A 3D visualization of a heterostructure composed of atoms, represented as spheres of different colors (red, orange, white, blue, purple) arranged in a layered, crystalline pattern. The spheres are arranged in a way that suggests a complex, multi-layered structure, likely representing the atomic arrangement in a heterostructure. The colors likely represent different elements: red for oxygen, orange for lanthanum (La), white for strontium (Sr), blue for titanium (Ti), and purple for aluminum (Al).

INTERFACIAL PHENOMENA IN ATOMICALLY ENGINEERED $\text{LaAlO}_3/\text{SrTiO}_3$ HETEROSTRUCTURES

Jeroen Huijben

INTERFACIAL PHENOMENA
IN ATOMICALLY ENGINEERED
 $\text{LaAlO}_3/\text{SrTiO}_3$ HETEROSTRUCTURES

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Cover: Artistic impression of atomically engineered $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures.

The research described in this thesis was performed in the Faculty of Science and Technology and the MESA⁺ Institute for Nanotechnology at the University of Twente. The work was financially supported by NanoNED, a national Nanotechnology R&D initiative, in flagship Nanoelectronic Materials with project number TOE.7008. In addition, support of the Dutch FOM and NWO foundations is acknowledged.

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Ph.D. Thesis, University of Twente

Printed by: Ipskamp Printing

ISBN 978-90-365-4524-2

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IN ATOMICALLY ENGINEERED
LAAlO₃/SrTiO₃ HETEROSTRUCTURES

DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
prof. dr. T.T.M. Palstra,
on account of the decision of the graduation committee,
to be publicly defended
on Thursday the 12th of April 2018 at 14:45 hours

by

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This dissertation has been approved by the supervisors:
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Voor Amy, Elena en Anita

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Preface

Before you lies the dissertation titled "Interfacial phenomena in atomically engineered $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures". The work that was to form the basis of this book was initiated roughly at the onset of 2006 when I was granted the opportunity to pursue a PhD degree in the field of oxide materials. The focus of research was to be on a discovery from about two years prior, when Akira Ohtomo and Harold Hwang found that the careful combination of two insulating oxides resulted in conductivity at their interface. Nature published their seminal article "A high mobility electron gas at the $\text{LaAlO}_3/\text{SrTiO}_3$ heterointerface" in January 2004. While that publication had already attracted quite some interest from the oxide materials community, early 2006 there had not yet been significant publications following up on the initial discovery. My research was to focus on furthering the understanding of behaviour at, and possible exploitation of, the 2DEG at the interface between LaAlO_3 and SrTiO_3 .

A lot of time was spent synthesizing and characterizing samples in the thin film laboratory at the University of Twente where the available experience and helpful nature of colleagues proved very valuable. Great collaborations with other research groups, also at other (inter)national institutes and universities, provided indispensable contributions for theoretical modelling or specialized tools for characterization such as synchrotron radiation source, high field magnet laboratory and low temperature scanning tunnelling microscopy. Coincidentally, when time for experiments drew to a close, the entire thin film laboratory was packed and moved to the newly built Nanolab facility at the University of Twente which was to open in November 2010.

During this period it became clear to me that scientific communication, specifically regarding the complex topics common to physics, could be improved by using visualizations of high quality. Some illustrations proved quite effective in reaching a broad audience, such as the illustration which also represented complex oxides

as "Beyond silicon?" as one of the runners-up for the Science Breakthrough of the year 2007. As requests for illustrative material came in from various other research groups, I started visualisation studio Nymus3D which rapidly grew into a viable company consisting of several artists. By the time that the PhD research ought to have come to a close, the work pressure in the start-up company was rising fast and in the end this precluded the time and focus required to write a dissertation.

By mid 2015, well running Nymus3D with its team of five artists was integrated, while remaining a separate entity, within the much larger DEMCON Group. For me things changed more considerably as I transferred my tasks within Nymus3D and shifted to a position as project manager in medical device development within DEMCON Advanced Mechatronics. In the end it brought more time and focus which I gladly used to return to my earlier research in order to finish my dissertation alongside a relatively normal job. While the described experiments originate from the period 2006 to 2010, reflections are included to take contemporary knowledge into account.

Outline with scientific motivation and collaboration

In Chapter 1 a brief introduction is given to oxide materials and the surprising conducting interface between the two band insulators LaAlO_3 and SrTiO_3 . Also, an overview of relevant literature is given with a focus on the exotic electron gas properties found and the debated origin of the charge carriers.

In Chapter 2 synthesis of epitaxial $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces, fundamental in order to study the behaviour of well defined materials of high quality, will be described with examples for single interfaces, heterostructures and superlattices. Furthermore a patterning method using Ar^+ ions is discussed. Lastly, some further points regarding strain build up and AFM patterning are considered.

In Chapter 3 a study has been described, which has explored the magnetic moments and dimensionality at the interface. Transport measurements on $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces have been studied down to 50 mK and in magnetic fields, B , up to 30 T, to verify the existence of induced magnetism. A large negative magnetoresistance of the interface is found, together with a logarithmic temperature dependence of the sheet resistance. A hysteresis artefact from the sample holder is evaluated separately. Magnetic effects in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces are discussed in retrospect. [In collaboration with the research group of prof. Zeitler, High Field Magnet Laboratory at Radboud University Nijmegen]

In Chapter 4 transport measurements on $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces at 50 mK have been studied in magnetic fields in order to provide further insight in the nature of the magnetic phenomena and dimensionality of the transport. Magnetoresistance oscillations are observed, which appear periodic in $\sqrt{B}$, and not periodic in $1/B$ as is the case for the well-known Shubnikov-de Haas oscillations. Several explanations are considered which would imply the existence of a highly mobile 2D electron gas at the interface. Concluding, the current state of research

into quantum oscillations in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces is evaluated. [In collaboration with the research group of prof. Zeitler, High Field Magnet Laboratory at Radboud University Nijmegen]

In Chapter 5 the atomic intermixing between LaAlO_3 overlayer and SrTiO_3 substrate is studied in order to understand its relation with the doping mechanism. The result shows a vacancy-rich A -site composition of neutrally charged $\text{Sr}_{1-1.5x}\text{La}_x\text{O}$ layers, the formation of which already starts at the onset of deposition. The measured A -site compositions do not take away the polar instability, which thus still requires a change from the nominal structure and/or composition at the B -sites. Evidence is given for such a mechanism starting at a thickness of 3 unit cells. [In collaboration with the research group of prof. Stierle, Universität Hamburg, measurements performed at the ANKA Synchrotron Radiation Source at Karlsruhe Institute of Technology]

In Chapter 6 $\text{LaAlO}_3/\text{SrTiO}_3$ bilayers on SrTiO_3 substrates are studied in order to understand the coupling between subnanometer spaced conducting interfaces. This is achieved by scanning tunnelling microscopy (STM) and spectroscopy (STS) experiments on STO-capped LAO layers on STO(001) substrates, revealing the individual interface (2DEG) and surface (2DHG) conducting sheets including their temperature dependent coupling. [In collaboration with the research group of prof. Zandvliet, University of Twente]

CHAPTER

1

Introduction

This chapter gives a brief introduction to oxide materials and the surprising conducting interface between the two band insulators LaAlO_3 and SrTiO_3 . Also, an overview of relevant literature is given with a focus on the exotic electron gas properties found and the debated origin of the charge carriers.

1.1 Introduction to $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces

1.1.1 Emergent phenomena by interface engineering

Exciting things happen at interfaces in general, whether this is formed by the interface between partners in a cooperation, the separate parts in a complex device or on the atomic level in materials science. It is the part most easily overlooked yet commonly the source of the biggest issues and interesting opportunities. Here the focus is on materials, where the interface turns them exotic. Or as Herbert Kroemer suggested during his Nobel lecture: "Often, it may be said that the interface is the device" [1].

Materials with exotic properties have, sparingly, been in use since ancient history with naturally occurring magnetite mineral lodestone forming a prime example. Used as a suspended compass it allowed early navigation even though the origin of its behaviour was not understood and remains a point for speculation even now. Yet the ascent of man through the ages has been more commonly ascribed to its industrial mastery of materials, leveraging improved tools and thereby gaining an edge on its surroundings. Well known are the stone, bronze and iron ages to specify this progression, for the first time clearly defined and published by Christian Jürgensen Thomsen in the 1830's [2]. With knowledge in metallurgy improved, the iron age extended to steel and may be considered to last to this day as the production of ferrous metals continues to be of prime importance to modern tools in terms of quantity. With regards to disruptive technology however it was quickly surpassed by advances in plastics, rubbers and semiconductor devices in the 20th century. Specifically semiconductors have opened up countless new opportunities, a trajectory which was sped up by the realization of the first solid-state electronic transistor by John Bardeen, William Shockley, and Walter Brattain at Bell labs in 1947. These new solid-state transistors quickly replaced vacuum tubes for most purposes as they proved to be smaller, cheaper, more reliable and efficient. Interface physics turned out to play a crucial role in semiconductor microelectronics, driving the success of e.g. metal-oxide-semiconductor field-effect transistors and allowing new discoveries in confined electron gasses at quantum wells and quantum dots. Currently the semiconductor industry is well established, realizing foremost the integrated circuits that are present in electronic devices which are now used in every corner of our society and support everyday life. Initially oxide materials played a supporting role here, for instance as high- κ gate oxides as ever increasing demands on miniaturization pushed the boundaries of what can be reached with conventional materials. More recently metal oxide materials have entered into the realm of active materials, for instance as transparent conducting oxides, diodes, random access memories and solar cells.

Transition-metal oxides (TMO) form a particularly interesting group of complex oxides as their phase diagrams are very diverse and exhibit spectacular phenomena [3]. The origin of these widely varying characteristics lies in the intricate electronic and magnetic correlations for the electrons in the partially filled 3d orbitals. As TMO's typically have high carrier densities in bulk which extend from 10^{17} to 10^{21} carriers/cm³, the electron-electron and inter-site coulomb repulsion is not completely screened and interactions take place on short length scales, such

as a few inter-atomic distances, becoming a dominant driver of the physics within these TMO materials. In contrast, the behaviour of electrons in bulk semiconductors such as doped silicon is of a lesser complexity due to the much lower carrier densities, typically ranging from 10^{13} to 10^{17} carriers/cm³. Within the crystal lattice of these bulk semiconductor materials, the electrons essentially move almost free of interactions with the other electrons. The increased interactions in the bulk of TMO's however result in the aforementioned spectacular phenomena, examples being colossal magnetoresistance in manganites, high transition temperature (T_c) superconductivity in cuprates, half-metallic ferromagnetism in LSMO and ferroelectricity in BaTiO_3 single-domain crystals.

Deposition of multiple TMO materials on substrates as artificially engineered heterostructures extends the parameter space available for manipulation due to the interplay between the constituent materials while also allowing integration of their functionality into devices. For instance, lattice mismatch induced strain, reduced dimensionality and proximity doping significantly affect the electronic behaviour of the constituent materials, substantially altering the physical properties from their bulk behaviour as a result. A major challenge for the all important functional properties however is the difficulty to achieve controlled epitaxially and stoichiometric deposition of these oxide heterostructures. It has taken the last few decades of intense research, partly incited by the focus on high T_c superconductivity in TMO materials, to realize atomic control over structure and composition in many compounds. Required advances have been well defined control over ionic plane termination of oxide substrate materials, improvements in physical vapor deposition techniques such as pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) and the development of reflection high energy electron diffraction (RHEED) as a means to visualize the growth per single atomic layer. In this way it is now possible to grow and study artificially engineered thin film heterostructures with a low amount of defects. An example is epitaxially deposited SrRuO_3 on SrTiO_3 , it abruptly transitions from metallic to insulating and loses ferromagnetic behaviour when film thickness is reduced below 4 unit cells [4].

The improved control over substrate surfaces and epitaxial deposition of TMO's now allows abrupt interfaces, changing from one material to another over the distance of a single unit cell. In analogy to semiconductors where interfaces gave rise to novel interfacial states, there are tremendous opportunities in TMO's to generate novel materials dictated by interfacial physics. As the interfacial states are easily influenced, both by intended and unintended causes, great care must be taken while engineering these interfaces to understand and control the influences from charge transfer, defects, interdiffusion and distortions. Besides the aforementioned deposition techniques, a wealth of tools are available to the researcher in order to characterize the resulting samples. While some of these are relatively readily available to most laboratories, others require large installations such as a synchrotron in order to obtain high quality data.

