the pulsed laser of a typical sample is presented in figure 3.10. In order to find the temperature dependence of the measured
quantities, the sample is positioned in a chamber to enable cooling of the system. More details on pyroelectric measurements can be found in [198]. The pyroelectric measurements were performed at the Institute for Solid State Physics, University of Tokyo.

3.3 Theoretical framework

In order to investigate the magnetic properties of the thin films, theoretical models of magnetic anisotropy have been used. The first two models, Stoner-Wohlfarth model and the temperature dependence model by Zener, have been employed to quantify and analyze the magnetic anisotropy. The other two models, the Néel model and the single ion model, have been used to couple the magnetic and the structural properties of the studied material systems.

3.3.1 Stoler-Wohlfarth model

A general model for a uniaxial anisotropy is as follows [199, 200]:

\[
\frac{E_a}{V} = K_u \sin^2(\theta - \phi)
\]  

(3.7)

where \(E_a\) is the anisotropy energy, \(V\) is the volume of the sample, \(K_u\) is
the uniaxial anisotropy constant, and $\phi$ is the direction of the easy axis. $K_u$ can be determined with the Stoner-Wohlfarth model. $K_u$ is found by calculating the anisotropy field, $H_{an}$, defined as

$$H_{an} = \frac{M_s}{(dM/dH)_{H=0}}$$

(3.8)

where $M_s$ is the saturation magnetization and $dM/dH$ is the derivative of the magnetization with respect to the field for the hard axis at remanence. The uniaxial anisotropy constant is then found using

$$2K_u = \mu_0 H_{an} M_s$$

(3.9)

with $\mu_0$ being the vacuum permeability. The Stoner-Wohlfarth is a model used for the magnetization of single domain ferromagnets, commonly small ferromagnetic particles, however, it has also been used in the analysis of La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films. This method of calculating the magnetic anisotropy has been used in (001)-oriented La$_{0.7}$Sr$_{0.3}$MnO$_3$ on NdGaO$_3$ [166] and as an approach to determine the switching mechanisms in La$_{0.7}$Sr$_{0.3}$MnO$_3$ on stepped SrTiO$_3$ [89].

### 3.3.2 Temperature dependence of magnetic anisotropy energy

In order to study the effects of structural transitions on the magnetic anisotropy a model of the temperature dependence is needed. Here a model first proposed by Zener [201] and further developed by Carr [202] is used. The model assumes a ferromagnetic material with spontaneous magnetization produced by parallel spin alignment driven by exchange interactions and that the atomic coupling constants are independent of temperature, resulting in the relation

$$\frac{K_u(T)}{K_u(T_0)} = \left(\frac{M_s(T)}{M_s(T_0)}\right)^{n(n+1)/2}$$

(3.10)

with $T$ being the temperature, $T_0$ is a temperature below the Curie temperature, and $n$ is the order of the symmetry. For uniaxial anisotropy $n = 2$, for biaxial anisotropy $n = 4$ and so on. For uniaxial anisotropy we thus arrive at the expression
This model has been applied to a wide range of materials. In addition to being used to analyze the step edge anisotropy of permalloy on Mo surfaces [203], the model by Zener is used to investigate the anisotropy in a wide range of materials, including to R$_2$Fe$_{14}$B single crystals where R = Pr, Th, or Dy [204], the layered semiconductors CrI$_3$ and CrBr$_3$ [205], epitaxial films of FePt [206], nanostructured Q-carbon [207], and the phase-separated perovskite manganite Eu$_{0.55}$Sr$_{0.45}$MnO$_3$ [208].

### 3.3.3 Néel model of magnetic anisotropy

Connecting the atomic structure and the magnetic anisotropy is important to gain an understanding of the magnetic interactions in the thin films studied here. The Néel model of anisotropy was developed by Louis Néel in 1954 [209]. It considers the interaction energies of two magnetic ions, where the energy is given by [210]:

$$E_i(r_{ij}, \zeta) = G(r_{ij}) + L(r_{ij}) \left( \cos^2(\zeta) - \frac{1}{3} \right) + Q(r_{ij}) \left( \cos^4(\zeta) - \frac{6}{7} \cos^2(\zeta) - \frac{3}{35} \right)$$

where $r_{ij}$ is the vector between the spins, $\zeta$ is the angle between the magnetization and $r_{ij}$, and $G(r_{ij}), L(r_{ij}), Q(r_{ij})$ are the isotropic, dipolar and quadrupolar Néel parameters. As it is the anisotropy that is studied here, i.e. the angular dependence of $E_i$, $G(r_{ij})$ can be disregarded. Likewise $Q(r_{ij})$ can be disregarded as it is typically a few orders smaller than $L(r_{ij})$ [209]. The dipolar parameter $L(r_{ij})$ can thus be approximated around an equilibrium value $r_0$:

$$L(r_{ij}) = L_0 + L' \epsilon$$

where $L_0 = L(r_0)$, $L' = dL/dr_{ij}(r_0)$, and the normalized strain $\epsilon = (r_{ij} - r_0)/r_0$. Through measurements of thin films of La$_{0.7}$Sr$_{0.3}$MnO$_3$ on (001)$_{pc}$ and (110)$_{pc}$-oriented substrates, both $L_0$ and $L'$ are found to be negative [211].
Here, the interactions between the Mn cations are considered. In order to find the anisotropy energy, \( E_i \) is summed over all nearest neighbours, i.e. the Mn-Mn bonds along each of the cardinal pseudo-cubic directions, resulting in a measure of the anisotropy as a function of in-plane angle. The Néel model here is used both to investigate the effect of different crystal symmetries, crystal parameters, and broken bonds on magnetic anisotropy, and is primarily solved numerically.

### 3.3.4 Single ion model

As the source of the magnetization in La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) is double exchange, both the angle and bond length of the Mn-O-Mn bonds are important for the magnetic characteristics. The Mn-O-Mn bond angle and length, and therefore the effect of octahedral rotations, can be introduced in the single ion model \[210\]. This model assumes that the crystal field is a sum of atomic crystal field and a strong spin-orbit coupling. The anisotropy energy from a single Mn-O bond is given as:

\[
E_i(\theta) = -\frac{eQQ_2}{16\pi\epsilon_0 R_i^3} (3\cos^2\theta_i - 1) \tag{3.14}
\]

where \( e \) is the electron charge, \( Q \) is the effective charge of the ligand, \( Q_2 \) is the quadrupole moment of the magnetic ion, \( \epsilon_0 \) is the vacuum permittivity, \( R_i \) is the Mn-O bond length, and \( \theta_i \) is the angle between the magnetization direction and the Mn-O bond. \( E_i \) is summed over three Mn-O bonds per pseudo-cubic unit cell in a 2x2x2 supercell in order to find the total anisotropy energy. The single model is used to investigate how octahedral rotations affect the magnetic anisotropy in addition to the effects of different crystal symmetries, crystal parameters, and broken bonds. It is for all structures solved numerically due to the complexity of the crystal structures.

Magnetocrystalline models such as the Néel model and single ion model have been previously used in literature to model the strain dependent anisotropy of relevant material systems. Examples include La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) on (001)\(_c\)-oriented SrTiO\(_3\) \[165\] and on (110)\(_o\)-, (001)\(_o\)-, (100)\(_o\)-, and (010)\(_o\)-oriented NdGaO\(_3\) \[50\]. However, to describe the anisotropy of La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) on (112)\(_o\) NdGaO\(_3\), a surface term needs to be added \[212\]. Furthermore, it has been used to explain the magnetocrystalline induced anisotropy of other manganites such as La\(_{0.67}\)Ca\(_{0.33}\)MnO\(_3\) on SrTiO\(_3\) \[213\], bulk Pr\(_{1-x}\)Ca\(_x\)MnO\(_3\) \[214\], and the antiferromagnetic ordering in LaMnO\(_3\) \[215, 216\].
Part II

Papers
Chapter 4

Author’s contribution

In this work, the consequences of the (111)$_{pc}$-orientation on the structural and functional properties of ferroelectric and ferromagnetic perovskites have been investigated. The results are summarized in the following part in the form of papers. Papers A and B report the surface preparation of various (111)$_{pc}$-oriented substrates and the effect of the polar stacking order and the octahedral stacking order along the [111]$_{pc}$-direction. Papers C and D discuss on how the magnetic anisotropy can be controlled using (111)$_{pc}$-oriented vicinal surfaces and strain. Finally, Paper E reports the growth and properties of (111)$_{pc}$-oriented BaTiO$_3$.

**Paper A**

In *Effect of Polar (111)-Oriented SrTiO$_3$ on Initial Perovskite Growth* the author performed the PLD deposition of BaTiO$_3$ and RHEED measurements. The author contributed to the data analysis and writing of the publication.


Crystal Growth & Design, 16 (4), 2357-2362, 2016

**Paper B**

In *Surface preparation of (111)-oriented DyScO$_3$, GdScO$_3$, and NdGaO$_3$ substrates* the author performed all synthesis and experiments except for PLD growth of LaFeO$_3$. The author, in close cooperation with the co-authors, carried out the data analysis and writing of the publication.


T. Bolstad, K. Kjærnes, Z. Čiperová, and T. Tybell
To be submitted

**Paper C**

In *Effect of (111)-oriented strain on the structure and magnetic properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films* the author performed all synthesis experiments except for the XMCD measurements. The author, in close cooperation with the co-authors, carried out the data analysis and writing of the publication.

T. Bolstad, E. Lysne, I. Hallsteinsen, E. Arenholz, U. L. Österberg, and T, Tybell
Journal of Physics: Condensed Matter, 30, 255702, 2018

**Paper D**

In *Thickness dependent uniaxial step edge anisotropy in (111)-oriented La$_{0.7}$Sr$_{0.3}$MnO$_3$* the author performed all synthesis and experiments. The author, in close cooperation with the co-authors, carried out the data analysis and writing of the publication.

T. Bolstad, E. Lysne, U. L. Österberg, and T. Tybell
Submitted

**Paper E**

In *Synthesis and characterization of (111)-oriented BaTiO$_3$ thin films* the author performed all synthesis experiments except for the PFM measurements and transversal electroresistance measurements. The author, in close cooperation with the co-authors, carried out the data analysis and writing of the publication.

T. Bolstad, K. Kjærnes, K. Raa, R. Takahashi, M. Lippmaa, and T. Tybell
Submitted
Publications not included in the thesis


Paper A

Effect of Polar (111)-Oriented SrTiO3 on Initial Perovskite Growth


Crystal Growth & Design, 16 (4), 2357-2362, 2016
Effect of Polar (111)-Oriented SrTiO3 on Initial Perovskite Growth
Effect of Polar (111)-Oriented SrTiO$_3$ on Initial Perovskite Growth

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ABSTRACT: In crystalline thin film growth a prerequisite is substrate surfaces with a stable and uniform structure and chemical composition. Various substrate treatments were used to obtain atomically smooth, step-and-terrace (111)-oriented SrTiO$_3$ with uniform cation layers at the surface, i.e., single termination. The surface control enables subsequent layer-by-layer epitaxial growth of perovskite thin films of La$_{1−x}$Sr$_x$MnO$_3$, LaFeO$_3$, and BaTiO$_3$. Reflection high-energy electron diffraction and electron energy loss spectroscopy revealed that a single chemically intermixed (AA′)BO$_3$ perovskite layer formed at the interface. As the terminating layer of (111) SrTiO$_3$ is polar, a surface reconstruction consisting of TiO$_2$ surface layers is expected, and the intermixing at the interface can be understood as A$^+$-cations from the film material compensating an A$^-$-cation deficient substrate surface during initial growth. This finding has important consequences for engineered interfaces between perovskite thin films and polar substrate facets.

The development of atomically well-defined substrate surfaces is a major driving force behind controlled epitaxial growth and recent advances in complex oxide thin film synthesis.$^1$ As complex oxides exhibit strong structure–property coupling, epitaxy can be used to control the functionality of the film, utilizing strain or crystalline orientation. Different orientations of a substrate will result in interfaces where symmetry, surface polarity, and octahedral coupling differ, possibly affecting the electronic states of the epitaxial film at the interface. To exploit such effects, substrates of stoichiometric crystals with atomically flat surfaces of single termination and without major reconstructions are required.$^2,3$ SrTiO$_3$ (STO) and different rare-earth scandates have been widely used as substrate materials for perovskite thin film growth due to the good lattice match with materials of interest and chemical stability. The surfaces of these materials have been extensively studied since the 1990s, and high-quality (001)-oriented substrates are commercially available.$^4,5$ However, for (111)-oriented STO, well-defined single-terminated stoichiometric surfaces have been more difficult to obtain due to the polarity of the terminating surface.$^6$ A schematic of the (111)-oriented STO surface is depicted in cross section and top views in Figure 1, panels a and b, respectively, where Ti is colored yellow, Sr blue, and O turquoise. The (111)-surface has a hexagonal symmetry, where the low-index in-plane crystallographic directions [110] and [112] are indicated in Figure 1b. Along the [111]-direction STO consists of alternating layers of SrO$_2^{−}$ and Ti$^{4+}$, which are each stacked in a “ABCABC...” manner as marked for the Ti$^{4+}$ layers in Figure 1a. The distance between two equally terminated planes is $d_{111} = a/\sqrt{3} = 2.25$ Å (Figure 1a), where $a$ represents the cubic lattice constant of STO ($a = 3.905$ Å). Ideally, single terminated STO(111) would solely have SrO$_2^{−}$- or Ti$^{4+}$- as the uppermost layer, in the schematic a Ti-terminated layer is shown. Hence, STO(111) has layers of nominal charge +4/-4, while STO in the (001) orientation consists of layers of SrO and TiO$_2$ and is thus nonpolar. Since the surface energy of an ideal polar surface diverges,$^7$ polar surfaces tend to facet or form stabilizing reconstructions. This makes film growth on a STO(111) substrate more challenging than on nonpolar STO(001), with a tendency to form a disordered interface.$^8$ We have earlier shown that by reducing the deposition temperature, it is possible to delay the onset of surface roughening, allowing for smooth surfaces in a certain thickness range.$^9$ Still, several reports point toward new phases and
Different reconstructions at the interface between a substrate and a (111)-oriented film.14,15 Substrates having uniform single terminations are necessary for obtaining structurally stable interfaces with a film material.16 For (001)-oriented STO, a uniform TiO2 termination can be achieved by selective wet etching in buffered hydrogen fluoride, which preferentially removes SrO from the surface.7 For (111)-oriented STO there are several reported surface preparation methods pointing toward the possibility of having a stable single termination. For instance, annealing in a reducing atmosphere has been reported to give single terminated surfaces.17 However, high-temperature treatment in a reducing atmosphere can result in oxygen deficiency, resulting in metallic conductivity and even ferromagnetic behavior.18,19 Annealing in O2-atmosphere and chemically etching with HCl/HNO3 give a surface, with Ti in yellow, Sr in blue, and O in turquoise. Ti4+ between the SrO3 1/2 monolayer, indicating that the terminating layer alternates step-and-terrace surface structure with steps corresponding to which preferentially removes SrO from the surface.4 For (111)-oriented STO the cubic lattice constant of SrTiO3 (a = 3.905 Å). (b) Top view. Arrows indicate the low-index in-plane crystallographic directions [101̅] and [112].