Leveraging these techniques and tools, an exciting interface state has for instance been found in the two-dimensional electron gas at $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ interfaces, showing mobilities over 1×10^6 cm²/Vs resulting in a pronounced quantum Hall effect[5]. Another exciting example is found at the interface between LaAlO_3 and SrTiO_3 , which forms the focus of this thesis and is introduced in more detail

in the following section.

1.1.2 Surprising conduction at $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces

As the possibilities of complex oxide engineering at the atomic level have made substantial leaps in recent years, laboratories around the world are now able to influence electronic structures on the nanometer scale which allows access to charge states that are not normally available in bulk materials.

Carefully combining perovskites allows manipulation and study of their structural and electronic properties. One such example is artificial charge modulation in superlattices comprised of $\text{LaTi}^{3+}\text{O}_3$ layers embedded in $\text{SrTi}^{4+}\text{O}_3$ [6], the individual materials are insulating in bulk yet their epitaxially grown combination is not. Here the structural transitions at the interfaces between both perovskite materials are atomically sharp while the charge modulation arising from Ti^{3+} and Ti^{4+} valence variation is spread over several nanometers giving rise to conduction confined to a thin layer.

In an effort to study the feasibility of two-dimensional electron gases in SrTiO_3 , Hwang et al. realized three approaches based on delta, oxygen vacancy and polar/non-polar doping [7] of which the last one is of particular interest. While it was known for some time that polar discontinuities may result in complex atomic and electronic structures in semiconductors such as GaAs on Ge [8, 9], the same effect holds for oxide materials. The ABO_3 structure of perovskites is comprised of alternating AO and BO_2 layers which in the ionic limit may yield polar layers having a charge difference with respect to each other. In the case of the previously mentioned $\text{LaTi}^{3+}\text{O}_3$ this would result in polar layers formed by $(\text{LaO})^+$ and $(\text{TiO}_2)^-$, yet due to the valence variation on the Ti atom this polarity may be diminished. To study the influence of interfacial polar discontinuities, LaAlO_3 was chosen as a candidate as Al does not allow valence values other than 3+. When epitaxially deposited with atomic perfection onto SrTiO_3 (001) substrates, the polar nature of the material may therefore remain to exist and influence neighbouring materials. Such an impact was indeed discovered in SrTiO_3 and LaAlO_3 heterostructures where the polar heterointerface was shown to result in an electron gas with mobilities exceeding $1 \times 10^4 \text{ cm}^2/\text{Vs}$ and magnetoresistance oscillations with periodicity in $1/H$ [10].

A polar discontinuity model was hypothesized where depending on substrate surface termination a discontinuous $(\text{LaO})^+ / (\text{TiO}_2)^0$ or $(\text{AlO})^- / (\text{SrO})^0$ interface was realized and an electrostatic potential would build up with increasing LaAlO_3 thickness. A transferred charge of $\pm e/2$ per two dimensional unit cell would be required in order to mitigate the potential build up, yielding either a transferred electron for a negatively charged interface (n-type) or hole for a positively charged interface (p-type). Indeed half an electron per unit cell was approached as carrier density for samples with $(\text{LaO})^+ / (\text{TiO}_2)^0$ interfaces grown at an oxygen pressure of 10^{-4} mbar. Much higher carrier densities were measured for samples grown at low oxygen pressures, these puzzling densities were described as being "unphysical". Oxygen vacancies were considered as an alternative origin of the conductivity yet subsequently ruled out based on two experimental observations. First, a substrate alone retained insulating behaviour when exposed to growth conditions. Second,

changing the termination layer of the substrate to SrO rendered the subsequently grown $(\text{AlO})^-/(\text{SrO})^0$ interfaces practically insulating leading to the conclusion that no Al oxygen gettering is happening at the interface. While it is now known that the very high carrier density samples are actually conductive throughout the SrTiO_3 substrate due to oxygen vacancy doping, there is a potential well for charge carriers at the interface exhibiting interesting behaviour.

Throughout the oxide materials community, the discovery quickly attracted a lot of interest inspiring early theoretical studies [11–13] and first experiments regarding the manipulation and origin of the carriers [14–17]. Growth conditions such as partial oxygen pressure were soon shown to play a distinct role [18, 19]. Also it was shown that the conduction had a very distinct onset based on a critical LaAlO_3 thickness and that by applying a gate voltage one was able to modulate the electron gas through a quantum phase transition from an insulating to a metallic state [20]. The $\text{LaAlO}_3/\text{SrTiO}_3$ interface was one of the runners-up in the Science Breakthrough of the year 2007 [21] and has since become a model system for polar discontinuity interfaces in oxides. Figure 1.1 shows an artist impression created by the author of this thesis which was also used in the mentioned Science Breakthrough of the year 2007 runners-up publication.

Figure 1.1: Artist impression on $\text{LaAlO}_3/\text{SrTiO}_3$ interface synthesis [21].

Many interesting phenomena have since been reported to occur at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface and are being avidly investigated. On-going progress has been summarized in a series of great reviews on the subject [22–28]. These phenomena span a wide spectrum from superconductivity to magnetism and spin-orbit in-

teraction, while allowing reversible carrier density manipulation by field effect or atomic force microscopy probe. Another point of on-going intense research is the origin of the charge carriers, which may be a combination of intrinsic effects such as the polar discontinuity and extrinsic effects such as oxygen vacancies, cation intermixing and lattice distortions. The exotic electron gas properties and possible origins are described according to literature in the next section.

1.2 Overview relevant $\text{LaAlO}_3/\text{SrTiO}_3$ literature

This section tries to highlight main advances and open issues, it does not intend to give a full overview of all literature concerning $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces. For further information the reader is referred to insightful reviews on the topic, such as by Joseph Sulpizio et al. [25] and Stefano Gariglio et al. [27].

1.2.1 Exotic electron gas properties

Superconductivity

When considering superconductivity in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces it is important to point out that the existence of superconductivity in doped bulk SrTiO_3 has been established for some time [29, 30]. As a function of carrier concentration, T_c in reduced SrTiO_3 was shown to exhibit a dome like appearance reaching a maximum superconducting critical temperature (T_c) of ~ 300 mK at an electron carrier concentration of $9 \times 10^{19} \text{ cm}^{-3}$ [31, 32]. It was actually work on SrTiO_3 that triggered the interest in superconductivity for Georg Bednorz [33] and ultimately led to a Nobel prize for Georg Bednorz and Alex Müller for their work on high- T_c superconductivity in perovskite-type oxides. As it turns out, SrTiO_3 was until recently the most dilute superconductor known [34], while the origin of superconductivity in these materials remains unclear [35].

The $\text{LaAlO}_3/\text{SrTiO}_3$ interface was found to be superconducting with a T_c of ~ 200 mK at a sheet carrier density of $\sim 1 \times 10^{13} \text{ cm}^{-2}$ with an estimated electron gas sheet thickness of ~ 10 nm [36, 37]. By using the electric field effect, carrier concentrations in these systems can be tuned continuously [20], in doing so the superconductivity can be turned on/off when driving the superconducting state to an insulating state [38]. The superconducting dome (carrier concentration vs T_c) shows similarities with the superconducting properties of bulk SrTiO_3 while the pseudogap behaviour is analogous to the high-transition-temperature cuprate superconductors [39]. The superfluid density is at $\sim 1 \times 10^{12} \text{ cm}^{-2}$ quite small compared to the total carrier concentration [38] and may be tuned by the electric field effect [40]. Interestingly and perhaps counter intuitively, cleaner interfaces may result in a lower T_c [41].

Magnetotransport studies have shed further light on the superconducting properties. Strong anisotropy of the transport properties confirms the two-dimensional nature of the superconducting gas and further analyses yield an estimate of ~ 10 nm for the superconducting layer thickness [42], which corresponds well with results found when using conducting tip atomic force microscopy techniques [43]. Perpendicular magnetic fields allow extraction of coherence lengths, estimated at

~ 70 nm [42] and ~ 50 nm [44]. While magnetic fields are known to reduce T_c , in the $\text{LaAlO}_3/\text{SrTiO}_3$ system it is shown that magnetic fields applied parallel to the two-dimensional electron gas (2DEG) may actually enhance this unconventional superconductive state [45].

Specialized superconducting devices based $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces are now a reality as superconducting quantum interference devices have been created where the critical currents of constriction-type Josephson junctions can be controlled independently via the side gates [46].

Not restricted to merely the model system in the (001) direction, superconductivity is also shown in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces along the (110) [47] and (111) [48] direction.

Magnetism

Within bulk SrTiO_3 , ferromagnetic ordering is possible using cation doping with at least several percent magnetic elements such as cobalt while carrier doping or oxygen vacancies yield no effect [49, 50]. Furthermore considering that superconductivity is demonstrated at $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces, magnetic ordering would appear counter intuitive as it would be expected to disrupt the pairing mechanism required for superconductivity. Such a combination of superconductivity and magnetism is therefore uncommon and only seen in some rare-earth bulk materials. Theoretically however a Ti^{4+} to Ti^{3+} filling of $3d_{xy}$ orbitals at the interface yields electrons carrying charge and spin which could result in magnetic order [13]. Indeed, signatures of ferromagnetic ordering and scattering at localized magnetic moments at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface have been found [19] (see also Chapter 3). Even though the details of magnetism in these interfaces are not fully understood, advances like this have spurred an interest into the ground state of the system and possible contribution levels from itinerant or localized electrons.

Magnetotransport was shown to be strongly anisotropic at low temperatures [51, 52]. Increased resistivity for perpendicular magnetic fields may be caused by orbital effects, reduced resistivity for in-plane magnetic fields may be due to alignment of magnetic ordering and thus reduced spin scattering which would provide evidence for magnetic ordering at the interface.

Remarkably both superconductivity and magnetic states may co-exist in a single sample. From density-functional theory it was suggested that the transferred electrons at the interface may occupy nearly 10 sub-bands, leading to a rich array of transport properties that appear concurrently [53]. Electronic phase separation due to the selective occupancy of interface sub-bands of the nearly degenerate Ti orbital in the SrTiO_3 was demonstrated by magnetoresistance and magnetization measurements [54]. This electronic phase separation was suggested to result in regions of a quasi-two-dimensional electron gas, a ferromagnetic phase, which persists above room temperature, and a (superconductor like) diamagnetic/paramagnetic phase below 60 K. The coexistence or phase separation of superconductivity and ferromagnetism was reported by multiple other groups using magnetoresistance, Hall, and electric-field dependence measurements [55], high-resolution magnetic torque magnetometry and transport measurements [56] or local imaging of the magnetization and magnetic susceptibility by SQUID mea-

measurements showing microscopic patches [57, 58]. Due to these patches, macroscopic signals such as the ferromagnetic response may be low. Similar to the thickness dependence of the conductivity, SQUID measurements have shown that magnetism only appears above a critical thickness and is independent of itinerant carriers [58]. Whether magnetic ordering and superconductivity are intrinsic properties of these interfaces is debated with some theoretical studies suggesting that while Ti $3d$ electrons generate both states, oxygen vacancies enhance the tendency for ferromagnetism [59]. The filling of the nearly degenerate sub-bands is probably very sensitive to material synthesis parameters, suggesting a possible cause for deviations between the results of separate groups.

In an effort to determine the origin of the magnetic signals, X-ray magnetic circular dichroism (XMCD) has been used. While one group determined that ferromagnetism is located in the topmost TiO_2 layer [60] another group concluded that in oxygenated samples the signal is considered negligible ruling it out as intrinsic effect [61].

Realizing control over a spin polarized 2DEG may lead to exotic magnetic states and could open up many technological opportunities. Therefore, it is promising that gate tunable coupling between itinerant electrons and localized moments has been demonstrated [62] while magnetic force microscopy was used to image how ferromagnetism emerges as electrons are depleted from the interface and diminishes when they are reintroduced [63]. Furthermore, gate-controlled spin injection [64] and recent demonstration of d-electron 2DEG spin transport at room temperature with a spin relaxation length of 300 nm [65] may open the field of d-electron spintronics.

Dimensionality

The thickness of the superconducting layer was initially limited to less than ~ 10 nm based on the equivalent superconducting critical temperature of ~ 200 mK in oxygen defect driven superconductivity in SrTiO_3 with similar carrier densities [36]. Further analysis of the anisotropic resistance response, in perpendicular and parallel magnetic fields, versus temperature near the superconducting transition yield an equivalent estimate of ~ 10 nm [42]. Direct imaging of the carrier density profile using conducting atomic force microscopy demonstrated once more the importance of synthesis protocols and determined the conducting layer confined to the interface to be as thin as 7 nm [43]. Similar estimations of the conducting layer thickness were obtained by combining infrared ellipsometry with transport measurements [66] and using time-resolved photoluminescence spectroscopy [67]. Cross-sectional scanning tunneling microscopy and spectroscopy suggested an even more confined electron gas of less than 1 nm [68].

A 2DEG with sufficient electron mobility may fulfill the requirements for quantum conductance oscillations and the signatures for such behaviour have been searched for since the initial discovery of interfacial conductivity in this system. Earlier results demonstrated oscillations regardless of perpendicularity of the magnetic field [10, 69], suggesting a three dimensional nature of the electron gas. Demonstration and investigation of two dimensional Shubnikov-de Haas oscillations was made possible by improvement of the electron mobility in the 2DEG

in two separate ways: optimization of the growth conditions [41] or manipulation by electric field effect [70]. The carrier density, which is deduced from these Shubnikov-de Haas oscillations, is notably lower than the value derived from Hall effect measurements, it is therefore suggested that only a small fraction of the carriers actually contribute. Further improvements to thin-film growth techniques may allow the observation of the remarkable quantum Hall effect. So far it has remained elusive in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces as it requires very high mobilities and low carrier densities but was recently demonstrated in an other perovskite oxide system [71, 72].

In lateral dimensions the electrons may be scattering from step edges resulting in magnetoresistance oscillations [73] (see also Chapter 4) or anisotropic conduction [74]. The striped tetragonal domain order in SrTiO_3 may yield further lateral anisotropic conductivity behaviour [75, 76].

Spin-orbit interaction

Spin-orbit interaction has attracted significant interest in the last decade, resulting in new discoveries and realizations of Rashba effect driven manipulation of spin currents in systems with a broken inversion symmetry [77]. In systems such as the $\text{LaAlO}_3/\text{SrTiO}_3$ 2DEG interface, spin-orbit interaction and specifically the Rashba effect may play an important role. Tunable spin-orbit interaction at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface was demonstrated simultaneously by two separate research groups by means of magnetotransport studies. One study specifically notes a correlation between the onset of spin-orbit interaction and quantum critical point toward superconductivity and furthermore a clear signature of a D'yakonov-Perel mechanism is shown, suggesting Rashba spin-orbit interaction [78]. The other study provides an explanation for the strong gate dependence of mobility and anomalous Hall signal, relating it to a spin-orbit interaction energy [44].

Comparing spin-orbit interactions in an inversion symmetry system to a broken inversion symmetry system is worthwhile in order to understand the relative influence of the Rashba effect which requires the latter. Initial work on spin orbit interaction and superconductivity in inversion symmetrical Nb-doped SrTiO_3 suggested an important role for spin orbit interaction [79]. A study comparing asymmetric $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces directly to symmetric Nb-doped SrTiO_3 concluded that Rashba spin-orbit interaction drives the first and atomic spin-orbit interaction drives the second, explaining the difference in transport properties [80]. Yet further work by another group concluded differently that the Rashba effect plays a minor role, using a band model allowing for atomic spin-orbit coupling to demonstrate a transition between d_{xy} and d_{xz}/d_{yz} orbital populations explaining observed behaviour [81].

Theoretical modeling by density-functional-theory calculations of the spin-orbit interactions points at the strong influence of multi-orbital effects and demonstrates that gate voltage does not directly drive spin-orbit interaction as the energies involved are too low [82]. Several experimental results are explained by a microscopic theory for the formation and interaction of local moments, most notably the co-existence of magnetism and superconductivity [83]. Based on measurements and theoretical modeling on a 2DEG at the surface of bulk SrTiO_3 , quantum confine-

ment and inversion symmetry breaking have been suggested to delicately balance charge, spin, orbital and lattice degrees of freedom in 2DEGs in SrTiO_3 -based surfaces and interfaces [84].

In recent years the complex influence of the Rashba effect on several specific phenomena has been demonstrated and theoretically described: in-plane rotation magnetoconductance oscillations [85], modulation of Shubnikov-de Haas oscillations [86], giant negative magnetoresistance of up to 70% [87]. The latter study provided an alternative explanation for the giant magnetoresistance, ascribing it to a combination of spin-orbit coupling and scattering from spatially correlated impurities [88] instead of conduction electron scattering from Kondo-screened magnetic impurities [19].

In order to pave the way towards more intricate device engineering, further control over the spin-orbit interaction is required. Recently it has been demonstrated that superconductivity and Rashba spin-orbit interaction may be directly controlled in top-gated field-effect devices, showing a linear increase of spin-splitting energy with interfacial electric field [89]. Another parameter is provided by crystal orientation, allowing selective 2DEG orbital occupancy driving spatial extension and anisotropy of the 2D superconductivity and the Rashba spin-orbit effect [90]. One particularly interesting field for the application of the spin-orbit interaction is in spintronics devices. Just several years ago, efficient spin-to-charge conversion using Rashba interaction has been realized in Bi/Ag interfaces by injecting a spin current into the 2DEG and measuring the charge current [91]. A similar approach has recently been used by two separate groups, demonstrating efficient and tunable spin-to-charge conversion through Rashba coupling in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces by spin pumping from a NiFe film [92, 93]. Both groups stress the importance of long scattering time on efficiency with regard to the larger effect seen versus the work in Bi/Ag interfaces.

Manipulation

While manipulation of the $\text{LaAlO}_3/\text{SrTiO}_3$ interface properties by synthesis parameters such as oxygen pressure and layer thickness have already been discussed, many more options are available to engineer the interface. An early example being the addition of a SrTiO_3 capping layer leading to electronically coupled n-type and p-type interfaces yielding conduction down to a single LaAlO_3 unit cell layer [17, 94, 95]. By introducing a single unit cell of SrCuO_2 in between the LaAlO_3 layer and SrTiO_3 capping layer, oxygen exchange is enhanced bringing reduced carrier densities and improved mobilities [96] which in turn resulted in multiple Shubnikov-de Haas frequencies providing further information about the band structure [97]. A further example allows tuning of the conductivity threshold and carrier density by the addition of $\text{La}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ layers, suggested to originate in the modulation of the amount of polarization in the combined over layers [98]. A very pronounced mobility enhancement by more than two orders of magnitude, resulting in Shubnikov-de Haas oscillations and suggesting a quantum Hall effect, is achieved at the related interface between disordered LaAlO_3 and crystalline SrTiO_3 by inserting a single unit cell of insulating polar $\text{La}_{1-1/3}\text{Sr}_{1/3}\text{MnO}_3$ [99]. Another method for manipulating interface properties by synthesis is by directed

and stable oxygen surface adsorbates from an oxygen plasma surface treatment. In this way the conductive state at the interface can be suppressed, the electrons are suggested to remain trapped in acceptor-like surface states [100]. Furthermore, surface polar adsorbates from common laboratory solvents have been shown to affect conductivity and even driving an insulator to metal transition, supporting a polarity based electronic transfer mechanism [101]. The addition of a metallic film of cobalt on top of a 1 unit cell LaAlO_3 film is shown to suppress the critical thickness threshold by inducing a charge transfer towards the Ti $3d$ bands [102].

Properties may be strongly manipulated by the electric field effect as well. It was shown that both bottom and top gating of the interface, by applying an external field over respectively the SrTiO_3 substrate or the LaAlO_3 layer, allows tuning of the 2DEG and a transition from insulating to conductive behaviour [20]. Using this field effect in a back gating setup it was demonstrated that a superconductive sample could be tuned toward an insulating state yielding similar magnetoresistance measurements as in earlier work [19], yet here it was suggested that the negative magnetoresistance was due to weak localization [38]. Using a back gating setup yields a potential envelope which pushes the carriers toward the interface where they are scattered more strongly. Top gating is a viable alternative [103, 104] which pushes carriers away from the interface; the reduced density situated in less disordered bulk SrTiO_3 , both structurally and electronically, results in a systematic increase in the Hall mobility as the sheet carrier density in the channel is depleted [105]. Besides voltage gating, electric field driven control may also be realized by adding a ferroelectric layer, allowing modulation of the conductivity and an insulator-to-metal transition [106]. Tuning the occupation of bands by a varying potential well allowed comparison of experimental data with band structure calculations from which it was concluded that electrostatics and electronic correlations play an equally important role [107].

In order to realize comprehensive measurements and devices, stable patterning of the $\text{LaAlO}_3/\text{SrTiO}_3$ interface is required. It was demonstrated early on that leveraging the LaAlO_3 thickness dependency of the conductivity combined with amorphous LaAlO_3 growth allows structuring of the 2DEG down to structures with a width of ~ 200 nm [108]. Another lithography approach uses low energy Ar^+ ion beam irradiation to bring the scale of structures down further, it allowed successful patterning down to ~ 50 nm [109]. Significantly smaller structures can be reversibly created by using voltages applied by a conducting atomic force microscope, lines written by this method were shown to be as small as ~ 3 nm [110]. It was suggested that the AFM tip facilitates removal or adsorption of oxygen from the LaAlO_3 surface when respectively writing or erasing metallic wires. Further experimental work demonstrated that conduction is indeed driven by written surface charges [111], may depend on the availability and dissociation of H_2O [112] and is also possible by oxygen ion transfer in a high vacuum environment [113]. Alternatively to the application of voltage, it has been shown that mechanical stress applied by a scanning probe tip may force oxygen vacancies out of the LaAlO_3 over layer into the SrTiO_3 and thereby modulating the conductivity [114].

1.2.2 Origin of the charge carriers

While the initial report on the discovery of conductivity at $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces noted the influence of oxygen pressure during sample synthesis, it dismissed extrinsic sources as the origin of the charge carriers [10]. As substrate alone retained insulating behaviour when exposed to similar growth conditions, while changing the termination layer of the substrate from TiO_2 to SrO rendered the subsequently grown interfaces practically insulating [10]. Later work by other groups showed that the highest carrier densities and mobilities were in fact caused by oxygen vacancy doping deep into the SrTiO_3 substrate [18, 115]. The debate on the true intrinsic origin of the charge carriers has never really subsided ever since, hampered in part by the large range of available synthesis parameters resulting in competing, possibly overlapping and sometimes meta stable phases that may co-exist in a single sample. This tunability between competing phases provides an interesting opportunity for novel functionality yet it hampers dependable growth and comparison of samples from procedures at different laboratories as the entire parameter space is never fully defined.

The main reconstructive mitigations at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface hypothesized to be an origin of the charge carriers are: polarity discontinuity driven electronic reconstruction [10, 14], oxygen vacancy formation [18, 115], cation intermixing [116, 117] and structural distortions [118, 119], see figure 1.2. The different hypotheses are discussed in more detail below.

Figure 1.2: Schematic overview depicting the different models hypothesized. Electronic reconstruction resulting in 0.5 electrons transferred per interface unit cell (a). Oxygen vacancies resulting in 2 released electrons per vacancy (b). Cation intermixing based doping (c). Structural distortions releasing electrons (d).

Electronic reconstruction

Inspired by polar discontinuities resulting in complex atomic and electronic structures in semiconductors such as GaAs on Ge [8, 9] it is intriguing to consider the polarity of ionic layers in heterostructures formed by (001) SrTiO_3 and LaAlO_3 . The polarity discontinuity driven electronic reconstruction model was introduced in the initial report on the discovery of conductivity at (001) oriented $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces [10] and further extended upon in later work, while the term "polar catastrophe" was introduced for the issue presented by the discontinuity [14]. The basic consideration here is that Ti atoms at the interface have access to mixed-valence states, which may provide an opportunity for electrons to move and mitigate the polar catastrophe in a more energy efficient way than by moving the atoms near the interface in some mitigating manner.