**Figure 1.** Schematic of an ideal cubic STO (111) Ti4+ terminated surface, with Ti in yellow, Sr in blue, and O in turquoise. The Ti4+ layers on adjacent terraces.17 Several authors have reported single monolayer step-and-terrace structure for STO(111) by combining buffered hydrogen fluoride etching with high-temperature annealing in O2 atmosphere.18,19 As SrO3− reacts with water to form Sr(OH)2, while Ti4+ is not water-soluble, an almost identical result was reported by using deionized water as the etching reactant;17,20 however the use of buffered hydrogen fluoride results in a more complete removal of Sr-related compounds.18 Here we present a study of how the polar surface of STO(111) influences the initial thin film growth. We discuss the effect of substrate preparation on thin film synthesis and how possible reconstructions affect the stoichiometry of the thin film/substrate interface, important for interface engineering of (111)-oriented thin films.

### EXPERIMENTAL SECTION

Two different treatments of the (111)-oriented STO substrates (Shinkosha, 10 × 10 mm2) are compared in this study, where deionized-water and buffered hydrofluoric acid are used as etching agents. Both etching chemicals have been reported to produce atomically smooth surfaces with a single terminating layer.17 For both methods the substrates were cleaned prior to etching in acetone and ethanol for 5 min under ultrasonic agitation. Annealing was done under oxygen flow after the etching process with a ramp rate of 5 K/min. The first treatment method (DI) consists of immersing the substrates in 80 mL of deionized water at 70 °C under high ultrasonic agitation for 30 min before annealing at 1200 °C for 2 h. In the second treatment method (BHF), the substrates were immersed in deionized water at 70 °C and held under ultrasonic agitation for 5 min, before being dipped in buffered hydrofluoric acid for 45 s and rinsed in deionized water, ending with an annealing at 1050 °C for 1 h. The buffered hydrofluoric acid solution was NH4F/HF 7:1, with a pH of 4.7. The annealing times and temperatures were chosen after optimization based on atomic force microscopy (AFM) investigations. Ultradiffusion films of La0.7Sr0.3MnO3 (LSMO), LaFeO3 (LFO), and BaTiO3 (BTO) were deposited by pulsed laser deposition at 520 °C in 0.5 mbar for 15 min. The substrates were cooled to room temperature in 100 mbar of oxygen at a rate of 15 K/min. Reflection high energy electron diffraction (RHEED) was used to monitor the growth in situ. AFM (Veeco NanoScope V) was used to study the surface topography. Friction force microscopy (FFM) with a cantilever spring constant of 0.9 N/m was used to study the termination of the substrates. Coatal impact...
An AFM image of an as-received substrate is shown in Figure 2a, revealing a relatively flat surface with a root-mean-square roughness of 0.36 nm. The surface is disordered with structures of multiples of half \( d_{111} \), indicating mixed termination. Figure 2b,c shows substrate morphologies after annealing, which were pretreated with the BHF and DI methods, respectively. In both cases, ordered surfaces were obtained with a clear step-and-terrace structure. In Figure 2d AFM line scan profiles are shown for both BHF and DI treated substrates, revealing that both methods result locally in step-heights of 0.23 nm and flat terraces of 100–130 nm widths, in agreement with the substrate miscut angle of 0.1°. The measured step height correspond to STO \( d_{111} \), indicating that all terraces are terminated by identical atomic layers in accordance with the findings of Chang et al.16

A morphological difference is observed between substrates prepared with BHF and DI methods. The substrates pretreated with BHF (Figure 2b) reveal steps and terraces that are straight. However, substrates pretreated with DI, as in Figure 2c, have faceted step edges forming triangular sections. The step edges make a zigzag pattern, where the direction of the edge changes by 60° or 120°. On the basis of the crystal orientation of the substrate, the step edges tend to follow the crystallographic axes, as indicated in Figure 2b,c. For the BHF substrates the step edges are parallel to one of the three \(<112>_{\text{in-plane}}\) directions in accordance with the miscut direction. This is also the case for the DI substrates, except that the step edges in this case make the zigzag pattern along all three \(<112>_{\text{in-plane}}\) directions. We note that for STO(001) such faceted step edges have earlier been reported for Sr-rich terminations.1 The morphologies of LSMO films of approximately 10 nm grown on as-received, BHF and DI substrates are compared in Figure 2e–g. The morphologies of the films replicate the substrate surfaces accurately, which means that the substrate surface is stable at the deposition temperature (500–600 °C) and acts as a mold for the film as long as the film grow layer by layer.12

To further investigate the termination and chemical composition of the substrates, friction force microscopy (FFM) was used. In Figure 3 we show the contact-mode topography and friction contrast for BHF (a, b) and DI (c, d) prepared substrate surfaces. For BHF substrates no significant friction contrast is observed, indicating no macroscopic chemical composition contrast on the surface. For the DI case, there is friction contrast visible, with two distinct levels compatible with areas of different cations. Comparing topography and friction data, it is a clear that the faceted terraces are split into triangles of different friction contrast. On the basis of comparison with FFM measurements of SrTiO\(_3\) (001) surfaces, the dark contrast are inferred to be Sr-rich areas and the bright contrast Ti-rich areas.26 AFM analysis also reveals that Sr-rich regions are rougher than the Ti-rich terraces, and that they lie approximately 1/2 and 3/2 \( d_{111} \) above the Ti-rich terraces.

One possible way for the substrate to stabilize the polar surface is by forming nonstoichiometric surface reconstructions.23–25 Different substrate pretreatments have shown a variety of surface reconstructions on (111)-oriented STO,26–28 where the polarity is screened by surface TiO\(_2\) layers. Angle-resolved CAICISS measurements were performed on DI and BHF treated substrates to test the chemical composition of the substrates. The time-of-flight surface composition analysis revealed increased presence of Sr on both DI and BHF prepared substrates as compared to as-received (see Supporting Information), suggesting the occurrence of Sr segregation during annealing. We note that the longer annealing time and higher annealing temperature for the DI (2 h, 1200 °C) compared to the BHF (1 h, 1050 °C) may lead to segregation of Sr,21 and the reason for the difference in FFM. To test if the Sr signal corresponds to segregated atomic Sr on the surface, we rinsed the DI substrate with DI-water 70 °C for 2 min in ultrasonic bath, followed by 5 min on a hot plate of 100 °C to evaporate all the remaining liquids. The results shown in Figure 3e,f reveal that the faceted step-and-terrace structure is still present; however, the FFM data now gave a homogeneous contrast. We interpret this as atomic Sr being removed from Sr-rich areas, resulting in a single termination state.

In thin film epitaxy, the ad-atom mobility and possible growth mode depend on the chemical environment of the underlying layer.1 Hence the growth of the first unit cell of a...
thin film on top of the substrate may indirectly identify the chemical environment of the substrate. Using substrates prepared by the BHF method and recording the intensity oscillations of the RHEED diffraction spots we investigate the growth of the first unit cells of a thin film. In Figure 4a RHEED oscillations for different film materials are plotted. The maximum of each oscillation is taken as a complete layer, consistent with the longest intensity recovery time for each pulse indicating no phase shift. For clarity the signals have been normalized to the growth period (number of laser pulses per RHEED oscillation) of each film material. As can be seen in Figure 4a, the growth period remains constant throughout the growth of the film except for the first complete layer. It is clear that for all three materials investigated here, the first RHEED oscillation is shorter than the growth period for the subsequent layers. In Figure 4b statistics for the first oscillation normalized to the growth period is shown, and the first layer has typically a growth period of 30–90% as compared to the subsequent layers. Hence, the amount of pulses needed to synthesize the first layer varies from film to film, but is observed to always be shorter than the growth period of the subsequent layers independent of film material or deposition parameters. Moreover, the growth period for the first layer is not consistent with half a period, which would indicate a change of termination, as observed for SrRuO₃ growth. In Figure 4c a RHEED intensity plot for an LSMO/LFO/STO(111) epilayer is shown. It is clear that for the first LFO layer the corresponding RHEED oscillation has a shorter period (26 s) as compared to the subsequent layers (33 s). However, for the top LSMO film the first RHEED oscillation has the same period as for the subsequent layers (15 s) for this particular sample. Hence we interpret that the shorter growth period at the substrate/thin film interface is an effect due to the substrate surface.

To further investigate the chemical interface between substrate and thin film, STEM and EELS investigations were performed across the substrate–film interface. The STEM data in Figure 5a indicate that the film is epitaxial, fully strained, and of high crystalline quality. Cross section composition analysis of the interface regions was obtained from EELS measurements across the LSMO/STO(111) and LFO/STO(111) interfaces, and is shown in Figure 5, panels b and c, respectively. Figure 5d
shows the LSMO/LFO(111) interface in the eplayer for comparison. For clarity the EELS intensities have been normalized to 100% at each side (see Supporting Information for non-normalized data). As can be seen, neither interface is compositionally abrupt toward the STO substrate. The signal for the substrate A-cation, Sr, decreases before the B-cation signal, Ti. Correspondingly, the A-cation signal from the thin films, La, increases before the B-cation signals, Fe/Mn, respectively. The distance between the change in A and B-cation signals is determined to be 0.25±0.3 nm, corresponding to the distance between two subsequent A-cation layers in the (111)-orientation. The spatial resolution of the EELS signal is determined to be 0.15 nm by the width of fitted Gaussian curves for the atomically resolved EELS map. Hence, the EELS measurements reveal that the layer at the interface between film and substrate is a mixture of cations, with B-cations from the substrate and A-cations from the film. 

Figure 6. Model of (111)-oriented STO(111) surface with Sr-deficient top layers and (b) interface with LFO, where La-atoms has filled in the Sr-vacancies, yielding a La(Sr)/TiO layer at the interface. Atoms are colored accordingly: Ti atoms are yellow, Sr blue, Sr vacancies transparent blue, La gray, Fe orange. Oxygens are shown as octahedral.

In conclusion, we have shown that the polar (111)-oriented STO surface can be pretreated to form single terminated, atomically smooth surfaces with both deionized water and buffered hydrogen fluoride, which promotes structurally abrupt interfaces and layer-by-layer film growth. However, the chemical interface between film and substrate is not abrupt, and one layer of chemical A-cation intermixing is found. We note that the effect is due to the substrate, and robust to the type perovskite thin film deposited. If the exact level of Sr surface vacancies can be controlled, the one interatomic thick (AA)BO interface layer could be utilized to establish particular interface properties.

**REFERENCES**


(9) Lee, M. K.; Eom, C. B.; Tian, W.; Pan, X. Q.; Smoak, M. C.; Tsui, F.; Krajewski, J. J. Synthesis and properties of epitaxial thin films of c-

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**ACKNOWLEDGMENTS**

This project was partially supported by the Norwegian Research Council under Project Number 221860 and 231290, and by JSPS Grants-in-Aid for Scientific Research Nos. 25706022 and 26105002. M. N. is supported by the Project NORTEM (Grant 197405) within the Programme INFRA-STRUCTURE of the Research Council of Norway (RCN). NORTEM was cofunded by the RCN and the project partners NTNU, UiO, and SINTEF.


Surface preparation of (111)-oriented DyScO$_3$, GdScO$_3$, and NdGaO$_3$ substrates

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To be submitted
Surface preparation of (111)-oriented DyScO$_3$, GdScO$_3$, and NdGaO$_3$ substrates
Surface preparation of (111)-oriented DyScO₃, GdScO₃, and NdGaO₃ substrates

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Abstract
The fabrication of well-defined, atomically flat (111)pc-oriented orthorhombic substrates of DyScO₃, GdScO₃, and NdGaO₃ by various preparation methods is reported (the subscripts pc and o refer to the pseudo-cubic and orthorhombic symmetry, respectively). It is found that the choice of orthorhombic orientation, (011)o or (101)o, both corresponding to (111)pc, results in step heights of either one or two (111)pc interplanar distances, respectively. The observed differences in step heights is explained by considering the rotations oxygen octahedra along the [011]o and [101]o direction. Growth thin films of La₀.₇Sr₀.₃MnO₃ and LaFeO₃ monitored by reflection high-energy electron diffraction suggest that the surfaces have reconstructed due to the polar stacking order along the [111]pc direction.
**Introduction**

Perovskite oxides constitute an interesting class of materials, due to their strong coupling between structure and functional properties, which include ferroelectricity, ferromagnetism, and superconductivity. With advances in deposition techniques the last decades, epitaxial perovskite heterostructures can be constructed, exhibiting a wide array of novel and enhanced functionality. An example is the induced superconductivity at the interface of SrTiO$_3$ (STO) and LaAlO$_3$ (LAO), two wide-bandgap insulators. Recently, the interest in thin films grown on facets other than the widely used (001)$_{pc}$ (the subscript pc, o, and c, refer to the pseudo-cubic, orthorhombic, and cubic symmetry, respectively) facet has increased. By utilizing (111)$_{pc}$-oriented substrates it has been shown that polar metals can be designed [1], exchange bias can be introduced at the interface between a ferromagnet and a paramagnet [2], a switchable ferrimagnetic moment can be created in an antiferromagnetic material at the interface with a ferromagnetic material [3], and with density functional theory it has been shown that a goldstone-like mode can be introduced in strained LAO [4].

However, to realize high quality heterostructures, atomically flat substrates with control over the termination are desired. The preparation of various (001)$_{pc}$-oriented substrates has been reported. TiO$_2$ terminated STO can be prepared by selectively etching SrO with buffered hydrogen fluoride [5]. ScO$_3$ terminated rare-earth scandates (REScO$_3$) are produced by annealing at 1000 °C in oxygen followed by a NaOH etch which selectively removes the rare earth cations [6]. For NdGaO$_3$ (NGO) both NdO and GaO$_2$ termination has been reported. NdO-termination is achieved by annealing in air at 1000 °C, while GaO$_2$-termination requires etching in buffered hydrofluoric acid with subsequent annealing in air at 1000 °C [7, 8]. Atomically flat LAO surfaces can be prepared by annealing in oxygen at 1000 °C [9], resulting in a termination dependent on surface temperature. Below 150 °C, the surface is AlO$_2$ terminated, above 250 °C LaO terminated, and between 150 °C and 250 °C there is a mix of AlO$_2$ and LaO terminations [10, 11].

With regards to (111)$_{pc}$-oriented substrates, achieving high quality surfaces has proven to be difficult [12, 13]. Thus far only reports of surface preparation of STO have been published. Etching in a mixture of HCl and HNO$_3$ and annealing in an
oxygen atmosphere at 850 °C give a step and terrace structure with an integer multiple of half unit cell high steps, indicating a mix of Sr and Ti termination [14]. Alternatively, etching in buffered hydrofluoric acid followed by high temperature annealing in oxygen is found to result in an atomically smooth surface with a chemically mixed termination due to chemical reconstruction [15-17].

In this work, the effect of surface preparation methods on (111)$_{pc}$-oriented NGO, DyScO$_3$ (DSO), and GdScO$_3$ (GSO) substrates are presented.