The electronic reconstruction model describes how depending on substrate surface termination a discontinuous $(\text{LaO})^+ / (\text{TiO}_2)^0$ or $(\text{AlO})^- / (\text{SrO})^0$ interface is realized and an electrostatic potential will build up with increasing LaAlO_3 thickness. A transferred charge of $\pm e/2$ per two dimensional unit cell would be required in order to mitigate the potential build up, yielding either a transferred electron for a n-type interface or hole for a p-type interface. For n-type interfaces the Ti atoms at the TiO_2 plane located at the interface may allow electronic reconstruction due to the available mixed valence state, resulting in $\text{Ti}^{3.5+}$. For p-type interfaces there is no such accommodating state available and in this case divergence is suggested to be avoided by removing half an electron from the SrO plane by creating oxygen vacancies.

The appeal of the model lies primarily in the explanation of a pronounced influence of surface termination on the resulting electronic behaviour [10, 120], the dependence on crystallinity [108] and the requirement of a critical thickness [20, 108] which was verified for various similar systems [121]. While the polar discontinuity should lead to a significant built-in electric field rendering the system metallic for any coverage of LaAlO_3 , density functional theory (DFT) calculations show that strong lattice polarization compensates the electric field resulting in insulating behaviour up to 5 unit cells of LaAlO_3 [122].

Further support for this model is provided by various approaches to experimental manipulation of the electric field. One such example is the modulation from insulating to a metallic state either by gate voltage [20] or polar adsorbates [101]. Other examples have to do with shifting the critical thickness threshold through for instance LaAlO_3 dilution with SrTiO_3 [123] or cobalt capping layer [102]. While significantly lower than expected, carrier densities have been shown to rise with increasing LaAlO_3 layers [124].

Measurement of the electric field within the LaAlO_3 overlayer was achieved by multiple groups using scanning tunneling spectroscopy (STS), the value for the electric field was determined at $\sim 80 \text{ meV/\AA}$ [125] and $\sim 30 \text{ meV/\AA}$ [68], although external effects such as bend bending from metal electrodes could not be excluded. Another method to probe whether an electric field exists within the LaAlO_3 overlayer is by measuring the electrostrictive effect using X-ray diffraction (XRD). This was used to demonstrate the expansion of the LaAlO_3 c-axis and relating it to the internal electric field by ab initio calculations [123, 126].

In the electronic reconstruction model the crystal orientation is important and

while SrTiO_3 (111) and (110)-oriented crystals are composed of polar planes, heterostructures with LaAlO_3 seemingly result in a discontinuity in the (111) direction but not for the (110) direction. The demonstration of conduction in (110) samples therefore called into question the polar catastrophe model [127], while other work measuring similar conduction in (110) samples attributed it to a buckled interface through which the polarization discontinuity is actually still present [128].

While this model does correctly describe many experimental findings, it may be too simplistic to ascribe all effects merely to electronic reconstruction alone. The following concerns have been raised over time: lower than expected carrier densities which are largely independent of LaAlO_3 thickness [53, 129], electric field not measurable by X-ray photoelectron spectroscopy (XPS) [130–134] or strongly reduced in STS and XRD measurements [68, 125, 126] and Ti^{3+} is detected already below critical thickness [124, 132, 135].

Apparently the situation is not quite so clear cut and early inspirational work already demonstrated the existence of intermixing and oxygen vacancies working in conjunction with electronic reconstruction to mitigate the polar catastrophe in distinct ways for both n-type and p-type interfaces [14].

Oxygen vacancy formation

Already in the initial report it was taken into consideration that SrTiO_3 may be easily doped by oxygen vacancies and therefore oxygen vacancy trapping or oxygen gettering could play a role [10]. However, oxygen vacancy doping was ruled out based on experimental observations yet open questions remained. Quickly thereafter, multiple reports demonstrated the significant influence of oxygen vacancy doping in similarly grown samples, demonstrating the very real occurrence of such doping in these interfaces and their reduction by additional annealing procedures [18, 69, 115]. In those studies it was argued that: the PLD process itself is sputtering off oxygen [18], oxygen exchange out of SrTiO_3 substrate is strongly enhanced by the reducing atmosphere during film growth [69], crystalline defects in SrTiO_3 provide enhanced diffusion removing oxygen which is not replaced as quickly through the LaAlO_3 layer [115]. It was shown, by using ^{18}O exchanged SrTiO_3 , that a substantial oxygen transfer between substrate and film is possible, suggesting that oxygen drawn from the substrate may provide the charge carriers for conductivity at these interfaces [136]. In a study comparing samples grown at high and low oxygen pressure it was noted that the high oxygen pressure samples were insulating, suggested to be due to: suppressed reduction of SrTiO_3 , higher oxidation state and lower mobility of the ablated species limiting cationic substitution [137]. The important role of oxygen pressure was singled out in this study, yet the combination of cationic substitution, oxygen vacancies, interfacial strain and local polar fields was also noted as important factors for the carrier concentration at these interfaces.

To gain further information on the formation of oxygen vacancies the behaviour in related systems has been studied. Perhaps most strikingly it was shown that amorphous LaAlO_3 grown on crystalline SrTiO_3 results in conductivity suggested to be from sputtering or redox reactions [138, 139]. While annealing removed the charge carriers completely for both studies an important role for redox reactions in

SrTiO_3 -based heterostructures was suggested [138]. Remarkably high mobilities of $1.4 \times 10^5 \text{ cm}^2/\text{Vs}$, allowing Shubnikov-de Haas oscillations, have been demonstrated at the spinel/perovskite interface of $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$. The effects being fully ascribed to interface-stabilized oxygen vacancies and presented as an alternative approach, alongside interface polarity, to create 2DEGs in complex oxide heterostructures [140]. Interestingly however, it has been pointed out that the polar catastrophe mechanism may actually play a role at this spinel/perovskite interface of $\gamma\text{-Al}_2\text{O}_3/\text{SrTiO}_3$ [141]. A study of the deposition of a wide variety of metals on SrTiO_3 suggests that often an interfacial layer of oxygen deficient SrTiO_3 is formed due to redox reactions [142].

While from the above studies it is clear that oxygen vacancies play an important role and are easily introduced, their effect in the ideal oxygen-annealed crystalline $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures was shown to be minimal [143]. From a purely oxygen vacancy doping point of view it is also hard to understand how SrO termination of SrTiO_3 would prevent their influence so markedly.

Reducing the influence of oxygen vacancy doping has been a concern from the start, using either higher partial oxygen pressure during deposition [19] or by post growth procedures such as annealing at high oxygen pressure [43]. In contrast, more recently the manipulation of oxygen vacancies using post growth treatment to tune electronic properties of the 2DEG has been demonstrated as a potentially useful tool [144].

Cation intermixing

Intermixing of cations across the interface may present a further route from which the charge carriers at these interfaces originate. It is well established that La may be used to effectively dope SrTiO_3 n-type, a nice example being epitaxial La-doped SrTiO_3 films exhibiting mobilities exceeding $10^4 \text{ cm}^2/\text{Vs}$ and Shubnikov-de Haas oscillations [145]. While an abrupt interface separating SrTiO_3 substrate and LaAlO_3 film is the ideal picture often used to model the system, intermixing of cations between SrTiO_3 substrate and film in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces was already demonstrated in early work [14].

Shortly thereafter, cationic mixing scenarios were studied in more detail, an early study claiming that the formation of metallic $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ alone explains the 2DEG [116]. Other work noted the role of cation disorder and described how it could result in the experimentally found 4 u.c. critical thickness for conductivity but merely suggested La doping as one of the possible scenarios for the conductivity itself [146]. Further notable work on this topic has been put forth by a group stressing the importance of intermixing [117, 131, 147, 148] while also pointing out similarities with behaviour found in similar systems such as La-doped SrTiO_3 films [149]. The critical thickness of 4 u.c. for the onset of conductivity is here suggested to be due to being the thickness required for enough La to diffuse into the SrTiO_3 substrate [117]. The pronounced influence of substrate termination was suggested to be due to excess Sr from SrO deposition filling Sr vacancies in the SrTiO_3 substrate which would otherwise facilitate La indiffusion [117].

However, others have pointed out that intermixing may not actually solve the polar catastrophe nor provide the straightforward doping mechanism it appears

to be. As intermixing Sr for La cations may reduce the interface dipole as a compensating mechanism, it would not remove the diverging potential itself [14]. Merely equal intermixing of cations across the interface is suggested to not result in effective doping as there would be as much donors and acceptors on either side of the interface, resulting in electrons annihilating at holes when located sufficiently near [150]. Partly compensated electrostatic energy build up and polar catastrophe retaining cation intermixing have also been demonstrated by surface X-ray diffraction (SXRD) in [151] (see also Chapter 5). Interestingly, thin SrTiO_3 films grown on LaAlO_3 substrates were shown to be fully insulating [152]. While the actual cause for the insulating behaviour proved difficult to determine, it was suggested that the lack of conductivity excludes intermixing of interface atoms as doping mechanism here.

Structural distortions

Structural distortions are commonly found in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures and typically suggested to be the result of a large range of other effects. Suggested causes for structural distortion are for instance charge repulsion [15, 153], Jahn-Teller effect [15, 116, 153], ionic radius of Ti^{3+} [116], strain [116, 154] or electrostrictive effect [126, 155, 156]. A depolarizing buckling was even suggested to counteract the internal field in polar LaAlO_3 and increase the critical thickness for the onset of conductivity [155]. Structural reconstruction was also suggested to be the cause for the lower than expected carrier densities measured and the largely thickness independence [98]. The existence of structural distortions was typically not considered as an origin for charge carriers and the main three hypotheses remained electronic reconstruction, oxygen vacancies and cation intermixing which had been introduced from the start [10, 14].

A fourth hypothesis has been put forth after carefully measuring the correlation between carrier density and strain in the LaAlO_3 layer [118]. It was suggested that large octahedral distortions in the LaAlO_3 layer get transferred into the topmost SrTiO_3 layers, changing band structure and releasing localized carriers on Ti^{3+} sites which themselves could originate from oxygen vacancies or La-diffusion. The distortion at the top most SrTiO_3 layers and their impact on interfacial transport was also noted by other work [157]

Recently, atomic-resolution imaging and electron spectroscopy has been used to demonstrate that the conductivity onset at the critical thickness of 4 unit cells is accompanied with head-to-head ferroelectric-like polarizations [119]. The divergent depolarization fields are suggested to form a screening electron gas in SrTiO_3 with LaAlO_3 hosting complementary localized holes. Polar catastrophe and cation intermixing as a cause for conductivity at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface are considered negligible in this study.

Discussion

A clear debate is still on-going regarding the origin of the charge carriers at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. Helpful reviews have been presented which try and aggregate the results of many experiments and single out one hypothesis able to

describe the origin of said effects. Sometimes such overviews may reach strikingly different conclusions however [158, 159].

Instead of one singular origin, it is probable that a combination of various competing effects are at play, intricately balanced and highly susceptible to synthesis parameters. Recent studies in this direction consider the energies required to create various non-stoichiometric defects and the influence exerted by the polar catastrophe [134, 159–162]. An approach in essence not quite different from much earlier work in which the polar discontinuity was suggested to go hand in hand with intermixing and oxygen vacancies [14]. In the end the discussion remains which of these effects may be considered intrinsic and whether non-stoichiometry can for instance be remedied by tuned synthesis as suggested by a broad study into extrinsic defects [141].

Finally, while LaAlO_3 layer deposition is crucial in most of the discussed hypotheses, there are some noteworthy similarities to be found in the electronic behaviour of SrTiO_3 lacking such a defined LaAlO_3 overlayer completely. Some examples being: manipulation by electric field effect [163, 164], 2DEG created at the surface by cleaving [165, 166] and Shubnikov-de Haas oscillations in delta La doped SrTiO_3 [149]. These effects may be to some extent also present in the prototypical $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces.

CHAPTER

2

Synthesis of epitaxial $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces

Synthesis of epitaxial $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces, fundamental in order to study the behaviour of well defined materials of high quality, will be described with examples for single interfaces, heterostructures and superlattices. Furthermore a patterning method using Ar^+ ions is discussed with an example showing a patterned single interface. Lastly, some further points regarding curved features resulting from strain build up, and mechanical AFM patterning are considered.

2.1 Introduction

In order to study the behaviour of well defined materials of high quality, it is important to establish control over their synthesis. It allows reproducible realization of samples and improves tunability for various competing factors driving their behaviour. It was shown in the groundbreaking paper by Ohtomo and Hwang [10] that epitaxial synthesis of $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces results in conductivity despite the fact that the constituent materials are insulators. Shortly thereafter subsequent STEM imaging results provided insights in the realized atomic structure [14, 17] and hypothesized on the necessity of defects found therein [14]. Unresolved questions in these early publications and critical considerations published afterwards remain partly unclarified to this day. As this system is highly sensitive to the wide range of fabrication parameters one may arrive at a wide spectrum of different samples with potentially seemingly conflicting results. Also, striving for the idealized stoichiometric materials combination with perfect separation between constituents in order to arrive at a purely "intrinsic" result from a single mechanism may prove infeasible [14]. Continued effort in understanding and improving the synthesis of these oxide materials systems will allow improved research into materials properties, functionality and may provide a route towards devices in viable applications. In this chapter the synthesis of epitaxial $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces will be described with examples for single interfaces, heterostructures and superlattices. Furthermore a patterning method using Ar^+ ions is discussed with an example showing a patterned single interface. Lastly, some further points regarding SrTiO_3 substrates, strain build up and AFM patterning are considered. While the performed experiments, using the synthesis methods described in this chapter, originate from the period 2006 to 2010, they are still relevant and their discussions connect with contemporary knowledge.

2.2 Thin film growth methodology

2.2.1 Material considerations

The oxide materials used to realize the polar discontinuity interfaces discussed herein, are of a perovskite structure which can be described by the generic formula ABO_3 where A and B are cations bonding with the oxygen anions as shown in figure 2.1. While the basic lattice system for a perovskite is cubic, stretching along one or two lattice vectors is common and results in respectively tetragonal or orthorhombic lattice systems. Distortions such as buckling, cation displacements and especially octahedral rotations provide additional degrees of freedom, potentially triggering completely new behaviour.

Interfaces comprised specifically of epitaxial LaAlO_3 and SrTiO_3 have been at the core of the research in this field but the prime attributes such as being of perovskite structure, non-conducting nature and able to form a polar discontinuity system is satisfied by many similar materials combinations. While the study of different material combinations, crystal orientations and even the inclusion of non-perovskite lattices is avidly being addressed and highly useful, here the focus is on furthering the understanding of the model system formed by the $\text{LaAlO}_3/\text{SrTiO}_3$

Figure 2.1: Schematic depiction of the perovskite structure with generic formula ABO_3 , showing sub-unit layers formed by AO and BO_2 . Schematic adapted from [167].

interfaces along the (001) crystallographic direction.

From an electronic point of view both LaAlO_3 and SrTiO_3 are insulating and non-magnetic materials in bulk, having wide bandgaps of ~ 5.6 eV and ~ 3.2 eV respectively. While both materials may be doped, specifically SrTiO_3 is sensitive to cation doping and oxygen vacancy doping from reducing environments. Where LaAlO_3 already features a relatively high dielectric constant of ~ 25 , SrTiO_3 has a markedly larger dielectric constant of 300 at room temperature which increases strongly toward $\sim 10^4$ at low temperatures. Due to these high dielectric constants, both materials are considered as gate dielectrics, e.g. in silicon electronics.

Structurally, SrTiO_3 is a cubic material with a lattice parameter of $3.905 \text{ \AA}$ at room temperature which distorts to a tetragonal structure below $\sim 110 \text{ K}$ [168]. LaAlO_3 on the other hand is of rhombohedral structure with a pseudocubic lattice parameter of $3.791 \text{ \AA}$ at room temperature which transforms to an ideal cubic structure above $\sim 820 \text{ K}$ [169–171]. Even though LaAlO_3 and SrTiO_3 are relatively well matched, having a lattice mismatch of $\sim 3\%$, the difference will result in strain when epitaxially combined. Directly at the interface this leads to distorted crystal structures affecting electronic properties while thicker overlayers may release this strain by the inclusion of a variety of defects.

Figure 2.2: Schematic depiction of heterostructures with n-type $(\text{LaO})^+ / (\text{TiO}_2)^0$ interface (a), p-type $(\text{AlO}_2)^- / (\text{SrO})^0$ interface (b), and coupled interfaces (c).

The AO en BO_2 layers in a perovskite, occurring in sequence along all three crystal directions of the structure, are shown in figure 2.1. For SrTiO_3 these layers are charge neutral in the ionic limit, being $(\text{Sr}^{2+}\text{O}^{2-})^0$ and $(\text{Ti}^{4+}\text{O}^{2-}_2)^0$. While for LaAlO_3 these layers are positively $(\text{La}^{3+}\text{O}^{2-})^+$ and negatively charged $(\text{Al}^{3+}\text{O}^{2-}_2)^-$. When combining these non-polar and polar materials with atomic control, a polar discontinuity is formed as the layer sequence will be maintained in the perovskite heterostructure. As shown in figure 2.2a and 2.2b, the stacking order at the interface results in either of the previously mentioned electrically conducting "n-type" or insulating "p-type" interfaces. In the case of a double heterostructure, the additional layer will introduce the counterpart to the initial type of interface, an example is shown in figure 2.2c.

As a synthetic polar discontinuity is directly dependent on sharp transitions between constituent materials at the atomic scale, a well defined initial substrate and substrate surface is crucial. Pure and single crystalline substrates for SrTiO_3 and LaAlO_3 are usually readily available from multiple suppliers and have been in broad use for research purposes. As received, a perovskite substrate surface is typically not sufficiently defined for atomically controlled growth as the cutting or cleaving process which shaped the surface left a mix of AO and BO_2 surface terminations. Established procedures are available for SrTiO_3 which, by combining chemical and thermal treatments, allow successful single termination of the surface with a crystalline TiO_2 atomic plane [172, 173]. A procedure resulting in stable single atomic plane termination of LaAlO_3 across the wide range of temperatures encountered during deposition is not currently available. Therefore, TiO_2 termi-

nated SrTiO_3 substrates are typically used to fabricate $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces.

2.2.2 Pulsed laser deposition

Initially demonstrated in 1965 [174], PLD did not gain much traction in the next two decades as resulting films were of inferior quality to other deposition techniques and availability of the required lasers with stable output and high repetition rates was low. This situation changed significantly when PLD was used to grow high temperature superconducting thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [175], showing improved quality compared to other deposition techniques. While the PLD process itself is quite complex, it has since proven to be a relatively simple to deploy and versatile deposition technique, yielding stoichiometric transfer for many materials at well controllable growth rates.

The first samples demonstrating conductivity at $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces were grown using PLD [10] and it has been the main deposition technique for the field. Alternative deposition techniques have been used however, primarily within the physical vapor deposition class, to compare with and extend upon earlier results, often to good effect. Molecular beam epitaxy was for instance employed with flux gradients, demonstrating the importance of cation stoichiometry and a La/Al ratio <1 requirement for 2DEG formation [141]. In another example, sputtering in high oxygen pressure yielded smooth films with atomically sharp interfaces, if only in a small parameter window, yet all interfaces remained insulating suggested to be due to the inability to reach the same La/Al ratio <1 requirement [176]. As a chemical vapor technique, atomic layer deposition was used to grow amorphous LaAlO_3 on crystalline SrTiO_3 substrates, yielding conductivity which was suggested to be due to the formation of oxygen vacancies [139]. As is the case for most research on $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces, all samples herein were prepared by pulsed laser deposition due to the advantages provided by the technique and as it allowed more direct comparison to results from other research groups, starting from the earliest days of $\text{LaAlO}_3/\text{SrTiO}_3$ interface property characterization.

All samples discussed herein were fabricated on the same pulsed laser deposition setup located at the MESA+ Institute for Nanotechnology at University of Twente. Here, the source for the required ablation energy is formed by a 248nm KrF ~ 25 ns pulsed excimer laser, operated at 1Hz repetition rate. This laser beam is shaped by a mask in order to select the most uniform inner section of the beam, yielding an improved definition of energy density per surface area. A focusing lens then projects this beam into a high vacuum chamber, illuminating a target under an angle of 45° with an energy density of 1.3 J/cm^2 , defined by a combination of laser energy and focal spot size. The target comprises either SrTiO_3 or LaAlO_3 single crystals, optionally both are mounted on a target carousel allowing these materials to be deposited in sequence on a single sample. Initially, the intense laser beam energy is absorbed at the surface of the target which evaporates, yielding further scattering and absorption of laser energy resulting in locally very high temperatures and pressure. As the electrons in the material are now in an excited state, photons are emitted and an illuminated plasma plume is visibly expanding outward into the low pressure of the vacuum chamber. The particles within the plasma plume are mediated by the background gas pressure, here composed of

Figure 2.3: Schematic overview of a typical PLD system (a) and close up of RHEED monitoring setup (b). RHEED patterns are shown for a clean SrTiO_3 substrate (c) and LaAlO_3 films with a smooth surface (d), some surface roughness (e) and the onset of 3-dimensional island growth (f)

O_2 , losing energy on their outward expansion. This reduces plasma plume size while also making it more directional as background pressure is increased, other more complex changes to plasma plume composition are driven by background pressure as well. For the samples discussed here, pressures ranging from 2.5×10^{-3} mbar to 1×10^{-6} mbar are used primarily to control oxygen content of the involved materials. By placing a substrate in the path of the expanding plasma plume, ablated material may be deposited and thereby a thin film grown. While some kinetic energy is still contained within the arriving material, the substrate is heated to 850° which is optimized to yield improved diffusivity for the particles on the surface, resulting in an ideal layer-by-layer growth mode. For an overview of the PLD setup used, see figure 2.3a.

2.2.3 Growth monitoring

A wide range of tools allow the characterization of a film after growth has been completed, either in-situ or ex-situ. However, in-situ monitoring during growth is crucial for efficient control and optimization of both stoichiometry and growth rate. For thin film deposition, monitoring is most often realized by reflection high-energy electron diffraction (RHEED) originating in the discovery of surface related diffraction patterns from grazing incidence cathode rays [177]. These patterns were demonstrated to modulate during deposition, notably yielding intensity oscillations providing information on sub-monolayer growth [178, 179]. RHEED became a dependable monitoring tool for pulsed laser deposition of complex oxide thin films after the introduction of a two-stage differential pumping system, allowing for the high oxygen pressures required and thereby opening up many materials for controlled growth by PLD [180].

RHEED employs high-energy electrons, typically in the range of 10-30 keV, which are directed toward a sample at a grazing incidence angle of several degrees. Due to this very shallow angle, interaction of the electrons with the sample is confined to the topmost layers only, rendering this technique highly surface sensitive. After interaction with the surface, the forward reflected electrons are visualized by a phosphor detector screen which is being captured by a CCD camera directly behind it, see figure 2.3b. The interaction between high-energy electrons of well defined wavelength with the crystalline lattice of the material results in interference leading to diffraction patterns on the detector. For very clean and atomically smooth surfaces, the electron interaction with the surface is dominated by single elastic scattering called kinematic scattering. In this case the diffraction pattern exhibits spots lying on concentric Laue circles which originate from the intersection of Ewald's Sphere with reciprocal lattice rods, satisfying interference requirements. Surfaces with 3D islands result in more pronounced multiple scattering of electrons, transforming the sharp reciprocal lattice rods into broadened reciprocal lattice points and resulting in a diffraction pattern exhibiting spots on a rectangular grid. See figure 2.3 for examples of associated RHEED patterns.