**Experimental**

Various treatments of (101)$_o$-oriented DSO (Pi KEM) and GSO (Pi KEM), and (011)$_o$ and (101)$_o$-oriented NGO (Shinkosha, Pi KEM) were compared in this study. Both (011)$_o$ and (101)$_o$ orientations correspond to the (111)$_{pc}$-orientation. The o and pc subscript corresponds to the orthorhombic and pseudo cubic symmetry, respectively. The DSO and GSO substrates were annealed at 1000 °C in an oxygen atmosphere for six hours followed by either no etching or etching in a 12 M NaOH/DI solution. The NGO substrates were either directly annealed at 1000 °C in an oxygen atmosphere for two hours, or etched for 45s or 120s before annealing. The etching was performed in a 12.5% buffered HF/NH$_4$F solution. DSO, GSO, and NGO have an orthorhombic symmetry at room temperature (space group Pbnm) with Glazer tilt pattern a’a’a’c’ [18]. The lattice parameters can be seen in table 1.

The substrate surfaces were investigated by atomic force microscopy (AFM, Veeco Nanoscope V) in tapping-mode and contact-mode. Friction force microscopy (FFM) was used to study the surface termination.

Thin films of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) and LaFeO$_3$ (LFO) were deposited by pulsed laser deposition (PLD) using a KrF excimer (248 nm) with a fluence of ~2 J/cm and a repetition rate of 1 Hz. The substrates were heated to 540 °C during deposition in a 0.35 mbar oxygen atmosphere and the substrate target distance was 45 mm. The growth was monitored by reflection high-energy electron diffraction (RHEED). After deposition the samples were cooled at 15 K/min in a 100 mbar oxygen atmosphere.
Results and discussion

Figure 1 (a) and (b) show the surface micrographs of as-received DSO and GSO substrates, respectively, obtained by contact mode AFM. The surfaces are flat without signs of steps and terraces. The unetched and etched DSO surfaces are shown in figure 1 (c) and (d), respectively, with corresponding line scans in (e) and (f). Likewise, the unetched and etched GSO surfaces are shown in figure 1 (g) and (h), respectively, with line scans in (i) and (j). For both materials and preparation methods the substrates exhibit clear step and terrace surfaces with the height of the steps (DSO: 0.48 nm, GSO: 0.47 nm) corresponding to the height of one (101)\textsubscript{o} layer, or two (111)\textsubscript{pc} layers (DSO: 0.448 nm, GSO: 0.451 nm). This is in contrast to reports of (001)\textsubscript{pc}-oriented scandates, where the step height corresponds to one (001)\textsubscript{pc} layer [19]. The same results are found for shorter annealing times (1 h, 2 h and 4 h, not shown).

An AFM micrograph of an as-received (011)\textsubscript{o}-oriented NGO substrate is shown in figure 2 (a) showing a relatively flat surface with no signs of steps. Figures 2 (b), (d), and (f) show AFM micrographs of the substrates prepared without etch, 45 s etch and 120 s etch, respectively. All show clear step-and-terrace surfaces with step heights of 0.24 nm as seen from the line profiles in figure 2 (c), (e), and (g). The step heights correspond to half the interplanar distance between two (011)\textsubscript{o} planes (0.223 nm), i.e. the interplanar distance between two pseudocubic (111)-planes. To further investigate the step height difference between two orthorhombic terminations, the surface of (101)\textsubscript{o}-oriented NGO substrate, etched in HF for 120 s followed by annealing, is presented in figure 2 (h). A line scan is shown in figure 2 (i) showing step heights of 0.47 nm, approximately equal to one (101)\textsubscript{o} interplanar distance (0.443 nm).

The difference in step height between the (101)\textsubscript{o}-oriented scandates, and (011)\textsubscript{o}-oriented NGO can be rationalized by looking at the rotational stacking sequence of an orthorhombic perovskite with an a’a’c’\textsuperscript{+} rotation pattern. The outermost layers of an (101)\textsubscript{o}-oriented and a (011)\textsubscript{o}-oriented surface are shown in figure 3 (a) and (b), respectively, with surface line scans of the differently oriented NGO substrates as comparisons in (c) and (d). As can be seen, with respect to the surface, the octahedra can exhibit two different rotation states, \(\text{u}\) and \(\text{v}\). For example, in (101)\textsubscript{o}-oriented DSO, the angle of the oxygen bonds oriented upwards for \(\text{u}\) form angles of 38°, 57°,
and 73° with respect to the surface normal, while the free oxygen bonds of \( v \) form angles of 37°, 59°, and 75° with respect to the surface normal. In (011),-oriented DSO the angles for \( u \) and \( v \) are (49°, 55°, 56°) and (36°, 66°, 72°), respectively, assuming no reconstruction. An important difference between the orientations is the stacking sequence of \( u \) and \( v \). Where the (101),-orientation have alternating layers of \( u \) and \( v \) along [101], the (011),-orientation layers along [011], each have a mix of \( u \) and \( v \). Assuming that the surface energy is linked to the angle of the free oxygen bonds, surface energy of the layers populated only by \( u \) or \( v \) along [101], will be different, while the mixed layers along [101], will have a surface energy given by an average of \( u \) and \( v \). A reconstruction of the surface will affect the bond angles and surface energy, however, the surface octahedra will still be limited by the bonds to the underlying layers, which will either be mixed or pure \( u \) or \( v \).

The friction force contrast and topography are shown in figure 4 for unetched DSO (a, b), etched DSO (c, d), unetched GSO (e, f), and etched GSO (g, h). For all the preparation methods, the surfaces appear homogeneous with respect to the friction force contrast. In figure 6 the friction contrast along with the related topography of the NGO surfaces prepared without etching (a, b), 45 s etching (c, d), and 120 s etching (e, f) can be seen. As the scandates, no significant friction contrast is observed for any of the preparation methods. However, this does not necessarily indicate a single terminated surface, as chemically intermixed reconstruction can form on the surface, which would appear homogeneous with respect to the friction contrast. The stacking sequence along [111]sc for DSO, GSO, and NGO is DyO3\(^{3-} + \text{Sc}^{3+} + \text{DyO}3^{3-} + \text{Sc}^{3+} + \ldots \), GdO3\(^{3-} + \text{Sc}^{3+} + \text{GdO}3^{3-} + \text{Sc}^{3+} + \ldots \), and NgO3\(^{3-} + \text{Ga}^{3+} + \text{NgO}3^{3-} + \text{Ga}^{3+} + \ldots \), respectively, resulting in polar layers. To stabilize a polar surface and overcome the polar discontinuity, a reconstructed, non-stoichiometric surface layer can form [13, 20]. Surface reconstructions due to polar stacking has been observed in (111),-oriented STO [16, 21], (110),-oriented STO [22], (110),-oriented DSO [19], (001),-oriented LAO [23], and (110),-oriented LAO [24, 25]. In order to study the surface reconstruction, thin films of LSMO and LFO were grown on the prepared substrates. The normalized oscillation lengths for the first four RHEED oscillations are shown in figure 5. For all the substrates, the first RHEED oscillation period is shorter than the following oscillation. A difference in the length of the first RHEED oscillation as compared to the following oscillations for thin films grown on (111),-oriented STO
have been linked to surface reconstruction, where the surface was found to be Ti-rich to screen the polarity [16]. Similar effects can take place for the polar surfaces reported on here. Although the termination of the unetched surfaces is unknown, the etching solutions employed selectively remove the A-site cations when applied to (001)pc-oriented surfaces, resulting in B-terminated substrates [6, 7]. Hence, taken together with the RHEED results, this suggests that the etched DSO and GSO surfaces are Sc-rich and the etched NGO surfaces are Ga-rich.

Conclusions
In conclusion, atomically flat surfaces of (111)pc-oriented DSO, GSO, and NGO are prepared by either etching, annealing, or in combination, with indications that the polar stacking order of along the [111]pc-direction results in a reconstructed surface. The choice of (111)pc-orientation, (110)_n or (101)_n, is found to be important for the step heights on the vicinal surface, resulting in step heights of one or two (111)pc interplanar distances, respectively. This step height dependency, which is not observed in (001)pc or (110)pc oriented materials, could be used to engineer certain interface properties.

Acknowledgements
The Research Council of Norway is acknowledged for providing funding through Grant No. 231290.
References:

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Figure 1: Tapping mode AFM of as received DSO (a) and GSO (b), annealed DSO (c) and GSO (d), and annealed and etched DSO (g) and GSO (h). Line scan for annealed DSO surface (e), annealed GSO surface (f), annealed and etched DSO (i), and annealed and etched GSO (j). The black lines in (c,d,g,h) indicate where the linescans are obtained. The dimensions of AFM micrographs are 3x3 μm².
Figure 2: Tapping mode AFM micrographs of NGO surfaces: (a) NGO(011)o, as-received, (b) NGO(011)o annealed 2 hours, (c) NGO(011)o annealed 2 hours and etched for 45 s, (f) NGO(011)o annealed 2 hours and etched for 120 s, and (h) NGO(101)o annealed 2 hours and etched for 120 s. Figures (c), (e), (g), and (i) are line scans corresponding to the surfaces shown in figures (b), (d), (f), and (h), respectively. The black lines in (b,d,f,h) indicate where the linescans are obtained. The dimensions of AFM micrographs are 3x3 μm².
Figure 3: The rotational patterns of a (101)$_o$-oriented and a (011)$_o$-oriented orthorhombic perovskite. The $u$ and $v$ labels indicate different octahedral rotations with regards to the surface. The figures are generated with VESTA [29]. (c) and (d) are line scans of the surfaces of (101)$_o$ and (011)$_o$-oriented NGO as comparison. The dashed orange lines indicate (111)$_{pc}$-layers.
Figure 4: Contact mode and friction force contrast for various treatments of (101)$_x$-oriented DSO, (101)$_y$-oriented GSO, and (110)$_z$-oriented NGO: unetched DSO (a, b), etched DSO (c, d), unetched GSO (e, f), etched GSO (g, h), unetched NGO (i, j), 45 s etched NGO (k, l), and 120 s etched NGO (m, n). The dimensions of all micrographs are 1x0.5 μm$^2$. 

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DSO   GSO   NGO
Figure 5: Statistics for the oscillation length for the first four oscillations for growth of LSMO grown on NGO(011)$_o$ and LFO on NGO(011)$_o$, DSO(101)$_o$, and GSO(101)$_o$. 
Paper C

Effect of (111)-oriented strain on the structure and magnetic properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films

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Journal of Physics: Condensed Matter, 30 255702, 2018
Effect of (111)-oriented strain on the structure and magnetic properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films
Effect of (1 1 1)-oriented strain on the structure and magnetic properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films

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Received 19 March 2018, revised 9 May 2018
Accepted for publication 14 May 2018
Published 31 May 2018

Abstract
Using strain, i.e. subtle changes in lattice constant in a thin film induced by the underlying substrate, opens up intriguing new ways to control material properties. We present a study of the effects of strain on structural and ferromagnetic properties of (1 1 1)$_{pc}$-oriented La$_{0.7}$Sr$_{0.3}$MnO$_3$ epitaxial thin films grown on NdGaO$_3$, SrTiO$_3$, and DyScO$_3$ substrates. (The subscript pc denotes the pseudo-cubic symmetry.) The results show that La$_{0.7}$Sr$_{0.3}$MnO$_3$ assumes a monoclinic unit cell on NdGaO$_3$ and DyScO$_3$ and a rhombohedral unit cell on SrTiO$_3$. For La$_{0.7}$Sr$_{0.3}$MnO$_3$ on NdGaO$_3$ and DyScO$_3$ a uniaxial magnetic anisotropy is found, while La$_{0.7}$Sr$_{0.3}$MnO$_3$ on SrTiO$_3$ is magnetically isotropic. The Néel model is used to explain the anisotropy of the thin films on NdGaO$_3$ and DyScO$_3$; however, for La$_{0.7}$Sr$_{0.3}$MnO$_3$ on DyScO$_3$ the effect of octahedral rotations needs to be included through the single ion model. Through examination of the Curie temperature of the strained films we suggest that (1 1 1)-strain has a different effect on the Jahn–Teller splitting of $e_g$ and $t_{2g}$ electron levels than what is seen in (0 0 1)$_{pc}$-oriented La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films.

Keywords: strain, LSMO, magnetic anisotropy, crystal symmetry

(Some figures may appear in colour only in the online journal)

Introduction
Control of magnetic properties is important for the realization of spintronic devices such as magnetic tunnel junctions. Central to the realization of such devices is the possibility to tune the magnetic anisotropy [1]. Epitaxial thin film synthesis allows tuning the magnetic properties by inducing tensile or compressive strain in thin films through suitable choice of substrate. Especially, the magnetic anisotropy has been shown to be susceptible to both strain and symmetry, controllable in thin films through the choice of substrate [2–6]. Connected to strain engineering is understanding the effect of octahedral rotations on thin film properties. Oxygen octahedral rotations are responsible for a thickness driven change in anisotropy direction for La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) films on (0 0 1)$_{pc}$-oriented substrates [7] (We use the subscripts c, pc, rh, o, m, and t for cubic, pseudocubic, rhombohedral, orthorhombic, monoclinic and triclinic, respectively.). In LSMO/ Eu$_{0.7}$Sr$_{0.3}$MnO$_3$ superlattices the creation of octahedral superstructures enables spatial control of the ferromagnetism and electronic bandwidth [8].

An intriguing material to study in this regard is LSMO, a room temperature ferromagnetic perovskite oxide with a near 100% spin-polarization, and a strong coupling between atomic structure on the one hand and electronic and magnetic properties on the other hand [9, 10]. In bulk, LSMO is...
twinned rhombohedral and reported to have either an \((1 \overline{1} 1)_{pc}\) easy plane of magnetization \([11, 12]\), or \((1 \overline{1} 1)_{pc}\) easy direction \([13]\). Extensive research has focused on tuning the magnetic anisotropy by strain in thin films with a \((001)_{pc}\) surface orientation \([12]\). For thin films of LSMO on cubic substrates, tetragonal and monoclinic unit cell structures have been reported under tensile strain on \((001)_{pc}\)-oriented \(SrTiO_3\) (STO), while under compressive strain on \((001)_{pc}\)-oriented \((LaAlO_3)_{0.3}-(Sr_2AlTaO_6)_{0.7}\) (LSAT) only monoclinic unit cell structures are reported \([14, 15]\). In both cases a biaxial anisotropy with magnetically easy axes along the \((1 \overline{1} 0)_{pc}\) directions are reported, with an additional uniaxial contribution in the case of LSAT \([2, 6]\). For orthorhombic substrates a monoclinic structure is found for both LSMO under tensile strain on \((110)_{pc}\)-oriented \(DyScO_3\) (DSO) and under compressive strain on \((001)_{pc}\)-oriented \(NiGaO_3\) (NGO) \([15]\). The anisotropy of tensile strained LSMO on orthorhombic substrates is uniaxial, with the easy axis aligned along the direction of the largest strain, except for \((111)_{pc}\)-oriented NGO where the easy axis has been reported to change with film thickness \([4, 5, 16]\). In addition to tuning the magnetic properties with strain, changing the crystallographic orientation opens further avenues for property engineering. For LSMO on STO it has been found that the interfaces of \((110)_{pc}\) and \((111)_{pc}\)-oriented LSMO are more bulk-like as a function of thickness than \((001)_{pc}\)-oriented interfaces \([17]\), while differences in switching mechanisms and anisotropy are observed between films of LSMO on \((001)_{pc}\), \((100)_{pc}\), and \((100)_{pc}\)-oriented NGO \([18]\).

Recently, the interest in \((111)_{pc}\)-oriented films has grown considerably due to the possibilities offered by symmetry engineering on such facets by strain. The three-fold symmetry has been shown to result in emerging properties like polar metals \([19]\), exchange bias at the interface between a ferromagnetic and a paramagnetic material \([20]\), switchable ferrimagnetic moments as result of interface oxygen octahedral rotations \([21]\), and predicted Goldstone-like behavior of compressively strained \(LaAlO_3\) (LAO) \([22]\). The magnetic anisotropy of LSMO on \((111)_{pc}\)-oriented STO has been found to have a weak in-plane anisotropy following the high symmetry directions of the substrate \([23]\), different from when deposited on \((001)_{pc}\)-oriented STO.

In order to address how \((111)_{pc}\)-strain affects the structural symmetry and magnetic anisotropy of LSMO thin films we synthesized LSMO thin film on a range of different substrates and determined material properties using x-ray diffraction and magnetic characterization techniques. The results point towards a distinct response to strain as compared to \((001)_{pc}\)-strain, and the possibility to employ strain in \((111)_{pc}\)-oriented thin films to tailor the magnetic anisotropy of LSMO.

### Experimental

Epitaxial LSMO films of 19nm to 26nm thickness were grown on \((011)_{pc}\)-oriented NGO, \((111)_{pc}\)-oriented STO, and \((101)_{pc}\)-oriented \(DyScO_3\) (DSO) substrates (all corresponding to \((111)_{pc}\) facets) by pulsed laser deposition. The substrates were prepared for deposition using two different methods. The NGO and DSO substrates was annealed for two hours at 1050 °C in oxygen flow. A KrF excimer laser (λ = 248 nm) with a fluence of ~2 J cm\(^{-2}\) and a repetition rate of 1 Hz was employed to ablate material from a stoichiometric LSMO target. The substrates were heated to 540 °C in a 0.35 mbar oxygen atmosphere during deposition with a target to substrate distance of 45 mm, in order to ensure 2D growth \([24]\).

During deposition, the growth was monitored with reflection high-energy electron diffraction (RHEED). The samples were cooled in a 100 mbar oxygen atmosphere after deposition. After deposition the film topography was characterized with atomic force microscopy (AFM, Veeco Nanoscope V).

Micrographs of the surfaces of the films grown on NGO, STO and DSO are shown in figures 1(a)–(c), respectively, with well-defined steps and terraces, indicating high film quality.

Bulk LSMO has a rhombohedral unit cell (space group R-3c) with \(a = 5.471\) Å and \(c = 60.43°\) \([25]\). Both NGO and DSO have an orthorhombic unit cell (space group Pbnm) with lattice parameters \(a = 5.427\) Å, \(b = 5.500\) Å, \(c = 7.705\) Å \([26]\), and \(a = 5.44\) Å, \(b = 5.71\) Å, \(c = 7.89\) Å \([27]\), respectively. STO is cubic (space group Pm-3m) with lattice constant \(a = 3.905\) Å \([28]\). The strain along an \(hk\) direction is defined as \(\varepsilon_{hl} = (d_{hl,sub} - d_{hl,bulk})/d_{hl,bulk}\), with \(d_{hl,sub}\) and \(d_{hl,bulk}\) being the lattice parameter of the substrate and bulk LSMO, respectively. The calculated strain values along the primary in-plane directions \((11 \overline{1})_{pc}\) and \((1 \overline{1} 11)_{pc}\) can be found in table 1.

The crystalline structure of the LSMO thin films was characterized using a four-circle, high-resolution x-ray diffractometer (XRD, Bruker D8). Rocking curves around the LSMO \((111)_{pc}\) reflection reveal full width at half maximum values between 0.035° and 0.04°, on the same order as for the substrates, indicating high quality films. Reciprocal space maps were recorded around asymmetrical reflections. For the thin film on NGO, the \((330)_{pc}\), \((114)_{pc}\), \((312)_{pc}\), and \((132)_{pc}\) reflections (in this work we use parenthesis to denote reflections...
to ease inclusion of crystal symmetry subscript) were used to determine the film’s unit cell. The same reflections (corresponding to (028), (060), (244), and (−244),) were used for the film on NGO. However, for the film deposited on DSO the (208), (600), (316), and (3−16), reflections (corresponding to (330), (114), (231), and (321),) were utilized, as substrate reflections overlap the film reflections for the (424), and (4 − 24), peaks. In addition, the symmetrical (111) reflection was used for all structures.

Magnetic measurements were performed using a vibrating sample magnetometer (VSM). Due to a strong paramagnetic signal from both NGO and DSO substrates, hysteresis measurements were also performed by MOKE at room temperature. Magnetic anisotropy was investigated using the magneto-optical Kerr effect in the longitudinal configuration (L-MOKE) at room temperature. Hysteresis curves were measured at different angles by rotating the samples in a sinusoidal H-field (in the plane of the film). An alternating magnetic field with an amplitude of 100 Oe and a frequency of 10 Hz was used to achieve full saturation of the samples. Each hysteretic curve was calculated as average of 1000 individual loops.

To ensure that the observed MOKE signal does not originate from the NGO and DSO substrates, element specific x-ray magnetic circular dichroism (XMCD) spectroscopy at beamline 4.0.2 at the advanced light source (ALS) has been performed (see supplementary materials figures S1 and S2 available online at stacks.iop.org/JPhysCM/30/255702/mmedia).

Results and discussion

Figure 2 depicts θ-2θ scans of the (111)pc peaks of LSMO deposited on DSO, STO, and NGO respectively. The position of the (111)pc reflection of LSMO shifts due to strain from the substrates, the average strain being −0.70%, 0.64%, and 2.44% for NGO, STO, and DSO, respectively. In figures 3(a)–(c) reciprocal space maps (RSM) of LSMO on the three substrates are shown. For all films the in-plane component of the film peak is coinciding with the value of the substrate, confirming coherent film growth. The features (Qpc) indicating the out of plane lattice constant in figure 3(a) for LSMO on STO does not depend on the choice of reflection. On (001)-oriented STO this would correspond to a tetragonal unit cell. However, due to the trigonal symmetry of the (111)pc STO surface, the constant Qpc value indicates a rhombohedral/hexagonal unit cell. Similarly, the RSM data for LSMO on NGO reveal a constant value for the out-of-plane parameter for the reflections investigated (figure 3(b)). Due to the orthorhombic symmetry of the DSO substrate, this is consistent with a monoclinic unit cell of LSMO. We note that the data for LSMO on DSO also can be represented by a strained hexagonal unit cell. To establish a hexagonal unit cell on a (111)pc-oriented surface the relation between the primary in-plane directions needs to be 1/√3. This is not the case for an orthorhombic unit cell, though due to the out-of-plane symmetry found in the RSM data, a strained hexagonal unit cell can be inferred with γ = 118.2° smaller than γ = 120° in a proper hexagonal unit cell. Figure 3(c) shows the reflections for LSMO on NGO. Here the out-of-plane peak positions vary, revealing a triclinic unit cell. The refined unit cell parameters are listed in table 2, while figure 4(a)–(c) depicts the resulting unit cells and their relationship to the substrate. Here, LSMO under compressive strain (NGO) is found to be triclinic while it is monoclinic when deposited on (001)-oriented NGO. However, it is possible to obtain a monoclinic unit cell for compressively strained (111)pc LSMO on NGO by tuning the laser-fluence during deposition (see supplementary materials, figure S3). The triclinic LSMO film on NGO presented here has been grown using the same laser-fluence as the rhombohedral and monoclinic films on STO and DSO, respectively.

The structure of rhombohedral LSMO can be expressed using a monoclinic unit cell, enabling a more detailed comparison between the different systems. In figure 4(d) the evolution of the lattice parameters and distortion angle as a function of average in-plane strain, ε∥,avg = (ε1∥−10pc + ε3∥−10pc)/2 is shown. The values for bulk unstrained LSMO are plotted as open circles. For all films, the b-parameter is chosen as the parameter locked to the substrate. This corresponds to the [100], [−100], and [010], directions for the NGO, STO and DSO substrates, respectively. All free parameters, a⊥, ε⊥, β, vary to accommodate the strain.

The β angle increases from β < 90° for compressive strain to β > 90° for tensile strain (β = 90.5° for bulk LSMO).

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<th>d1−2 (Å)</th>
<th>ε1−10 (%)</th>
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ε, which for LSMO as compared to the tensile strained films. In (0 0 1)pc-oriented the compressive regime, where all lattice parameters change the films on STO and DSO. This is not the case moving in to distortion, of orientation, has a higher symmetry as compared to com-

pressed strained LSMO.

The film strain affects the magnetic properties of the thin films. The magnetization of (1 1 1) oriented LSMO on STO is macroscopically isotropic, as seen in figure 5(a). This is in full agreement with previously reported results [23] of a weak microscopic anisotropy with a six-fold symmetry, resulting in a macroscopically isotropic response. By utilizing the Néel model of magnetic anisotropy [31], which has been used to explain the magnetic anisotropy of (001) SrTiO3 and (110) SrTiO3-oriented LSMO thin films, an analytical expression for the anisotropy energy of a rhombohedral unit cell can be found [32]:

\[ E = -6\lambda L(r_0) \left( \cos^2 \theta - \frac{1}{2} \right) \]

where the largest angle on each side face of the rhombohe-
dral unit cell is modeled as 90° + 2b, L(r_0) is the dipolar Néel parameter at the equilibrium value r_0, which for LSMO is found to be negative, and θ is the angle of the magnetization with the [1 1 1]c direction. This results in an easy (1 1 1)c plane, corroborating the experimental results. A surface plot of the anisotropy energy can be seen in the insert of figure 5(a).

Figures 5(b) and (c) show MOKE data for LSMO on NGO and DSO, respectively, exhibiting a strong in-plane aniso-

tropy. LSMO on NGO shows a clear difference between the [100]c and [01 –1]c in-plane directions (figure 5(b)), with [100]c, as magnetically hard axis with a close to linear response to the applied field, while the response to the applied magnetic field along the [01 –1]c easy axis leads to nearly square hysteresis curve. The Néel model predicts an easy axis along the most tensile strained direction, which in this case is [01 –1]c. Solving the Néel model for a triclinic unit cell numerically (supplementary material figure S4) a two-fold magnetic anisotropy is found with easy axis and hard axis along [01 –1]c and [100]c, respectively.

From the Néel model it is expected that LSMO films on DSO will have an easy axis along the direction of largest tensile strain, i.e. [010]c. However, the data reveals a hard axis along the [010]c direction and an easy axis along [10 –1]c, as shown in figure 5(c). Hence, applying the Néel model does not replicate the observed effective magnetic anisotropy (supplementary material figure S5). We note that the Néel model only considers bond length and angle between the Mn atoms. As the source of the magnetization in LSMO is the double exchange mechanism, the angle and length of the Mn–O–Mn bonds are important for the magnetic characteristics, and can be incorporated in a single ion model [33]. This model

![Figure 3. Reciprocal space maps of the LSMO films on (a) STO ([312], [312], [330], and [114] reflections), (b) DSO ([4 –2 4], [424], [208], and [600] reflections), and (c) NGO ([2 -4 4], [244], [028], and [060] reflections). The out-of-plane reciprocal space vector is defined as \( Q_{\perp} = 4\pi / \lambda \sin(\theta) \) with \( \lambda = 1.540598 \ \text{Å}. \)](image_url)
Table 2. The refined unit cell parameters for LSMO films deposited on NGO(0 1 1)o, STO(1 1 1)c, and DSO(1 0 1)o.

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<td>7.75</td>
<td>90.1</td>
<td>89.5</td>
<td>90.1</td>
</tr>
<tr>
<td>STO</td>
<td>Rhombohedral</td>
<td>5.47</td>
<td></td>
<td></td>
<td>60.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DSO</td>
<td>Monoclinic</td>
<td>5.47</td>
<td>5.73</td>
<td>7.78</td>
<td>90</td>
<td>90.9</td>
<td>90</td>
</tr>
</tbody>
</table>

Figure 4. Sketches of the resulting unit cells obtained from the RSM data. (a) Triclinic (t) LSMO on (01 1)o-oriented NGO. (b) Rhombohedral (rh, black) or hexagonal (h, blue) LSMO on (1 1 1)c-oriented STO. (c) Monoclinic (m, black) or distorted hexagonal (h∗, blue) LSMO on (1 0 1)o-oriented DSO. (d) Normalized lattice parameters and angle \(\alpha\) as a function of average in-plane strain. The unit cell volumes for bulk LSMO and LSMO on STO are found by expressing their rhombohedral unit cells as monoclinic. The values for bulk LSMO are shown as open circles. (e) Measured out-of-plane strain and volume versus average in-plane strain. Bulk values are marked at open circles.

Figure 5. (a) Magnetization data for LSMO on STO. 0° corresponds to the \([1−1 0]c\) direction. The insert shows a surface plot of the magnetic anisotropy energy of LSMO on STO. (b) Magnetization data for LSMO on NGO. 0° corresponds to the \([1 0 0]o\) \([1−1 0]pc\) direction. (c) Magnetization data for LSMO on DSO. 0° corresponds to the \([0 1 0]o\) \([1−1 0]pc\) direction.
assumes that the crystal field is a sum of the atomic crystal fields and a strong spin–orbit coupling. The anisotropy energy from a single Mn–O bond is given by:

\[ E_i = -\frac{eQ_i}{16\pi\varepsilon_0R_i} (3\cos^2\theta_i - 1) \]

where \( e \) is the electron charge, \( Q_i \) is the effective charge of the ligand, \( \varepsilon_0 \) is the vacuum permittivity, \( R_i \) is the Mn–O bond length, and \( \theta_i \) is the angle between the magnetization direction and the Mn–O bond. \( E_i \) is summed over all bonds in a two by two by two structure of pseudo-cubic unit cells to find the total anisotropy energy \( E \). By applying the single ion model, without octahedral rotations, the same result as for the Néel model must be obtained. This results in \( Q_{22} \) being negative for LSMO on DSO and NGO.

Using the single ion model, the magnetic anisotropy of LSMO films on DSO and NGO can be expressed as a function of octahedral rotations. For LSMO on DSO the monoclinic unit cell can have three possible rotation patterns in the Glazer tilt system \([34]\), \( a' b' c'^2 \) \((\neq 12)\), \( a' a' c' \) \((\neq 15)\), or \( a' b' c' \) \((\neq 11)\). As the \( a_{pc} \) and \( b_{pc} \) are mirror symmetrical across the \((010)_{pc}\) plane, the rotations need to be symmetrical across that plane and consequently \( a' a' c' \), \( a' a' c' \), or \( a' a' c' \) are possible. For LSMO on NGO the triclinic unit cell can only have the rotation system \( a' b' c' \) \((\#2)\). Since triclinic distortion in this case is small \((\alpha \approx 90.1^\circ, \gamma \approx 90.1^\circ)\), the difference in rotation magnitudes around \( a_{pc} \) and \( b_{pc} \) will be small, and are therefore here treated as equal. The resulting anisotropy phase diagram can be seen in figure 6, with the shaded regions indicating the intervals of rotation magnitudes that recreate the observed anisotropy for LSMO on DSO and NGO.