Growth monitoring is performed by measuring the intensity of a bright diffraction spot originating from and therefore depending on the initially smooth surface. With the wavelength of the high-energy electrons much smaller than surface step edges, the electrons are easily scattered from such out-of-plane components. In the case of layer-by-layer growth mode, a surface is initially roughened as a new monolayer is forming. The resulting increase in step edges, and therefore out-of-plane scattering, is accompanied with a decrease of intensity at the initial diffraction spot. At roughly half a monolayer, step edge density is at a maximum, resulting in a minimum of the spot intensity. Further growth fills up the monolayer, resulting in a smooth surface with the associated high initial diffraction spot intensity. Continued growth leads to the process repeating itself sequentially. In effect, this oscillatory increase and decrease of step edge density on the surface allows layer-by-layer growth monitoring with sub monolayer resolution. However, deviations from ideal layer-by-layer growth has a strong influence on the oscillatory behaviour, e.g. a transition to island- or step flow growth modes will reduce the oscillation amplitude, inhibiting further growth monitoring.

2.3 Engineering of epitaxial interfaces

The growth methodology described above enables interfaces based on a wide range of material combinations to be realized and studied. Indeed, as the phenomena found in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces have been debated from the onset, related interface systems were created with various techniques yielding sometimes conflicting conclusions [115, 139, 181, 182]. In a similar vein, systems based on LaAlO_3 and SrTiO_3 are for instance created with intermixed [123] or off-stoichiometric [141] constituents on purpose. The approach taken here is to pursue ideal interfaces formed by the $\text{LaAlO}_3/\text{SrTiO}_3$ model system, spanning three main categories as shown in Figure 2.4: single interfaces, coupled interfaces and superlattices.

Figure 2.4: Schematic depiction of the different type of systems synthesized: single interface (a), coupled interfaces (b) and superlattice (c).

2.3.1 Single interfaces

The single n-type $\text{LaAlO}_3/\text{SrTiO}_3$ interface has been the model system in its purest form since the original discovery of conduction [10]. While this system may appear deceptively straightforward, many growth parameters actually affect resulting structural composition and electronic behaviour in a striking way. This versatile tunability may be one of the most promising aspects of these interfaces, yet it also imposes strict requirements on the level of control over the growth of these interfaces.

Typical deposition parameters for the single interface samples shown here are as follows. A single crystal LaAlO_3 (001) target is ablated at a laser fluence of $\sim 1.3 \text{ J/cm}^2$ and a repetition rate of 1 Hz. The substrate is held at 850°C during deposition, while typically an oxygen pressure between 2×10^{-3} mbar and 3×10^{-5}

mbar is used. After growth, the sample is slowly cooled to room temperature in the oxygen deposition pressure at a rate of $10^\circ\text{C}/\text{min}$.

Figure 2.5: RHEED pattern with AFM image of the initial TiO_2 -terminated SrTiO_3 (100) substrate (a), RHEED intensity monitoring during growth of a thin 13 uc LaAlO_3 layer at 2×10^{-3} mbar (b) and RHEED pattern with AFM image of the final surface of the LaAlO_3 toplayer (c).

Prior to the start of LaAlO_3 growth, both ex-situ AFM topography and in-situ RHEED pattern for the TiO_2 -terminated SrTiO_3 (001) substrate verify the smoothness of the initial substrate surface, as shown in Figure 2.5a. RHEED analysis during growth of a relatively thin 13 unit cells LaAlO_3 layer is shown in Figure 2.5b. Clear intensity oscillations indicate control on the unit cell scale due to the layer-by-layer growth mode. The constant number of laser pulses, which is required to form one unit cell, and the constant intensity at the maximum of the oscillation suggest the growth of individual unit cells of LaAlO_3 with a constant surface roughness. The sharp decrease in RHEED intensity for the first LaAlO_3 unit cells can be explained by the difference in the optimal diffraction conditions for both materials, because the RHEED monitoring was initially aligned with the SrTiO_3 unit cell of the substrate [120]. The difference in c-axis length between the initial SrTiO_3 unit cell ($3.905 \text{ \AA}$) and the deposited LaAlO_3 unit cell ($3.791 \text{ \AA}$) requires a new alignment of the RHEED monitoring for optimal surface analysis. After deposition, both in-situ RHEED pattern and ex-situ AFM topography for the AlO_2 -terminated LaAlO_3 overlayer verify the smoothness of the resulting sample surface, as shown in Figure 2.5c.

Figure 2.6: RHEED patterns with AFM images of the initial TiO_2 -terminated SrTiO_3 (100) substrates (a,d), RHEED intensity monitoring during growth of thick 52 uc LaAlO_3 layers at 2×10^{-3} mbar and 3×10^{-5} mbar (b,e) and RHEED patterns with AFM images of the final surfaces of the LaAlO_3 toplayer layers (c,f).

With thickness and oxygen background pressure as important tuning parameters, correct growth of LaAlO_3 throughout an extended range has been established by the growth of relatively thick 52 unit cell LaAlO_3 layers at both 2×10^{-3} mbar and 3×10^{-5} mbar. Prior to the start of LaAlO_3 growth, both ex-situ AFM topography and in-situ RHEED pattern for the TiO_2 -terminated SrTiO_3 (001) substrates verify the smoothness of the initial substrate surface, as shown in Figure 2.6(a,d). RHEED analysis during growth of 52 unit cells LaAlO_3 layers is shown in Figure 2.6(b,e). Clear intensity oscillations, indicating control on the unit cell scale, are maintained throughout the entire 52 unit cell deposition sequence suggesting the growth of individual unit cells of LaAlO_3 with a constant surface roughness. After deposition, both in-situ RHEED pattern and ex-situ AFM topography for the AlO_2 -terminated LaAlO_3 overlayers verify the smoothness of the resulting sample surface, as shown in Figure 2.6(c,f). Therefore in this way, one is able to study samples engineered with unit cell fidelity up to relatively high thicknesses at a wide range of background pressures.

The above single interfaces are all n-type due to TiO_2 -termination of the used SrTiO_3 interfaces. As there is no similar and dependable SrO -termination procedure available, growth of single p-type interfaces is dependent on in-situ growth,

by interval pulsed laser deposition, of a single unit cell SrO as terminating layer [183, 184] prior to LaAlO_3 deposition. Subsequent control over correct growth of LaAlO_3 on these SrO terminated SrTiO_3 substrates has been established by the growth of relatively thick 52 unit cell LaAlO_3 layers at both 2×10^{-3} mbar and 3×10^{-5} mbar. Prior to the start of SrO growth, both ex-situ AFM topography and in-situ RHEED pattern for the TiO_2 -terminated SrTiO_3 (001) substrates verify the smoothness of the initial substrate surface, as shown in Figure 2.7(a,e)

RHEED analysis during growth of 1 unit cell SrO is shown in Figure 2.7(b,f). As all SrO material for 1 unit cell is deposited almost instantly during interval pulsed laser deposition, the RHEED intensity drops sharply to a minimum. As a smooth single unit cell is formed over the subsequent ~ 80 seconds, RHEED intensity largely recovers and the resulting RHEED pattern, as shown in the insets of Figure 2.7(b,f), verifies the smoothness of the now SrO terminated sample surface prior to the start of LaAlO_3 growth. RHEED analysis during growth of the subsequent 52 unit cells LaAlO_3 layers is shown in Figure 2.7(c,g). Clear intensity oscillations are maintained throughout the entire 52 unit cell deposition sequence, albeit at a reduced amplitude compared to deposition directly on TiO_2 -terminated SrTiO_3 (100) substrates, suggesting the growth of individual unit cells of LaAlO_3 with somewhat increased surface roughness. After deposition, both in-situ RHEED pattern and ex-situ AFM topography for the now LaO-terminated LaAlO_3 overlayers verify the somewhat reduced smoothness of the resulting sample surface, as shown in Figure 2.7(d,h). Therefore in this way, one is able to study samples engineered with unit cell fidelity up to relatively high thicknesses at a wide range of background pressures.

Carefully engineered samples created by this procedure have subsequently been used for the research presented in Chapter 3, 4 and 5 and further studies on for instance electronic phase separation [54].

Figure 2.7: RHEED patterns with AFM images of the initial TiO_2 -terminated SrTiO_3 (100) substrates (a,e), RHEED intensity monitoring during growth of 1 uc SrO layers at 0.13 mbar (b,f), RHEED intensity monitoring during growth of thick 52 uc LaAlO_3 layers at 2×10^{-3} mbar and 3×10^{-5} mbar (c,g) and RHEED patterns with AFM images of the final surfaces of the LaAlO_3 top layers (d,h).

2.3.2 Coupled interfaces

The single interfaces presented in the previous section may be of either n-type or p-type sequence order, yet an interesting situation appears when a SrTiO_3 capping layer is introduced. While for LaAlO_3 films grown on TiO_2 -terminated SrTiO_3 substrates an insulator to metal transition is found when the LAO film exceeds a thickness of 3 unit cells [20], metallic behaviour is seen already for single LaAlO_3 unit cell thickness when an SrTiO_3 capping layer is grown on top of the LaAlO_3 film [17]. Furthermore, in this case both n-type and p-type interfaces co-exist in a single sample, potentially leading to interesting interaction phenomena as their proximity is modulated. Samples have been prepared, allowing these and other interesting characteristics to be studied methodically.

For all samples, substrates had vicinal angles of $\sim 0.1^\circ$. Single crystal $\text{STO}(001)$ and $\text{LAO}(001)$ targets were ablated at a laser fluence of $\sim 1.3 \text{ J/cm}^2$ and a repetition rate of 1 Hz. The substrate was held at 850°C during deposition of both layers, while an oxygen pressure of $2 \times 10^{-3} \text{ mbar}$ was used. After growth, the heterostructures are slowly cooled to room temperature in the oxygen deposition pressure at a rate of 10°C/min .

Figure 2.8: RHEED intensity and FWHM monitoring during growth of a $\text{SrTiO}_3(001)/(5 \text{ uc } \text{LaAlO}_3)/(10 \text{ uc } \text{SrTiO}_3)$ heterostructure by RHEED-assisted pulsed laser deposition. The insets show the RHEED patterns of (left) the initial TiO_2 -terminated SrTiO_3 (100) substrate and (right) the final surface of the SrTiO_3 toplayer.

RHEED analysis during growth of one $\text{STO}(001)/\text{LAO}/\text{STO}$ heterostructure comprised of 5 unit cells LaAlO_3 and 10 unit cells SrTiO_3 is shown in Figure 2.8. Clear intensity oscillations during growth of each individual layer indicate control on the unit cell scale due to the layer-by-layer growth mode. The constant number of laser pulses, which is required to form one unit cell, and the constant intensity at the maximum of the oscillation suggest the growth of individual unit cells of LaAlO_3 with a constant surface roughness. The sharp decrease in intensity for the first LaAlO_3 unit cells is partly recovered after a few unit cells SrTiO_3 as the c -axis length for the deposited SrTiO_3 unit cell ($3.905 \text{ \AA}$) returns RHEED monitoring back toward optimal diffraction conditions.

Growth of individual unit cells layers with a constant surface roughness was confirmed by the fluctuations in the full width at half maximum (FWHM) of the specular RHEED spot, which exhibit identical oscillations, but inverted compared to the specular spot amplitude [120]. The lower half of Figure 2.8 shows the constant FWHM value, after growth of each LaAlO_3 and SrTiO_3 unit cell, indicating constant surface roughness without the formation of islands. The corresponding RHEED patterns are shown in the insets of Figure 2.8 for the TiO_2 -terminated SrTiO_3 (001) substrate and SrTiO_3 toplayer. The clear two-dimensional spots in the RHEED patterns demonstrate the conservation of (1×1) surface reconstruction from the initial TiO_2 -terminated STO (100) substrate [185] surface to the final surface of the STO top layer with low surface roughness.

Figure 2.9: RHEED intensity analysis during epitaxial growth of two $\text{SrTiO}_3(001)/(2 \text{ uc } \text{LaAlO}_3)/(1 \text{ uc } \text{SrTiO}_3)$ heterostructures by RHEED-assisted pulsed laser deposition showing identical characteristics (a). Temperature dependent scanning tunneling microscopy (STM) and spectroscopy (STS) are performed by monitoring the tunneling current I_t between the tip and the sample as a function of V_s , voltage at the sample relative to the tip. Surface topography image (b) and corresponding height profile recorded by STM at -1.0 V and 300 K (c).