With regards to LSMO on DSO, rotations of at least 3.3° around \( c_{pc} \) is needed, ruling out \( a' a' c' \) as a possible rotation pattern. Both \( a' a' c' \) and \( a' a' c' \) can result in a hard axis along \([010]\), for a certain range of rotation angles. The rotation pattern \( a' a' c' \) requires, for a given rotation around \( c_{pc} \) and \( b_{pc} \), a larger rotation around \( c_{pc} \), than is the case for the rotation pattern \( a' a' c' \). The rotation angle of bulk LSMO is 4.48° \([25]\), while rotations of 6° with a rotation pattern of \( a' a' c' \) been found for LSMO on \((111)\)-oriented STO by DFT calculations \([35]\). LSMO on DSO has a larger average tensile strain than for LSMO on NGO. We note that rotations in \((111)\)-oriented LAO are found by DFT to increase close to linear with amount of tensile strain \([22]\), allowing us to extrapolate an expected 10.3° rotational angle for LSMO on DSO. In \((001)\)-oriented thin films, the effective rotations are larger around the most tensile strained direction \([36]\). Assuming this is also true for \((111)\)-oriented LSMO, the rotations should be largest around the \( a_{pc} \) and \( b_{pc} \) directions \((a_{pc} = b_{pc} = 3.96 \text{°})\), whilst \( c_{pc} = 3.89 \text{°}\). However, from the single ion model calculations, (shown in figure 6) we note that both for \( a' a' c' \) and \( a' a' c' \) the rotation around \( c_{pc} \) is expected to be largest. For a 10.3° rotational angle around \( a_{pc} \) and \( b_{pc} \), a minimum of \( c_{pc} = 13 \text{°} \) and \( c_{pc} = 10.7 \text{°} \) is needed to establish the observed anisotropy for \( a' a' c' \) and \( a' a' c' \) respectively. For the triclinic structure of LSMO on NGO the results from the single ion model calculation in figure 6 indicates that the observed anisotropy is energetically favorable for a range of rotations including no octahedral rotations. DFT studies of \((111)\)-strain indicate that compressive strain results in smaller than bulk rotations around the pseudo-cubic axes \([36]\), consistent with the phase diagram in figure 6.

The remanent magnetization close to the Curie temperature \(T_C\) for strained LSMO is shown in figure 7. The data were taken while increasing the temperature. The Curie temperature is determined by taking the lowest temperature at which the remanent magnetization vanishes, a method that provides a reliable measure of \(T_C\), though often lower values than when the saturation magnetization is used \([37]\). The Curie temperatures are found at 328 K, 334 K, and 338 K for the films on

Figure 6. Octahedral rotation angle dependence of the hard axis direction for LSMO on DSO for \(a' a' c' \) and \(a' a' c' \). For a certain range of rotation angles, the rotation pattern are calculated using the single ion model. The octahedral rotation combinations that result in an anisotropy matching the experimentally found anisotropy are shown as striped areas for the film on DSO and as shaded blue for the film on NGO.

Figure 7. Remanent magnetization of the LSMO films on NGO, STO and DSO for the temperature range around the Curie temperatures.
GSO, STO and NGO, respectively. Millis, Darling [38] has proposed a model to describe the effects of strain on the Curie temperature of manganites. 

\[ T_C(\varepsilon B, \varepsilon') = T_C(0, 0) \left[ 1 - a \varepsilon - b \varepsilon' \right]. \]

With \( \varepsilon B = 1/2(2\varepsilon_{1110} + \varepsilon_{1000} + \varepsilon_{0110} - \varepsilon_{1100}) \), a measure of the bulk compression and \( \varepsilon' = 1/4(2\varepsilon_{1110} - \varepsilon_{1000} - \varepsilon_{0110} - \varepsilon_{1100}) \), a measure of the biaxial distortion. An increase in compressive strain and therefore an increased \( \varepsilon B \) tends to increase the electron hopping probability, decreasing the effect of the electron lattice coupling and therefore the Curie temperature. The biaxial distortion, \( \varepsilon' \), is related to the Jahn–Teller splitting of the \( eg \) and \( t_{2g} \) electron levels. A deviation from \( \varepsilon' = 0 \) will increase the localization of the electrons and therefore lower the Curie temperature. Corresponding to \( \varepsilon B \) and \( \varepsilon' \) are the experimental quantities \( a = \frac{1}{2} \left[ \frac{d_T}{d_B} \right] \) and \( b = \frac{1}{4} \left[ \frac{d_B}{d_T} \right] \), predicted to be approximately 6 and 1400, respectively, for \( La_{1/3}Sr_{1/3}MnO_3 \) [38]. For (0 0 1)-oriented LSMO, there are several reports of the values of \( T_C(0, 0) \), \( \alpha \), and \( b \). Adamo [30] found \( T_C(0, 0) = 345 \) K, \( \alpha = 1.55 \), \( b = 1460 \). Tsui [2] reported \( T_C(0, 0) \), \( \alpha \), and \( b \) values of 334 K, 2, and 187, respectively, and Ranno [40] reported a \( b \) value of 1400. From the measured Curie temperatures we find \( T_C(0, 0) = 333 \) K, \( \alpha = 3.9 \), and \( b = -125 \). The values of \( T_C(0, 0) \) and \( \alpha \) obtained for LSMO from our set of strain data are in good agreement with the predictions and reported values for (0 0 1)-oriented films, while \( b \) is an order of magnitude lower than most values obtained from (0 0 1)-oriented films and have opposite sign. From the results of Adamo [30], both the LSMO film on NGO and the LSMO film on DSO are predicted to have a lower \( T_C \) than the LSMO film on STO due to the biaxial strain from the orthorhombic substrates. However, here the Curie temperature of the LSMO film on NGO is larger than for LSMO on STO, suggesting that \( T_C \) in (1 1 1)_pc-oriented LSMO thin films is to a smaller degree affected by biaxial strain. This can possibly indicate a smaller degree of Jahn–Teller splitting of the \( eg \) energy levels when applying strain to (1 1 1)_pc-oriented LSMO films, consistent with that the \( eg \) energy levels do not split due to (1 1 1)_pc-oriented strain contrary to what is found for (0 0 1)_pc-oriented strain [41].

Conclusions

In conclusion, (1 1 1)_pc-oriented LSMO thin films have been grown on NGO, STO, and DSO substrates in order to investigate the effects of strain on structural and magnetic properties. Compressively strained films on NGO are found to be triclinic or monoclinic, while films with tensile strain are found to be rhombohedral on STO and monoclinic on DSO, different from that obtained from (001)_pc-oriented strain. A uniaxial magnetic anisotropy is found for the LSMO films on both NGO and DSO with the hard axes along [1 0 0], and [0 1 0], respectively. For LSMO on STO, no macroscopic anisotropy is observed. The anisotropy of the LSMO films on NGO and NGO is well described by the Néel model of magnetic anisotropy, while for LSMO on DSO, incorporation of octahedral rotations through the single ion model is needed to explain the uniaxial anisotropy. Lastly, it was found through looking at the Curie temperatures as a function of strain that (1 1 1)_pc-oriented biaxial strain has a different effect on the Jahn–Teller splitting of \( eg \) and \( t_{2g} \) electron levels than observed in (0 0 1)_pc-oriented LSMO films.

Acknowledgements

The Research Council of Norway is acknowledged for providing funding through Grant No. 231290. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

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References

[5] Nishihara H, Houwman E, Boschker H, Mathews M, Blank D H A and Rijnders G 2009 Rotation of the magnetic easy axis in La_{0.67}Sr_{0.33}MnO_3 thin films on NdGaO_3 (1 1 2) Appl. Phys. Lett. 94 042502

https://orcid.org/0000-0003-0787-8476


[14] Boschker J E, Monsen Å F, Nord M, Mathieu R, Gregstad J K, Holnestad R, Wahlströsm E and Tybell T 2013 In-plane structural order of domain engineered La$_{0.3}$Sr$_{0.7}$MnO$_3$ thin films Phil. Mag. 93 1549–62


[16] Mathews M, Houwman E P, Boschker H, Rijnders G and Blank D H A 2010 Magnetization reversal mechanism in La$_{0.7}$Sr$_{0.3}$MnO$_3$/LaFeO$_3$ reconstructions at the interface of (1 11)-oriented Crystalline symmetry controlled magnetic switching in perovskite ABO$_3$ heterostructures (arXiv:1710.10996)


[21] Hallsteinseim I et al 2016 Concurrent magnetic and structural reconstructions at the interface of (1 1 1)-oriented La$_{0.3}$Sr$_{0.7}$MnO$_3$/LaFeO$_3$ Phys. Rev. B 94 201115

[22] Moreau M, Martihsen A, Selbach S M and Tybell T 2017 First principles study of the effect of (1 1 1) strain on octahedral rotations and structural phases of LaAIO$_3$ Phys. Rev. B 95 064109

[23] Hallsteinseim I, Folven E, Olsen F K, Choupdekar R V, Rzchowski M S, Eom C B, Gregstad J K and Tybell T 2015 Crystalline symmetry controlled magnetic switching in epitaxial La$_{0.3}$Sr$_{0.7}$MnO$_3$ thin films APL Mater. 3 062501


[27] Pies W and Weiss A 1976 c74, XVI. 1.2 Hydroxo-Compounds of Scandium (Hydroxoscostandates), XVI. 2 Oxo-Compounds of Yttrium (Oxystroct Key Elements: d9, d10, d1, d3, $f$-Elements (Berlin: Springer)) p 13


[35] Moreau M, Selbach S M and Tybell T 2017 Octahedral coupling in (1 1 1)- and (001)-oriented La$_{0.3}$Sr$_{0.7}$MnO$_3$/ SrTiO$_3$ heterostructures (arXiv:1710.10996)


Supplementary materials

Effect of (111)-oriented strain on the structure and magnetic properties of La$_{2/3}$Sr$_{1/3}$MnO$_3$ thin films

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X-ray magnetic circular dichroism

Element specific x-ray magnetic circular dichroism (XMCD) spectroscopy was done at beamline 4.0.2 at the Advanced Light Source (ALS). The XMCD spectra were measured in total-electron-yield mode by monitoring the sample drain current. The x-rays were incident at 30° to the sample surface. The hysteresis measurements were performed by a sweeping field, using an eight-pole electromagnet, between ±0.3 T parallel to the x-ray beam, and probing at element specific dichroism from the two circular polarizations.

Figure S1 and S2 shows hysteresis curves acquired from XMCD measurements for La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) on NdGaO$_3$ (NGO) and DyScO$_3$ (DSO), respectively, which are consistent with the other magnetic measurements presented.
Figure S1: Magnetization data for LSMO on NGO obtained by XMCD. 0° corresponds to the [100]₀ lattice direction.

Figure S2: Magnetization data for LSMO on DSO obtained by XMCD. 0° corresponds to the [010]₀ lattice direction.
Notes on structure refinement
Structure refinement was done by finding the symmetry elements through the positions of $Q_\perp$ and $Q_{||}$. For example an epitaxial thin film on a cubic substrate, equal $Q_\perp$ positions indicate a rhombohedral/hexagonal or cubic unit cell. Only one value of $Q_\perp$ results in a cubic unit cell ($Q_{film} = Q_{substrate}$), other values indicate a rhombohedral/hexagonal unit cell, which is the case for LSMO on SrTiO$_3$ (STO). With regards to the DSO substrate, the in-plane symmetry removes the possibility of a cubic unit cell and a hexagonal unit cell in the (001)$_h$ orientation (the subscripts $h$ and $o$ refers to the hexagonal and orthorhombic symmetry, respectively) for the LSMO thin film. A (101)$_h$-oriented hexagonal or orthorhombic unit cell is also possible, though not consistent with the measured $Q_\perp$ values, leaving a monoclinic unit. For the LSMO film on NGO, the same possible unit cell symmetries must be considered, though here only a triclinic unit is coherent with the $Q_\perp$ values. Knowing the symmetry, the parameters were found through minimization of the equations for the interplanar distance of the relevant planes.

Alternative unit cell structure of LSMO on (011)-oriented NGO
By changing the deposition laser fluence, the structure of LSMO on (011)$_o$-oriented NGO can change from a triclinic to a monoclinic unit cell. Figure S3 shows linear scans of a 21 nm LSMO film on (011)$_o$-oriented NGO. The overlapping peak positions of (-136)$_o$ and (-336)$_o$ along with the unequal positions of (152)$_o$ and (352)$_o$ indicate a monoclinic unit cell.
Figure S3: Linear scans of (-136), (-336), (152), and (352), peaks of a 21 nm LSMO film on NGO(011). The film peak positions indicate a monoclinic LSMO unit cell.

Anisotropy energy calculated using the Néel model

Figures S4 and S5 shows the calculated anisotropy energy obtained from the Néel model of magnetic anisotropy for triclinic LSMO on (011),-oriented NGO and monoclinic LSMO on (101),-oriented DSO, respectively. In the same figures are the squareness of the hysteresis curves plotted. The squareness is here defined as $1 - M_r / M_s$ where $M_r$ is the remanent magnetization and $M_s$ is the saturation magnetization. In the case of LSMO on (011),-oriented NGO, the experimental data follows Néel model. However, that is not the case for LSMO on (101),-oriented DSO, where the peaks of the experimental data and results from the Néel model are shifted 90° with respect to each other.
Figure S4: The in-plane anisotropy (blue line) calculated from the Néel model of triclinic LSMO on (011)$_c$-oriented NGO with the squareness (orange stars) of the experimentally obtained hysteresis curves. 0° corresponds to the [100]$_c$ lattice direction.

Figure S5: The in-plane anisotropy calculated from the Néel model of monoclinic LSMO on (101)$_a$-oriented DSO with the squareness (orange stars) of the experimentally obtained hysteresis curves. 0° corresponds to the [010]$_a$ lattice direction.
Effect of (111)-oriented strain on the structure and magnetic properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films
Paper D

Thickness dependent
uniaxial step edge anisotropy
in (111)-oriented
La_{0.7}Sr_{0.3}MnO_3

T. Bolstad, E. Lysne, U. L. Österberg, and T. Tybell
Submitted
Thickness dependent uniaxial step edge anisotropy in (111)-oriented $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$
Article type: Full paper

Thickness dependent uniaxial step edge anisotropy in (111)-oriented La$_{0.7}$Sr$_{0.3}$MnO$_3$

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Keywords: LSMO, magnetic anisotropy, step edges, (111)-orientation

Abstract

The magnetic anisotropy of films of La$_{0.7}$Sr$_{0.3}$MnO$_3$ grown on vicinal (111)-oriented SrTiO$_3$ substrates are investigated. For temperatures above the phase transition temperature of the substrate, a step edge induced uniaxial magnetic anisotropy is found at remanence with a thickness-driven change in easy axis direction, from perpendicular to the steps edges to parallel to the step edges with increasing thickness.

The anisotropy constant for the investigated (111)-oriented samples is of the same magnitude as for previously reported (001)-oriented samples. The data is discussed in the framework of in-plane rotations of the oxygen octahedra resulting in a uniaxial anisotropy. Furthermore, the magnetic anisotropy is sensitive to the structural phase transition at 105K of the substrate, and the anisotropy constant increases drastically as the temperature is lowered below 105K.
1. Introduction

Magnetic anisotropy in thin films has extensively been studied for the last 60 years, since control of the anisotropy opens for potential applications in electronic device technology.\(^1\) Important magnetic characteristics such as coercive field, magnetization, and domain structure are in part controlled by the magnetic anisotropy. Thus, engineering of the magnetic anisotropy is central to the development of spintronic technology. For example, control of the magnetic anisotropy is essential in the realization of magnetic tunnel junctions, where the resistance through the structure is controlled by the spin-orbit coupling at the interfaces and hence the two ferromagnetic electrodes ideally should have different switching dynamics.\(^2\)

Magnetic anisotropy control is also important for proposed devices based on domain wall movement such as racetrack memories.\(^3\) Albeit, large effort is focused on metallic systems, complex manganite oxides are interesting in this regard due their strong coupling between functional properties and detailed atomistic structure.\(^4\) \(\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\) (LSMO), especially, has received a significant amount of interest due to its robust room temperature ferromagnetism and a near 100 % spin polarization.\(^5,6\)

An experimental route to inducing anisotropy in thin films is to rely on stepped surfaces to break the magnetic symmetry. Such step edges provide both a change in shape, and a vertical interface between film and substrate. The effects of step edges on perovskite oxides thin films have been extensively studied. In LSMO, magnetic anisotropy effected by step edges was first observed in 13 nm thick films on highly vicinal, with a miss-cut of 10°, (001)-oriented \(\text{SrTiO}_3\) (STO) (all crystallographic designations in this article are in the pseudo cubic symmetry) at low temperature (80
K).\cite{7} The steps edges were found to induce a uniaxial anisotropy with the easy axis parallel to the step edges. Later, the effect was also observed at room temperature in 7 nm and 25 nm thick films LSMO grown on STO(001) with very low vicinal angles of 0.13° and 0.24°, respectively.\cite{8} For lower temperatures and in thicker samples, the biaxial magnetocrystalline anisotropy is found to dominate.\cite{8,9} The step density, i.e. vicinal angle, affects the thickness at which the uniaxial anisotropy disappears. For example, for a thickness of 120 nm, the uniaxial anisotropy is present in LSMO films grown on substrates with miss-cut angles larger than 4°.\cite{10}

The magnetic switching is found to proceed through nucleation and subsequent domain wall movement when the magnetic field is applied parallel to the step edges, and through coherent magnetization rotation when the field is applied perpendicular to the steps.\cite{7,11} The magnetic anisotropy due to step edges are in $La_{1-x}Ca_xMnO_3$ observed to induce a measurable anisotropy in both transport and thermoelectric properties.\cite{12,13} Anisotropic transport properties due to a step and terrace topology are also found in the double perovskite LaBaCo$_2$O$_{5.5-δ}$ on STO.\cite{14} For Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ on MgO, step edges are found to induce structural antiphase boundaries.\cite{15} By utilizing step edges in structural domain engineering in films of BiFeO$_3$ on STO, the ferroelectric coercive field can be lowered through the generation of nucleation sites at the steps.\cite{16} The effect of step edges on magnetic anisotropy has also been explored in metallic ferromagnetic thin films.\cite{17-22} For films of Co grown on Cu and Fe grown on Ag, the easy axis is seen to lie parallel to the step edges,\cite{17,20,21} while for Fe films on W, the easy axis is observed to lie either parallel or perpendicular to the step edges.\cite{18,19}
Advances in surface preparation techniques have recently enabled the exploration of (111)-oriented thin perovskite films.\textsuperscript{[23,24]} Due to the trigonal in-plane symmetry of (111)-oriented STO, deposited thin films of LSMO assumes a rhombohedral unit cell with no macroscopic in-plane anisotropy at saturation magnetization,\textsuperscript{[25]} albeit a 6-fold symmetry microscopically.\textsuperscript{[26]} In order to study the effects of step edges on (111)-oriented films of LSMO, which may have magnetic anisotropy, a small fields study of (111)-oriented LSMO is presented revealing subtle uniaxial anisotropy mechanisms due to the step edges with the easy axis direction dependent on film thickness, in addition to sensitivity to structural phase transitions of the substrate.

2. Experimental and theoretical framework

LSMO thin films with thicknesses ranging from 9.5 nm to 40 nm were grown on (111)-oriented STO substrates (miss-cut angle in the range 0.05° - 0.15°) using a pulsed laser deposition (PLD) system. A KrF excimer laser with wavelength $\lambda = 248$ nm, fluence of $\sim 2$ J cm$^{-2}$ and a repetition rate of 1 Hz was employed to ablate material from a stoichiometric LSMO target. The STO substrates were prepared by etching in buffered hydrofluoric acid for 45 seconds followed by annealing for one hour in oxygen flow at 1050 °C resulting in atomically smooth step and terrace substrate.\textsuperscript{[24]} During deposition the substrates were heated to 540 °C in a 0.35 mbar O$_2$ atmosphere with a distance of 45 mm from target to substrate, in order to ensure 2D growth.\textsuperscript{[27]} The growth was monitored by reflection high-energy electron diffraction (RHEED), and after deposition the samples were cooled in a 100 mbar oxygen atmosphere.

The crystalline structure of the films was examined using a four-circle, high-resolution x-ray diffractometer (XRD, Bruker D8). In Figure 1 (a) a typical linear
diffraction profile around the (111) reflections of STO and LSMO can be seen. The film thicknesses were determined from the thickness fringes. Rocking curves around the (111)-peak of LSMO reveal full width half maximum values of 0.035° and 0.04°, on the same order as for the substrates, indicating high quality films. Bulk LSMO has a rhombohedral unit cell (space group R-3c with lattice constant $a = 5.471$ Å and $\alpha = 60.43^\circ$), while STO is cubic at room temperature (space group Pm-3m with lattice constant $a = 3.905$). The low index in-plane directions for (111)-oriented LSMO are the $<1\bar{1}0>$ and $<11\bar{2}>$ family of directions and are illustrated in Figure 1 (b). The degree of strain relaxation was determined by linear scans of asymmetric substrate and film reflection peaks. For each sample, two reflections were studied, one with the in-plane component close to parallel to the step edges and one with the in-plane component close to perpendicular to the step edges. A reciprocal space map (RSM) of the 141 peak (in-plane component perpendicular to the step edges) of the 40 nm thick film with linear scan profiles is shown in Figure 1 (c-e). It has previously been found that (111)-oriented LSMO on STO assumes a rhombohedral unit cell,[25] which is consistent with the XRD results obtained in this study for all thicknesses. Surface characterization using atomic force microscopy (AFM, Veeco Nanoscope V) revealed a step and terrace structure with step heights of ~2.25 Å, consistent with the out-of-plane interplanar distance of ~2.22Å found from the XRD data.

The magnetic anisotropy was investigated using a magneto-optical Kerr effect setup in the longitudinal configuration (L-MOKE) at room temperature. Hysteresis measurements were obtained by applying a sinusoidal alternating magnetic field in the plane of the sample with amplitude 20 Oe and a frequency of 10 Hz to achieve full saturation. By rotating the sample in the plane of the sample, the magnetic response as
a function of the angle of the applied field was measured. Additionally, the
temperature dependency of the magnetic properties was determined using a vibrating
sample magnetometer (VSM). In order to investigate temperature dependency of the
anisotropy, the sample was rotated in increments of 30° with the field aligned along
the low index in-plane directions. In all cases, the anisotropy is probed by considering
the magnetization in remanence, at zero applied external field.

In order to quantify the anisotropy, a general model for the energy of uniaxial
anisotropy is used.\(^\text{[28]}\)

\[
\frac{E_a}{V} = K_u \sin^2(\theta - \phi)
\]  

(1)

where \(E_a\) is the anisotropy energy, \(V\) is the volume of the sample, \(K_u\) is the uniaxial
anisotropy constant, and \(\phi\) is the direction of the easy axis. \(K_u\) can be determined by
finding the anisotropy field, \(H_{an}\), defined as

\[
H_{an} = \frac{M_s}{(dM/dH)_{H=0}}
\]  

(2)

where \(M_s\) is the saturation magnetization and \(dM/dH\) is the derivative of the
magnetization with respect to the field for the hard axis at remanence. The uniaxial
anisotropy constant is then found using

\[
2K_u = \mu_0 H_{an} M_s
\]  

(3)
with $\mu_0$ being the vacuum permeability. By using a model first proposed by Zener,\textsuperscript{[29]} and further developed by Carr,\textsuperscript{[30]} the temperature dependence of the anisotropy constant can be modeled. The model assumes a ferromagnetic material with spontaneous magnetization produced by parallel spin alignment driven by exchange interactions, and temperature independent atomic coupling constants, resulting in, for uniaxial symmetry:

$$
\frac{K_u(T)}{K_u(T_0)} = \left( \frac{M_s(T)}{M_s(T_0)} \right)^3
$$

(4)

with $T$ being the temperature, and $T_0$ is a temperature below the Curie temperature. Here, $T_0$ is taken at 120 K due to the structural phase transition of the substrate at 105K, where STO undergoes a second order phase transition from cubic to tetragonal symmetry.

In the case of two sources of anisotropy, the total anisotropy energy is proportional to

$$
\frac{E_a}{V} \propto |K_{u,1} - K_{u,2}| \sin^2(\theta) = K_u \sin^2(\theta)
$$

(5)

where $K_{u,1}$ and $K_{u,2}$ are the anisotropy constants of the two sources of anisotropy. If two perpendicular anisotropy mechanisms are present, the easy axis will be dictated by the direction of the largest anisotropy constant. With two non-perpendicular anisotropies contributing, the resulting easy axis direction will lie between the two competing easy axes.
To investigate the role of unit cell symmetry, octahedral rotations and broken bonds as a source of magnetic anisotropy, the single ion model is utilized. The energy of a single Mn-O bond is given by

\[ E_i = -\frac{eQ_2}{16\pi\varepsilon_0 R_i^2} (3\cos^2\theta - 1) \]  \hspace{1cm} (6)

where \( e \) is the electron charge, \( Q \) is the effective charge of the ligand, \( Q_2 \) is the quadrupole moment of the magnetic ion, \( \varepsilon_0 \) is the vacuum permittivity, \( R_i \) is the Mn-O bond length, and \( \theta_i \) is the angle between the magnetization direction and the Mn-O bond. It has previously been found that \( QQ_2 \) is negative for LSMO. \( E_i \) is summed over all bonds in a structure of eight (111)-oriented pseudo-cubic units with bonds broken along a plane perpendicular to the surface representing the step edge.

3. Results and discussion

In order to illustrate the step edge anisotropy in (111)-oriented LSMO, the details of two typical films, 19 nm and 40 nm thick, are presented. Figure 2 (a) and (b) show AFM micrographs of the two films, respectively, along with corresponding remanent magnetization as a function of azimuthal angle in Figure 2 (c) and (d). Both films exhibit a uniaxial anisotropy, the 19 nm film with the easy axis perpendicular to the step edges, and the 40 nm film with the easy axis parallel to the step edges. The experimentally found anisotropy constants for the 19 nm and 40 nm films are shown in Figure 2 (e) and (f), respectively, along with the predicted temperature dependence from the model by Zener, showing good correspondence in the temperature range 110 K to 350 K. Below this range, the experimental value and theoretical values of \( K_u \)
diverges sharply, indicating a change in the origin of the anisotropy, linked to the structural changes in substrate at 105 K.

In Figure 3 (a) the easy axis direction relative to the step edge direction as a function of film thickness is shown, where an abrupt change in the relative direction of the easy axis occurs around a critical film thickness of 20 nm. In the same figure the anisotropy constants measured at 120 K, for each film respectively, are presented, showing no dependence on thickness, all being in the 100 J cm$^{-3}$ – 300 J cm$^{-3}$ range except from the film with a thickness of 30.2 nm, which exhibits a significantly higher value of the anisotropy constant. The surface of the 30.2 nm thick sample was characterized by circular indentations, indicating poorer film quality, not observed for the other samples and this sample will not be focused on for the rest of this article. The observed uniaxial anisotropy constants are of the same size order as what is found for (001)-oriented LSMO on STO (∼375 J cm$^{-3}$ at 150 K for 7 nm and 18 nm thick films).[32]

Figure 3 (b) depicts the degree of strain relaxation along and perpendicular to the step edges as a function of film thickness. In all samples, signs of micro relaxation were observed, with the film peak being shifted towards higher reciprocal lattice unit values as expected as LSMO has a smaller lattice constant than STO. However, no trend is observed with respect to thickness or direction relative to the step edges, nor to which of the high crystalline in-plane family of directions, $<1\bar{1}0>$ or $<1\bar{1}2>$, the relaxation was measured along. The relaxation is in all cases measured to be smaller than 2.5e-4 ± 2.5e-4 % employing the full width half maximum of the relevant peak as an estimate of the error bar.
Figure 3 (c) reveals the evolution of the out-of-plane parameter, $d_{111}$, along with the remanent moment along the easy axis at 120 K as a function of thickness. Both values increase with thickness and saturates between 20 - 25 nm.

The room temperature anisotropy obtained by MOKE is confirmed with VSM measurements, as shown in Figure 4 (a) where the remanent moment at 120 K and 50 K as a function of in-plane direction for the 19 nm film is presented. The remanent field as a function of temperature and magnetization direction for the 19 nm thick sample is shown in Figure 4 (b). A marked transition in the remanent magnetization is observed at the same temperature range as the change in $K_u$. The remanent magnetization along the [112], [10\bar{1}], and [2\bar{1}\bar{1}] in-plane directions drop in the tetragonal phase of STO, while along the [1\bar{1}0], [1\bar{2}1], and [0\bar{1}1] in-plane directions remanent magnetization increases. The same trend is seen for all samples, however, the exact in-plane directions with increased and decreased remanent magnetization is sample dependent. In order to explore the function of possible structural domains in the tetragonal phase,[33] measurements of evolution of the remanent magnetization at 50 K and 150 K upon repeated cooling and heating through the structural transition point is shown in Figure 5 (a), revealing an increase of magnetization upon subsequent cooling below 105K, as compared to the first run. The easy axis direction in the tetragonal phase as a function of thickness along with the anisotropy constant is plotted in Figure 5 (b), where no thickness-driven transition is observed.

One possible explanation for the observed thickness dependence of the anisotropy constant, is the presence of two competing, perpendicular, thickness dependent
anisotropies, $K_{u,1}$ and $K_{u,2}$, each dominant on different sides of the transition thickness. In such a scenario the total anisotropy constant, $K_u = |K_{u,1} - K_{u,2}|$, would decrease towards the transition point where $K_{u,1} = K_{u,2}$ before increasing again below, a development not perceived in the presented data, see Figure 3 (a). The data hence suggest a change in the structure of the magnetization at the critical thickness.