Demonstrating the high level of control and reproducibility of the growth procedure, RHEED intensity analysis of the growth of two $\text{SrTiO}_3(001)/(2 \text{ uc } \text{LaAlO}_3)/(1 \text{ uc } \text{SrTiO}_3)$ heterostructures is shown in Figure 2.9a. Identical char-

acteristics were observed in the RHEED analysis displaying the reproducibility of RHEED-assisted pulsed laser deposition. The deposition of LaAlO_3 was stopped exactly in the second maximum of the RHEED intensity, indicating the growth of two unit cells. The deposition of the SrTiO_3 toplayer was interrupted after a single unit cell. However, one extra laser pulse, more than required for the maximum of the RHEED intensity oscillation, was given to be certain that the SrTiO_3 toplayer was fully closed. This can be observed in Figure 2.9a where the intensity after the last laser pulse is slightly lower than the intensity of the maximum. Smoothness of the resulting surface is confirmed by STM imaging shown in Figure 2.9b and c.

Figure 2.10: Epitaxial growth of $\text{SrTiO}_3(001)/\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures by RHEED-assisted pulsed laser deposition. Four different heterostructures are shown with a thickness combination of the $\text{LaAlO}_3/\text{SrTiO}_3$ layers of 2/1, 2/2, 2/5 and 5/10 unit cells. Clear intensity oscillations indicate layer-by-layer growth of single unit cells.

RHEED analysis during growth of the $\text{STO}(001)/\text{LAO}/\text{STO}$ heterostructures for various thicknesses of the LaAlO_3 and SrTiO_3 layers is shown in Figure 2.10. Data is shown for four different heterostructures with a thickness combination of the $\text{LaAlO}_3/\text{SrTiO}_3$ layers of 2/1, 2/2, 2/5 and 5/10 unit cells.

Carefully engineered samples created by this procedure have subsequently been used for the research presented in Chapter 6 and further studies on parallel electron-hole bilayer conductivity [94].

2.3.3 Superlattices

While both n-type and p-type interfaces are present in the samples described in the previous section, one could envision additional benefit from being able to realize superlattice samples containing a multitude of such interfaces. Superlattices with varying spacing between interfaces could provide further insight on location,

thickness and type of conducting sheets when measured by cross-sectional conducting probe microscopy. Superlattices with strictly constant layer thicknesses could on the other hand provide increased signal strengths when probing for atomic structure by e.g. x-ray diffraction.

For superlattice samples, the procedure is an extension on the one described for coupled interfaces in the previous section. By repeated growth of periods comprised of LaAlO_3 and SrTiO_3 layers, the superlattice is formed. Typically, total deposition layer thicknesses are much larger than for single and coupled interfaces, placing additional requirements on the extent of control over growth.

Figure 2.11: RHEED intensity analysis during epitaxial growth of an ~ 80 nm $[(\text{LaAlO}_3)_5/(\text{SrTiO}_3)_5]_{20}$ superlattice, showing the initial two and the final twentieth period.

RHEED analysis during growth of an ~ 80 nm $[(\text{LaAlO}_3)_5/(\text{SrTiO}_3)_5]_{20}$ superlattice is shown in Figure 2.11. Clear and identical intensity oscillations are shown for the first two periods of 5 unit cells LaAlO_3 and 5 unit cells SrTiO_3 each, indicating unit cell control of a constant quality. Intensity oscillations are maintained all throughout the growth of the superlattice, including the final twentieth period. Here it may be seen that while by now the oscillation amplitude

has diminished somewhat, indicating increased surface roughness, the amount of pulses per oscillation has remained the same, indicating continued layer-by-layer growth mode.

Figure 2.12: X-ray diffraction θ - 2θ scan of superlattice $[(\text{LaAlO}_3)_6/(\text{SrTiO}_3)_6]_{10}$ (a), zoom-in on (001) peak for $[(\text{LaAlO}_3)_6/(\text{SrTiO}_3)_6]_{10}$ (b).

In order to verify epitaxial growth and atomic structure, superlattices were measured by X-ray diffraction in a θ - 2θ setup. The diffraction profile for a $[(\text{LaAlO}_3)_6/(\text{SrTiO}_3)_6]_{10}$ superlattice is shown in 2.12a. The main SrTiO_3 substrate reflections are clearly visible and straddled by sharp equidistant superlattice satellite peaks. The spacing between satellite peaks allows the calculation of superlattice modulation lengths by the following equation:

$$\Lambda = \frac{\lambda}{2|\sin\theta_{n\pm1} - \sin\theta_n|}, \quad (2.1)$$

with λ the wavelength of the radiation (here Cu K- α based 0.154 nm) and θ_n the angle of the n^{th} order satellite peak. The satellite peaks shown in 2.12b for a $[(\text{LaAlO}_3)_6/(\text{SrTiO}_3)_6]_{10}$ superlattice allow calculation of a modulation length of ~ 4.5 nm. This is somewhat lower than the nominal expected value of 4.616 nm for the periodic superlattice thickness as intended and derived by RHEED monitoring, probably caused by strain due to the SrTiO_3 substrate reducing the LaAlO_3 c-axis lattice parameter.

Samples created by this procedure have subsequently been used for such studies as cross-sectional scanning probe microscopy at Stanford University, STEM and EELS studies at University of Antwerp and Forschungszentrum Jülich and synchrotron X-ray diffraction at The European Synchrotron Radiation Facility, these studies are not included in this thesis.

2.4 Patterning

Various methods for $\text{LaAlO}_3/\text{SrTiO}_3$ patterning have been described in Chapter 1. Lithography using either amorphous LaAlO_3 deposition [108] or Ar^+ ion beam etching [109] and scanning probe writing by application of voltage [110] are probably most prominent. For the work described here, structured samples were also occasionally required. In these cases a UV lithography technique based on Ar^+

ion beam etching was typically used, see Figure 2.13 for a schematic overview. The sample containing an interface under study would have a lithographic resist mask applied through which gold contacts are deposited by sputtering. These contacts are to allow easier contacting and subsequent lithography resist mask alignment. This second resist mask allows Ar^+ ion etching based removal of the LaAlO_3 layer to a thickness below the critical thickness for conductivity, 0 to 3 unit cell LaAlO_3 [20], with reasonably good controllability and uniformity. Wire bonding to the gold pads allows good ohmic contacts to the underlying interface to be studied. This approach has for instance been used for the patterned samples studied in Chapter 4.

Figure 2.13: Schematic overview of patterning technique. Initial heterostructure (a), sputter deposited gold contacts (b), Ar^+ ion etched structure (c), contacting by wire bonding (d).

While the process described is simple in terms of steps involved, several remarks can be made regarding this process. First, using Ar^+ ion beam etching to remove LaAlO_3 is not without risks as removal of LaAlO_3 exposes the SrTiO_3 for atomic intermixing and Ar^+ -ion beam driven oxygen vacancy creation which may render the entire region highly conductive instead of insulating. Indeed, this was the primary consideration for the earlier mentioned alternate method based on amorphous LaAlO_3 . Replacing Ar^+ ion beam etching by a wet etch method would also mitigate such doping risks, however the process required was more difficult to control in terms of uniformity and resist stability. Second, as the gold contacts

are not directly touching the interfacial conductive layer the use of contact probes is less suitable. Adding an extra process step which creates Ar^+ ion beam etched holes in advance into which gold is then deposited would help in these situations.

2.5 Further considerations

When working with these types of samples for some years, certain approaches may prove more difficult than originally envisioned and unexpected results may present themselves. From the subset of such encounters on the meandering path that is research, two are included here as interesting further considerations.

Strain

As unit cell lattices of heterostructure candidates are typically not entirely matched in size, the lattice of thin deposited films is strained to match the lattice of the substrate. Even though this may potentially provide an extra tool to effectively influence structural and electronic properties of the material outside of the normal boundaries, significant strain may be induced locally. For $\text{SrTiO}_3/\text{LaAlO}_3$ samples with relatively defect free and thick layers of high crystalline quality, the accompanying strain forces may build up significantly and eventually break and curve the top layers into spectacular features upon sample cool down as shown in figure 2.14. The break lines of the structures are formed perpendicular, perfectly oriented along the in-plane crystal directions (100) and (010).

Figure 2.14: Strain release features on the surface of samples comprised of $\sim 50\text{nm}$ LaAlO_3 (a) and $\sim 100\text{nm}$ $[(\text{LaAlO}_3)_{10}/(\text{SrTiO}_3)_6]_{17}$ superlattice (b).

This effect may occur on thick single overlayers such as $\sim 50\text{nm}$ LaAlO_3 as shown in Figure 2.14 a; and superlattices such as $\sim 100\text{nm}$ $[(\text{LaAlO}_3)_{10}/(\text{SrTiO}_3)_6]_{17}$ shown in Figure 2.14 b. While shape clearly plays a pronounced role, a general aspect that stands out from these examples is the brightness contrast between overlayer and exposed substrate. This contrast may be due to the lack of conduction in the SrTiO_3 substrate resulting in charging and the lower atomic number of SrTiO_3 resulting in higher electron penetration depth, both leading to less scattered electron brightness on such locations. For the superlattice sample

the contrast is less pronounced however, this may be due to the overlayer being of mixed composition and the higher acceleration voltages used, causing higher penetration depths in general. Even where material is not actually released, structural domain formation is readily visible in images such as Figure 2.14a.

With regard to the $\sim 50\text{nm}$ LaAlO_3 sample, the released layer appears to be of $\sim 100\text{nm}$ thickness while the radius of the resulting circular features is $\sim 5\mu\text{m}$, see also Figure 2.15a. It is interesting that a roughly equivalent amount of SrTiO_3 appears to be released as one single material. Apparently the strain is not released directly at the interface or somewhere within the grown overlayer, one could readily envision a deposited layer as being of lesser quality than an ideally crystalline substrate. The exposed surface appears relatively, but not completely, smooth with minor rippling morphology along the largest length of material release. One may hypothesize the curved outer SrTiO_3 surface and inner LaAlO_3 surface to be relaxed to their respective lattice constants, respectively $3.905\text{ \AA}$ and $3.789\text{ \AA}$, while the material in between is strained. In such a scenario the inner LaAlO_3 surface circumference and thus radius would be 3% smaller. Here the difference between outer and inner radius is naturally defined by released material thickness which is $\sim 2\%$. Therefore it is suggested that for these striking features, the underlying cause for them to release and curl is strain which is largely relaxed on the outermost surfaces. Residual strain or defects may explain the deviation from the ideal 3% difference.

Figure 2.15: Thickness and radius of features on samples comprised of $\sim 50\text{nm}$ LaAlO_3 (a) and $\sim 100\text{nm}$ $[(\text{LaAlO}_3)_{10}/(\text{SrTiO}_3)_6]_{17}$ superlattice (b).

Regarding the $\sim 100\text{nm}$ superlattice, the released layer appears to be of $\sim 200\text{nm}$ thickness while the radius of the resulting circular features is $\sim 10\mu\text{m}$, see also Figure 2.15b. Like before, the difference between feature radius and released layer thickness is $\sim 2\%$. This value is actually equal to the difference between the lattice parameter of the SrTiO_3 substrate and the average lattice parameter of the superlattice, respectively $3.905\text{ \AA}$ and $3.832\text{ \AA}$. This suggest that this time the outermost surfaces may have relaxed to nominal values and defects play a minor role. The lower amount of defects may be in line with the general experience that $\text{LaAlO}_3/\text{SrTiO}_3$ superlattices tend to be easier to grow coherently to higher thicknesses than single LaAlO_3 layers. These features seem to signify that layers up

to 100 nm may be grown with little defects which would otherwise have mitigated the strain.

The layers discussed here are of considerable thickness, leading to potentially larger impact for strain. Yet possibly this effect is already present, to a lesser extent, in thinner sample layers which are more common. In such cases the initial domain forming could result in anisotropic conduction on the microscopic scale, potentially even forming periodic barriers. It could be worthwhile to verify by high resolution piezoresponse force microscopy methods whether such structural domain boundaries play a role when anisotropic conductance is found in these systems. One would imagine that the conductance of the interface is strongly impacted on such areas. In such instances it would be advisable to evaluate sample cooling procedures after growth and slow them down further to possibly reduce this effect.