The observed dependence of the anisotropy on step edge directions above 105K, points towards a step-induced anisotropy. There are several possible reasons for this behavior, as reported reported in literature; broken bonds or missing atoms at the steps,$^{[20]}$ strain relaxation either along or perpendicular to the step edges, shape anisotropy, or uniaxial roughening at the interface.$^{[34]}$ Both shape anisotropy and uniaxial interface roughening are interfacial effects, which would lead to a decreasing $K_u$ with increasing thickness.$^{[8]}$ In the thickness range investigated, no clear trend with thickness is observed and the anisotropy constant is rather constant, pointing towards the cause of the anisotropy as not, primarily, an interface effect. With regards to the broken bonds model, it is found with the single ion model that regardless of step edge direction, the easy axis is aligned parallel to the step edge.

In (001)-oriented LSMO on $(LaAlO_3)_{0.3}-(Sr_2AlTaO_6)_{0.7}$, octahedral rotations are suggested to result in an uniaxial contribution to the biaxial magnetocrystalline anisotropy from LSMO strained to a substrate with cubic symmetry.$^{[35]}$ From the single ion model it can be shown that while a rhombohedral unit cell with an $\alpha'\alpha'\alpha'$ tilt pattern does not give an in-plane anisotropy, an infinitesimal deviation can give rise to a uniaxial anisotropy. Even though the XRD measurements are consistent with a rhombohedral unit cell for all thicknesses, a slight perturbation of the $\alpha'\alpha'\alpha'$ rotation
pattern, below the XRD resolution, could hence result in an in-plane easy axis. The elongation of $d_{111}$ with thickness affects the magnetic structure as seen from Figure 3 (c), where the remanent magnetization along the easy axis increases with $d_{111}$. As the in-plane lattice component is locked to the substrate, the change in magnetization does not occur due to bond elongation along the in-plane direction. Alternatively, the increase in magnetization can originate in a change in the Mn-O-Mn bond angle from octahedral rotations. For example, from the single ion model, it is found that an in-plane rotation along the step edge direction will result in an easy axis perpendicular to the rotation and vice versa. Hence, one possible interpretation of the presented data is a picture where non-symmetric octahedral rotations governs the magnetic easy axis, resulting from the change in out-of-plane parameter as the film thickness is reduced favoring in-plane octahedral rotations along the step edges.

From the temperature evolution of the uniaxial anisotropy constant and the remanent magnetization, shown in Figures 2 (e,f) and 4 (a), respectively, there is a change in anisotropy at the phase transition of STO. The transition of STO from cubic to tetragonal appears as an elongation along one of the $<001>$ directions, which corresponds to an elongation along the $<11\bar{2}>$ in-plane directions for a (111)-surface. According to the single ion model of magnetic anisotropy, this results in lower anisotropy energy along the direction of elongation for LSMO. In the tetragonal phase, the surface of STO is made up of a random pattern of twinned regions and large single-twin areas, which changes upon subsequent cooling and heating.[33] We speculate that this can give rise to a complex anisotropy, largely controlled by the interplay between step-induced anisotropy and magnetocrystalline anisotropy from the different structural domains. This is confirmed by repeated transitions through the
phase transition, where it is observed that the remanent moment (along [10\overline{1}]) changes after run one. while the remanent moment in the cubic phase has a smaller variation (Figure 5 (a)). The moment in the tetragonal phase trends towards a saturation value, possibly due to a locking in of the structural domains. Although, the relation between the easy axis of each structural domain and the step edge direction can in principle be known, the macroscopic easy axis direction of the low temperature phase is dependent on the exact domain distribution, and the value of $K_u$ under 105 K is thus only an approximation (Figure 5 (b)). However, measuring along the different low index in-plane directions gives values of $K_u$ of the same order. In the tetragonal phase of STO the easy axis directions for all samples except the 10.4 nm thick film is less than 45° away from the step edge direction, Figure 5 (b). The experimentally obtained macroscopic easy axis at different angles to the step-edges is consistent with two non-perpendicular competing anisotropies; one contribution to the anisotropy given by the step edges, the other by magnetcocrystalline effects with different directional contributions from different structural domains.

4. Conclusions

In conclusion, LSMO has been grown on (111)-oriented STO in a range of thicknesses from 9.5 nm to 40 nm in order to study the effect of vicinal substrates on magnetic anisotropy. We have shown that step edges induce a macroscopic uniaxial anisotropy with a thickness depended easy axis above 105K; the easy axis lies perpendicular to the step edges for thin films, while for films thicker than a critical thickness the easy axis aligns parallel to the step edges. These results are consistent with the six-fold microscopic anisotropy observed in previous work on (111)-oriented LSMO.\cite{26} Below 105 K, the effect of the substrate phase transition from a cubic to
tetragonal unit cell results in a competition between step-edge contributions to the
magnetic anisotropy and magnetocrystalline contributions from each crystalline
domain, and hence no thickness transition is observed except for a varying magnetic
easy-axis from sample to sample.

Acknowledgements

The Research Council of Norway is acknowledged for providing funding through
Grant No. 231290.

References

Electrical and Electronics Engineering, 2005.
R127.
[6] M. Bowen, M. Bibes, A. Barthélémy, J.-P. Contour, A. Anane, Y. Lemaitre,
3731.
2010, 12, 103033.
322, 41.
3188.
Figure 1: (a) A linear 0/20 scan of the (111) peaks of 40 nm LSMO on STO. (b) A schematic of the atomic configuration of the (111) surface with the low index direction indicated. (c) A reciprocal space map of the 141 reflections of 40 nm LSMO on STO, with in-plane component perpendicular to the step edges. The orange arrow indicates the linear scan shown in Figure (d), while the yellow and blue arrows indicate the linear scans shown in Figure (e).

Figure 2: The top row shows AFM micrographs of a (a) 19 nm and (b) 40 nm LSMO film. The second row shows the remanent magnetization of the (c) 19 nm and (d) 40 nm LSMO film as a function of in-plane angle obtained by MOKE. The relation between the field angle and step edge is shown in Figure (a). In Figures (e) and (f) the anisotropy constants obtained by VSM for the 19 nm and 40 nm films, respectively, as functions of temperature is shown. The measured values are shown as open, orange circles and the theoretical values are shown as filled blue circles.

Figure 3: (a) The difference in direction between step edge and easy axis (blue, open circles) obtained by MOKE at room temperature and the anisotropy constant at 120 K (orange stars) obtained by VSM as a function of film thickness. (b) The degree of relaxation as a function of thickness parallel (blue circles) and perpendicular (orange stars) to the steps. (c) The out-of-plane parameter d_{111} (blue, open circles) and the remanent magnetization obtained by VSM at 120 K along the easy axis (orange stars) as functions of film thickness.

Figure 4: (a) The remanent moment of the 19 nm thick film as a function of magnetization direction obtained at 50 K and 120 K, with the STO substrate in the tetragonal and cubic phase, respectively. (b) The remanent magnetization field as a function of temperature and film thickness. The data in both figures were obtained by VSM.

Figure 5: (a) The remanent magnetization of a 30 nm LSMO film at 50 K and 150 K upon repeated heating and cooling. (b) The difference between the easy angle direction and step edge direction (blue, open circles) and the anisotropy constant (orange stars) at 50 K as a function of film thickness. All data in this figure was obtained by VSM.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Thickness dependent uniaxial step edge anisotropy in (111)-oriented La$_{0.7}$Sr$_{0.3}$MnO$_3$. 
Paper E

Synthesis and characterization of (111)-oriented BaTiO$_3$ thin films

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Submitted
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Abstract

The synthesis of (111)-oriented BaTiO$_3$ thin films on Nb-doped SrTiO$_3$ and bilayers
of BaTiO$_3$ and La$_{0.7}$Sr$_{0.3}$MnO$_3$ on SrTiO$_3$ are investigated. With increasing thickness
the films are found to exhibit a decreasing out-of-plane lattice parameter and
increased surface roughness. The BaTiO$_3$ films on doped SrTiO$_3$ are found to be
relaxed with indications of increasing defect density with increasing thickness.
Through piezoresponse force microscopy, pyroelectric measurements, and tunneling
electroresistance measurements, indications of ferroelectric behavior are found in
(111)-oriented BaTiO$_3$ down to a thickness of 5 nm.
Introduction

Ferroelectrics are a technologically important class of materials due to the presence of switchable polarization, large dielectric constants, piezoelectricity, pyroelectricity, and high non-linear optical activity. Therefore, these materials have an important role in devices such as capacitors, actuators, and MEMS applications [1-4]. The switchable polarization is especially interesting for use in non-volatile random access memory (FeRAM). However, due to low storage density, FeRAM has been primarily used in niche applications. Central to the realization of such devices is a thorough understanding of routes to control the properties of ferroelectric thin films.

BaTiO$_3$ (BTO) is a widely studied ferroelectric material due to its prototypical polarization mechanism where the central Ti cation is displaced relative to the surrounding oxygen octahedron. In bulk and at room temperature, BTO is ferroelectric with a tetragonal unit cell and the polarization is along the [001] direction [5]. For films deposited on (001)-oriented SrTiO$_3$ (STO), it has been found that ferroelectricity is present in films as thin as 7 unit cells or 2.8 nm [6] and that the magnitude of polarization decreases below the bulk value for thicknesses of less than 10 nm [7]. For thicker films, the polarization is higher than bulk due to the elongation of the tetragonal c-axis along with a decrease of the a-axis for compressively strained BTO. For films strained to GdScO$_3$ and DyScO$_3$ substrates the polarization of 200-nm-thick films has been observed to be $\sim$50 $\mu$C/cm$^2$ and $\sim$70 $\mu$C/cm$^2$, respectively, compared to 27 $\mu$C/cm$^2$ in bulk [8] with an increase in Curie temperature [9]. However, growing high-quality epitaxial films has proven difficult due to the mixed Stranski-Krastanov growth mode, resulting in oxygen vacancies and misfit dislocations [10, 11].
Until recently, with regards to perovskite oxides in general and BTO in particular, most of the research effort has been focused on (001)-oriented films. However, due to advances in substrate preparation techniques [12, 13], there is an increased interest in films grown on (111)-oriented substrates, which have novel properties such as polar metals [14], exchange bias in a paramagnetic-ferromagnetic LaNiO$_3$-LaMnO$_3$ superlattice [15, 16], and an induced switchable magnetic moment in an antiferromagnetic-ferromagnetic bilayer of La$_{0.3}$Sr$_{0.7}$MnO$_3$ (LSMO)-LaFeO$_3$ without charge transfer [13]. Additionally, it has been theoretically predicted that SrIrO$_3$ can exhibit non-trivial band topologies when embedded in a STO/SrIrO$_3$/STO stack [17, 18], and that compressively strained LaAlO$_3$ and SrMnO$_3$ will exhibit a Goldstone-like mode [19, 20].

In the (111)-orientation, the [001]-direction of BTO is at a 54.7° angle relative to the surface normal, which, assuming a tetragonal unit cell, would imply a different polarization behavior than for (001)-oriented films, where the polarization direction lies either in- or out-of-plane. There are a few reports on BTO grown on (111)-oriented substrates. 300 nm thick BTO films grown on (111)-oriented STO have been found to have a lower leakage current compared to the (001) and (110)-orientation [21], while in superlattices of BTO/STO a very high dielectric constant is found although the remanent polarization is only 1.35 μC/cm$^2$, approximately an order of magnitude lower than similar superlattices in the (001)-orientation [22]. Interestingly, theoretical studies predict a lowering of the out-of-plane polarization for compressively strained (111)-oriented BTO compared to the unstrained case [23, 24], opposite to what is observed in (001)-oriented films. In both cases the out-of-plane
lattice parameter increases with applied compressive strain, although in the (111) orientation the compressive strain forces the oxygen atoms in the (111)-plane together, filling the space available for the Ti cation to move out of the plane.

Regarding other ferroelectric perovskites, giant surface flexoelectric effect has been found in (111)-oriented BiFeO$_3$ on STO [25], in addition to a higher polarization than in the (001)- and (110)-orientations due to the rhombohedral structure of (111)-oriented BiFeO$_3$ films [26, 27]. However, (111)-oriented BiFeO$_3$ films suffer from fatigue, due to domain wall pinning. In PbTiO$_3$ grown on (111)-oriented LaAlO$_3$ a high degree of dislocations at the interface has been found by transmission electron microscopy [28].

In this work, we report on the synthesis and characterization of (111)-oriented BTO thin films, and the data points towards a change in defect density with thickness affecting the structural properties, albeit samples down to 5 nm are shown to exhibit ferroelectricity.

**Experimental**

A series of BTO films with varying thickness were grown on (111)-oriented niobium-doped STO (Nb:STO) substrates, as well as bilayers of BTO on 10-nm-thick LSMO on (111)-oriented undoped STO. The films were grown by pulsed laser deposition (PLD) using a KrF excimer laser (248 nm) at a fluence of ~2 J/cm$^2$ and a repetition rate of 1 Hz. During deposition, the substrate was heated to 540 °C in an oxygen atmosphere of 0.05 mbar while an oxygen pressure of 0.35 mbar was used for BTO and LSMO growth. The growth was monitored by reflection high-energy electron
diffraction (RHEED). Clear RHEED specular intensity oscillation peaks were observed (Figure 1), although with monotonically decreasing amplitude. The oscillation period was observed to be ~5.5 seconds. After deposition the films were cooled in a 100 mbar oxygen atmosphere with a cooling rate of 15 °C/min. The substrates were prepared before deposition by etching in buffered HF for 45 s, followed by annealing for 1 h at 1050 °C, resulting in atomically flat surfaces with unit cell high steps [29]. Information regarding the LSMO growth can be found in [30].

The film crystallinity was characterized using x-ray diffraction (XRD, Bruker D8) with linear scans and rocking curves taken around the 111 film and substrate peaks. Atomic force microscopy (AFM, Veeco Nanoscope V) and piezoelectric force microscopy (PFM, Veeco Nanoscope V) were used for surface characterization of the topography and ferroelectric properties, respectively. The ferroelectric properties of the bilayers were measured using a pyroelectric measurement setup, where 100 nm thick circular electrodes with a diameter of 1 mm were deposited using a sputter coater and contacted with silver paste to electrical leads, while the LSMO electrode was contacted by wire bonding. The temperature of the electrodes was modulated by illuminating with a modulated diode laser (\( \lambda = 1080 \) nm, 60 mW, 35 Hz) resulting in the generation of a pyroelectric current, which was converted to a voltage signal [31-34].

As a proof of concept, a ferroelectric tunnel junction (FTJ) was constructed from a BTO/LSMO bilayer by depositing top electrodes of magnetic permalloy capped with gold by electron beam evaporation through a mask with circular 0.2 mm diameter
holes. The thickness of the permalloy was 10 nm, while the gold caps were 100 nm thick. Silver paste was used to bond the top electrodes to enable the characterization of the tunneling electroresistance (TER). The TER measurements were performed with a commercially available system (VersaLab with the electrical transport option).

To pole the junctions, a series of DC voltages were applied in a triangular fashion with steps of 0.5 V between +2.5 V and −2.5 V. Between each poling step the resistance was determined from low amplitude (10 mV) IV-curves.

Results and discussion

Symmetric 0/20 XRD profiles taken around the 111 film and substrate peaks are presented in figure 2 (a). The BTO film thickness on Nb:STO was calculated from the width of the 111 reflection peaks to be 10 nm, 19 nm, 37 nm, and 110 nm, giving deposition rates of 5.7 s/layer, 6 s/layer, 6 s/layer, and 16.2 s/layer, respectively. We note that for the 10 nm, 19 nm and 37 nm samples the estimated thickness from XRD agrees well with the deposition rate obtained by RHEED. The uncertainty in these values increases with thickness due to a lack of thickness fringes for the thicker films. The out-of-plane parameter, d_{111}, was calculated from the peak position and is presented in figure 2 (b) as a function of the film thickness. The out-of-plane parameter was for all thicknesses larger than bulk (2.316 Å, indicated with a solid line), but relaxed towards the bulk value with increasing thickness. The full-width-at-half-maximum (FWHM) values of the film peak rocking curves are presented in the same figure. Approximately equal FWHM values are observed for the three thinnest samples (0.027°, 0.025°, and 0.027° for 10 nm, 19 nm, 37 nm, respectively), while the thickest film possesses an order of magnitude larger width (0.753°) due to a mosaic spread. The 0.015° FWHM of the substrate peak is marked with a dashed line in the
figure. A reciprocal space map (RSM) of the 114 film and substrate reflections of the 37 nm thick film is shown in figure 2 (c). The unequal in-plane positions of the film and substrate peaks suggest that the BTO film had relaxed. Using the center of the BTO peak, the in-plane lattice parameter along the \([11\bar{2}]\)-direction is found to be 1.64 Å. By comparison, in bulk BTO and STO the interplanar distance along the \([11\bar{2}]\) family of lattice planes is on average 1.638 Å and 1.594 Å, respectively, indicating a fully relaxed film. Comparable results are found for the other films (not shown). The BTO films are relaxed for all thicknesses with the peak centered in plane around the BTO bulk value. Due to a low film-substrate peak intensity ratio, XRD measurements of the two thinnest films had to be done with relatively large slit openings, making comparisons of peak widths difficult.

Figures 3 (a-d) show AFM micrographs of the 10 nm, 19 nm, 37 nm and 110 nm thick BTO films on Nb:STO with corresponding line scans in figures 3 (e-h). The sample surfaces became rougher with increasing thickness and a clear step-and-terrace structure was found only for the three thinnest samples, although some step bunching can be observed. However, we also observe occasionally step bunching for the Nb:STO substrates rendering is difficult to determine if the bunching is due to the growth conditions or the substrates used. Turning to the BTO/LSMO bilayers, AFM micrographs of the surfaces of 5 nm BTO, 10 nm BTO and 100 nm BTO, all grown on 10 nm LSMO, are shown in figures 4 (a-c), respectively. All films exhibit a step-and-terrace surface morphology with a step height that is equal to \(d_{111}\), following the template of the substrate.
There are several signs of defect formation and lattice relaxation with thickness in the samples investigated. The decrease of the $d_{111}$ parameter with thickness (figure 2 (b)) is contrary to what is observed for epitaxial (001)-oriented films of BTO on STO, where the out-of-plane parameter is constant for thicknesses above 10 nm, with a ~6.7 % expansion compared to bulk [7]. An expansion of the out-of-plane parameter of comparable magnitude would result in a $d_{111}$ of 2.47 Å ($d_{111} \approx 2.316$ Å in bulk).

Whereas the out-of-plane parameter for the 10 nm film reported here is significantly lower, $d_{111} = 2.341$ Å. By comparison, utilizing a Poisson’s ratio of 0.35 (polycrystalline bulk BTO at room temperature [35]) and assuming a fully strained film in the (111)-plane would yield a $d_{111}$ value of 2.386 Å. Theoretical predictions find a lower out-of-plane expansion under compressive in-plane strain for (111)-oriented BTO with R3m symmetry compared to (001)-oriented BTO with P4mm symmetry [23]. Again, assuming a fully strained film on STO, these results give an expansion of approximately 0.4 % or $d_{111} \approx 2.325$ Å. However, that RSM data reveal that all samples are relaxed as discussed above. A possible explanation for the decreasing out-of-plane parameter is the presence of a multiphase system, where the first unit cells of the film are strained, followed by a section with a strain gradient, and finally a fully relaxed section. This could result in linear XRD scans where the resulting film peak position is a combination of the respective sections. However, the RSM measurements indicate that the film reflections are centered on the bulk in-plane value (figure 2 (c)), whereas the scenario described above would result in either two separate peaks located at the strained and unstrained values of $Q_{||}$, or a peak centered around a midway point between the two extremes. Instead, the x-ray peak position and width indicate the presence of defects, albeit the observed peak width may hide contributions from film phases with different strain states. As all films are relaxed, the
decreasing out-of-plane parameter with thickness rather suggests a change in the
defect density with increasing thickness. In compressively strained films, cation
cavancies are expected [36], however, in the (001)-orientation, mainly misfit
dislocations and oxygen vacancies are observed as strain relief mechanisms [10, 11].

In order to study the ferroelectric properties of the BTO films three different
techniques were used; PFM, pyroelectric measurements and TER in order to
circumvent the challenges with leakage due to the defects present.

Room temperature PFM measurements were performed on the thickest sample grown
on Nb:STO. By sweeping the applied field, a hysteresis behavior of the PFM signal
amplitude and phase was observed as a function of the applied DC voltage (figure 5),
indicating the presence of ferroelectricity. The phase difference between the start and
end state is ~155°, indicative of the reversal of ferroelectric domains.

A hysteresis behavior was observed in pyroelectric measurements at 80 K for the
switching current and phase as a function of the applied DC voltage, here shown in
figure 6 (a) for the bilayer of 10 nm BTO on LSMO. The phase difference between
the up and down states is ~166°. In figure 6 (b) the pyroelectric current obtained from
another 10 nm BTO/LSMO bilayer is shown as a function of temperature. The non-
zero current at 300 K indicates that the Curie temperature is above room temperature.
We note that there is a clear kink in the pyroelectric current amplitude near 105 K,
similar to behavior observed in ferroelectric La$_2$NiMnO$_6$ thin films [31, 34]. This
indicates a coupling of the ferroelectric state of (111)-oriented BTO to the symmetry
and strain of the underlying substrate as STO undergoes a structural phase transition between cubic \((T > 105 \text{ K})\) to tetragonal \((T < 105 \text{ K})\) at 105 K.

Finally, the resistance as a function of the poling voltage, measured at 50 K for an FTJ consisting of a bilayer with 5 nm BTO is shown in figure 6 (c). The insert shows the measurement procedure, with the blue and yellow bars symbolizing interleaved poling and measurement, respectively. The resistance shows hysteresis as expected for a ferroelectric tunnel junction, a further indication of ferroelectricity in the \((111)\)-oriented BTO films. The tunneling electroresistance, \(TER = (R_{\text{off}} - R_{\text{on}})/R_{\text{on}}\), is found to be 4.1 %.

Despite indications of a high defect density, the \((111)\)-oriented BTO films are ferroelectric at room temperature and below as seen from the PFM, pyroelectric, and tunneling electroresistance measurements, with signs of ferroelectricity in films of 5 nm, 10 nm and 110 nm thickness.

**Conclusion**

In conclusion, BTO films and BTO/LSMO bilayers were deposited on Nb:STO and STO substrates, respectively. The out-of-plane parameters decrease with increasing thickness. From XRD scans of asymmetric peaks, it was found that the films are relaxed, indicating that of origin of the decreasing \(d_{111}\) is increased defect density. Still, the BTO films were found to exhibit ferroelectric behavior.
Acknowledgements

This project was partially supported by the Norwegian Research Council under project number 221860 and 231290, and through support of the Norwegian Micro- and Nano-Fabrication Facility, NorFab, project number 245963/F50. The project was also partially supported by JSPS Grants-in-Aid for Scientific Research Nos. 17H04895 and 26105002, and JST PRESTO (Grant No. JPMJPR16R3).
References
Figure 1: The first RHEED oscillations of a typical BTO deposition. The arrow indicates the starting point of the deposition.
Figure 2: (a) Linear XRD scans of the 111 reflection for substrate and film peaks. (b) The out-of-plane parameter, $d_{111}$, and the rocking curve FWHM of the films as a function of temperature. (c) RSM of 114 reflection for the 37 nm thick film. The in-plane and out-of-plane directions are [11-2] and [111], respectively. The orange line indicates the in-plane value of bulk BTO.
Figure 3: (a-d) AFM micrographs of the surfaces of the 10 nm, 19 nm, 37 nm, and 110 nm, respectively. The dimensions of AFM micrographs are 3x3 μm². (e-h) Line scans corresponding to the white lines in the micrographs in (a-d), respectively.
Figure 4: (a-c) AFM micrographs of the surfaces of bilayers of 5 nm, 10 nm, and 100 nm BTO, respectively, on 10 nm LSMO on STO. The dimensions of AFM micrographs are 3x3 μm².
Figure 5: The PFM amplitude and phase as a function of applied bias voltage.
Figure 6: (a) The pyroelectric current (blue line) and phase (orange line) at 80 K of a 10 nm BTO, 10 nm LSMO bilayer. (b) The temperature dependence of the pyroelectric current of a 10 nm BTO, 10 nm LSMO bilayer. (c) The tunneling electroresistance as a function of poling voltage of 50 K for a 5 nm BTO, 10 nm LSMO bilayer. The central inset shows the poling (blue bars) and measurement (yellow bars) procedure.
Synthesis and characterization of (111)-oriented BaTiO$_3$ thin films
Part III

Epilogue
Chapter 5

Conclusions and outlook

The growth and engineering of perovskite oxides in the (001)-orientation is well understood, with extensive research into how the interface, morphology, and strain affects the structure and properties of thin films. Although, to realize high quality devices with functional materials, further avenues towards material design need to be explored. The utilization of other orientations, such as the (111)-orientation, has been shown to have the potential to induce novel properties and open new pathways towards property control. However, research into (111)-oriented films is still in its starting phase.

In this work we have investigated the effect of (111)-oriented strain and symmetry on the structural and functional properties of thin films. Our model systems have been ferromagnetic La$_{0.7}$Sr$_{0.3}$MnO$_3$ and ferroelectric BaTiO$_3$. Both materials have been thoroughly investigated in the (001)-orientation in addition to a strong structure-property relationship, making them well suited for these purposes. To facilitate the deposition of high quality films, substrate surface preparation procedures of SrTiO$_3$, DyScO$_3$, GdScO$_3$, and NdGaO$_3$ have been developed and investigated.

Our most prominent findings are as follows:

- Optimizing the surface preparation procedures for (111)-oriented surfaces of SrTiO$_3$, DyScO$_3$, GdScO$_3$, and NdGaO$_3$ result in atomically smooth step and terrace structures. However, there are several signs of surface reconstructions due to the polar stacking along the surface normals. The reconstruction can result in the first layer being intermixed at the interface of the film and substrate.
Conclusions and outlook

- For the orthorhombic substrates the step heights can be controlled through considering the octahedral layering of the \((111)_{\text{pc}}\) surfaces, \((011)_o\) or \((101)_o\). Using the \((011)_o\)-orientation or the \((101)_o\)-orientation results in step heights of one or two \((111)_{\text{pc}}\) interplanar distances, respectively.

- Through strain and substrate symmetry, \((111)\)-oriented \(\La_{0.7}\Sr_{0.3}\MnO_3\) can assume multiple crystal structures: rhombohedral, monoclinic and triclinic, and the crystal structures are shown to influence the magnetic anisotropy. Considering only strain does not fully explain the observed anisotropy, but can be resolved by including octahedral rotations. A phase diagram of anisotropy versus octahedral rotations was therefore constructed using theoretical models of magnetic anisotropy.

- While \((111)\)-oriented \(\La_{0.7}\Sr_{0.3}\MnO_3\) is magnetically isotropic at larger applied fields, at remanence a uniaxial anisotropy is observed. The anisotropy is found to be linked to the step and terrace structure of the surface. The easy axis of the anisotropy is thickness dependent: under a critical thickness (~20 nm) the easy axis direction is perpendicular to the step edges, while above the critical thickness the easy axis is aligned parallel to the step edges. It is found through the single ion model that in-plane octahedral rotations induced by the step edges, can lead to a uniaxial anisotropy.

- Using the second order structural phase transition of the \(\SrTiO_3\) the magnetic properties of \((111)\)-oriented \(\La_{0.7}\Sr_{0.3}\MnO_3\) are changed due to the structural changes of the substrate, which results in an anisotropy controlled by both strain and interface morphology.

- The structure of \(\BaTiO_3\) on \((111)\)-oriented \(\SrTiO_3\) is found to be dominated by defect formation. Films of 10 nm and thicker are found to be fully relaxed in-plane, with signs of increasing defect density with increasing thickness. Indications of ferroelectricity are found in films down to 5 nm thickness.

- A marked change in the pyroelectric current in thin films of \((111)\)-oriented \(\BaTiO_3\) is observed at 105 K, concurrent with the phase transition of the \(\SrTiO_3\) substrate, showing that the ferroelectric properties are sensitive to small structural changes.

In this work, we demonstrate that utilizing the \((111)\)-orientation on well known materials results in novel responses to commonly employed control
parameters. The wide array of functionality and control options demonstrated in perovskite oxides opens for a future in electronic devices, in addition to being interesting from a fundamental perspective.

As the structure and properties of the thin films are so closely linked to the growth process, depositing films on orthorhombic substrates with different step heights could give further insight into the influence of morphology on functionality.

On (111)-oriented SrTiO$_3$, La$_{0.7}$Sr$_{0.3}$MnO$_3$ is seen to assume a rhombohedral unit cell. The symmetry constraints imposed by the (111)-oriented substrate may lead other material systems to assume the same crystal structure. A range of interesting properties are observed in hexagonal materials such as multiferroicity and topological defects in the hexagonal manganites, high electronic and thermal conductivity in graphene. Further, the orthorhombic substrates open for the possibility of straining these materials along an in-plane direction as seen for La$_{0.7}$Sr$_{0.3}$MnO$_3$ on DyScO$_3$ where a strained hexagonal structure is found.

The octahedral response of (111)-oriented strain is interesting as many functional properties are highly linked to the octahedral rotation pattern. Moreover, there are several reports of novel interface effects originating in the tilt pattern imposed by geometrical constraints and from coupling of octahedral rotations across an interface. The octahedral rotations in (111)-oriented films appear highly sensitive to both strain and thickness. Thus, offering a wide range of opportunities in engineering emerging functionality.

The functional properties of the thin film materials studied here are found to be highly sensitive to small structural changes, such as those induced by a second order substrate phase transition, providing an avenue towards control of properties in functional oxide electronic devices.

In summary, the (111)-orientation provides for an array of possibilities, which can hopefully inspire further research into the use of the (111)-orientation as a control parameter.
References


REFERENCES


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