Fully released features may be found, such as the one in Figure 2.15a. The strongly reduced brightness on the feature seems to point to charging and it being electrically insulated from its environment. Possibly one may use this technique to realize and study unique structures where ideal in-plane crystalline interface based 2DEG's are curled out of plane onto itself.

Mechanical AFM writing

While larger structures are typically realized by lithography techniques which define the structural composition at the interface [108], smaller feature sizes may be reached by PFM based methods which manipulate the electrical reconstruction at the interface [110]. Using a PFM method to directly define the structural composition at the interface may allow small feature sizes with stable electronic behaviour. This definition could be based on SrTiO_3 substrate termination and for this the manipulation of thin SrO layers by AFM has been studied. If successful, in this way one would also be able to study in-plane proximity interaction of n-type and p-type interfaces.

As initial step, a TiO_2 terminated SrTiO_3 substrate is covered with a thin layer of amorphous SrO deposited at room temperature by PLD, the amount of SrO being roughly equivalent to 1 mono layer. The atoms in this amorphous layer of SrO are expected to be much more loosely bound than the crystalline atoms comprising the SrTiO_3 substrate surface, allowing easier mechanical removal of SrO while maintaining substrate surface integrity. Subsequently scanning the surface of the sample by AFM within a range of increased applied tip forces, SrO may be removed resulting in an exposed smooth and clean SrTiO_3 substrate, see Figure 2.16a. Continued scanning does not result in any further material removed, verifying the transition to a surface comprised of much stronger material composition and structure. The layer removed appears to be of roughly 0.5nm thickness, see Figure 2.16 b, more than double the amount expected for a single SrO monolayer. This is probably due to a lower density of the SrO layer following from the amorphous nature of the layer. Care must be taken when choosing tip forces as one may pass through a spectrum of results. At low forces the SrO surface is seemingly unaffected, medium forces removes the SrO and excessive forces combined with high tip stiffness may eventually also remove substrate atoms which was verified by scanning on clean SrTiO_3 substrates.

Figure 2.16: AFM topography image showing removed material and clear step edges after scratching (a) with resulting line scans showing depth of removed material (b). Example feature of $\sim 50\text{nm}$ width (c). Intended measurement structure allowing variable widths and lengths from 0.5 to 2.5 μm (d).

In this way it was possible to create feature sizes thinner than 50 nm with no obvious limit to length, see Figure 2.16 c. The intention was to follow up with a subsequent LaAlO_3 deposition step, at reduced initial deposition temperatures if required to lower SrO diffusion. And finally to measure electronic behaviour of various lengths and widths of features by contacting to lithographically defined leads, see Figure 2.16 d. Unfortunately, it proved difficult to realize a reliable connection from defined contacts in order to measure a possible conductive channel. This was mostly hampered by alignment to the mechanical AFM written features and possible material diffusion at elevated temperatures. A more thorough study of the separate process steps involved may shed some light on the feasibility of this approach. If successful it could form another interesting approach towards structural definition at interfaces and aid in device fabrication.

CHAPTER

3

Magnetic effects at the interface between non-magnetic oxides

To verify the existence of induced magnetism and low dimensionality at the interface, transport properties on $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces have been studied down to 300 mK and in magnetic fields, B , up to 30 T. A large negative magnetoresistance of the interface is found, together with a logarithmic temperature dependence of the sheet resistance. A hysteresis artefact is evaluated separately and ascribed to a magnetocaloric effect in the sample holder. Furthermore, these earliest results on magnetic effects in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces are discussed in retrospect. [In collaboration with the research group of prof. Zeitler, High Field Magnet Laboratory at Radboud University Nijmegen]

This chapter contains parts of the following publication:

A. Brinkman, M. Huijben, M. van Zalk, **J. Huijben**, U. Zeitler, J. C. Maan, W. G. van der Wiel, G. Rijnders, D. H. A. Blank, and H. Hilgenkamp, *Magnetic effects at the interface between non-magnetic oxides*, Nature Materials **6**, 493 (2007)

The author of this PhD thesis has contributed to this publication by the fabrication of samples, the performed measurements and the discussion of results.

3.1 Magnetic effects ¹

The electronic reconstruction at the interface between two insulating oxides can give rise to a highly-conductive interface [6, 10]. Here we show how, in analogy to the remarkable interface-induced conductivity, magnetism can be induced at the interface between the otherwise nonmagnetic insulating perovskites SrTiO_3 and LaAlO_3 . A large negative magnetoresistance of the interface is found, together with a logarithmic temperature dependence of the sheet resistance. Magnetic ordering is a key issue in solid-state science and its underlying mechanisms are still the subject of intense research. In particular, the interplay between localized magnetic moments and the spin of itinerant conduction electrons in a solid gives rise to intriguing many-body effects such as Ruderman-Kittel-Kasuya-Yosida interactions [186], the Kondo effect [187], and carrier-induced ferromagnetism in diluted magnetic semiconductors [188]. The conducting oxide interface now provides a versatile system to induce and manipulate magnetic moments in otherwise non-magnetic materials.

The discovery [6, 10] of conduction caused by electronic reconstruction at oxide interfaces has attracted a lot of interest [12, 14–17, 20, 189, 190]. The general structure of the perovskites ABO_3 , with A and B being cations, can be regarded as a stack of alternating sub-unit-cell layers of AO and BO_2 . A heterointerface introduces polarity discontinuities when both elements A and B on either side of the interface have different valence states. Recently, Ohtomo and Hwang [10] found different electronic behaviour for thin LaAlO_3 films on either SrO or TiO_2 terminated SrTiO_3 substrates, the former interface being insulating and the latter interface being an n-type conductor. Assuming the formal valence states, the polarity discontinuities can be described by either the $(\text{SrO})^0/(\text{AlO}_2)^-$ or $(\text{TiO}_2)^0/(\text{LaO})^+$ sequence [14]. Similar behaviour was found for the $\text{LaTiO}_3/\text{SrTiO}_3$ interface [6], resulting in a surplus of half an electron per unit cell at the TiO_2/LaO interface, entering the otherwise empty conduction band. In addition to charge degrees of freedom at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, also an induction of spin states at interfaces can be expected. Following this scenario, a ferromagnetic alignment of the induced electron spins within the Ti-3d conduction band was theoretically predicted for the $\text{LaTiO}_3/\text{SrTiO}_3$ interface [11] as well as for the $\text{LaAlO}_3/\text{SrTiO}_3$ interface [13].

To appreciate the novelty of this predicted interface magnetism, the comparison can be made to doped SrTiO_3 . SrTiO_3 is a band insulator with a bandgap of about 3.2 eV. Doping with La^{3+} on the Sr^{2+} site introduces itinerant charge carriers in the conduction band. This doping gives rise to conductivity, but not to magnetism, since the Ti remains in its nominal valence 4+ state, with itinerant electrons in hybridized *spd* bands rather than localized in the 3d shell, i.e. $3d^0$. Only when almost all Sr is replaced by La, the Ti obtains a formal valence of 3+ with a spin-1/2 local moment [191], i.e. $3d^1$. The limiting case is LaTiO_3 , which is an antiferromagnetic Mott insulator. The search for ferromagnetism in these systems is ongoing, but has only been successful when large amounts of magnetic elements

¹The original publication [19] contained a discussion on the observation of hysteresis in magnetoresistance curves. These hysteresis loops have since been established as resulting from a magnetocaloric effect in the sample holder, see the following section for a revised discussion.

like several percent of Co or at least 10% of Cr on the Ti site are added [49, 50]. In this case, the local moments, such as the spin-3/2 $\text{Cr}^{3+} 3d^3$ moment, give rise to magnetic effects on the transport properties when they are coupled to doping-induced itinerant charge carriers [50].

To realize the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, we used a $\text{SrTiO}_3(001)$ substrate that was TiO_2 -terminated by a buffered-HF and annealing treatment[173]. An atomically smooth surface with clear unit-cell-height steps was observed with atomic force microscopy (AFM). On top of that, a LaAlO_3 film was grown at 850 °C in a wide range of partial oxygen pressures by pulsed laser deposition using a single crystal LaAlO_3 target. The growth was monitored by in-situ reflective high energy electron diffraction (RHEED)[180]. The observed intensity oscillations indicated clearly a layer-by-layer growth mode with a very smooth surface and without any island growth. The thickness of the LaAlO_3 layer was 26 unit cells, approximately 10 nm, as determined from the RHEED oscillations. After growth, the sample was slowly cooled down to room temperature in oxygen at the deposition pressure. A smooth surface morphology and the correct crystal structure of the final sample were confirmed by AFM and x-ray diffraction. X-ray photoelectron spectroscopy (XPS) at a treated SrTiO_3 substrate and a deposited film did not show any trace of magnetic elements such as Fe, Co, Cr, and Mn within a resolution of 0.1%. Four ohmic Al contacts were wire-bonded to the corners of the samples, allowing to contact the interface and measure the transport properties without structuring the sample, which could induce damage to the interface.

The sheet resistance, R_s as measured in a Van-der-Pauw geometry is shown in figure 3.1a for different n-type $\text{SrTiO}_3/\text{LaAlO}_3$ interfaces, grown at various partial oxygen pressures (while still maintaining a two-dimensional growth mode), from which the presence of a conducting interface is evident. The temperature dependencies of the corresponding Hall coefficients, $-1/eR_H$, are shown and described as Supplementary Information. Several groups have found that oxygen vacancies give rise to conduction in oxide interfaces when the oxide layers are deposited at low oxygen pressure [18, 115], which also becomes clear from the dependence of R_s on the deposition conditions. From here on we will focus on the transport properties of the samples deposited at 1.0 and 2.5×10^{-3} mbar in which the influence of oxygen vacancies is the lowest (see the supplementary information).

To investigate the magnetic properties of the interface, the magnetic field dependence of R_s is measured. Figure 3.2 shows the measured R_s as function of magnetic field at different temperatures. We define the magnetoresistance as the change in resistance relative to the zero-field resistance, $[R_s(H) - R_s(0)]/R_s(0)$. A large negative magnetoresistance effect is observed in both samples on the order of 30% over a magnetic field range of 30 T.

The magnetoresistance of the conducting interface is independent of the orientation of the magnetic field relative to the interface, which shows that the large magnetoresistance is related to spin physics and not to orbital effects (such as weak localization). We therefore suppose that the observed behaviour must be ascribed to spin scattering of conduction electrons off localized magnetic moments at the interface, as we will substantiate below.

Most theoretical treatments of spin scattering in metals are elaborations of the *s-d* model, the non-degenerate Anderson model, or the Kondo model, all of which

Figure 3.1: Sheet resistance of n-type $SrTiO_3/LaAlO_3$ interfaces. **a**, Temperature dependence of the sheet resistance R_s for n-type $SrTiO_3/LaAlO_3$ conducting interfaces, grown at various partial oxygen pressures. **b**, Temperature dependence of the sheet resistance R_s for two conducting interfaces, grown respectively at a partial oxygen pressure of 2.5×10^{-3} mbar ($\square$) and 1.0×10^{-3} mbar ($\bullet$). The low temperature logarithmic dependencies are indicated by dashed lines. Inset: four-point differential resistance dV/dI as function of applied voltage, at a constant temperature of 2.0 K (1), 10.0 K (2), 50.0 K (3) and 180.0 K (4). **c**, Schematic representation of the electron transfer from the LaO layer into the TiO_2 layer. The electrons either form localized $3d$ magnetic moments on the Ti site, or conduction electrons that can scatter off the Kondo cloud surrounding the localized moments.

describe the interaction between itinerant charge carriers and localized magnetic moments [192]. The scattering cross-section of conduction electrons off localized magnetic moments depends on the relative spin orientation. Under an applied magnetic field, spin-flip scattering off localized moments is suppressed at the Fermi level, because of the finite Zeeman splitting between the spin-up and spin-down levels of the localized magnetic moments. The Zeeman splitting thus turns the spin scattering into an inelastic process, requiring energy exchange with the environment. The large negative magnetoresistance (up to 70%) observed in $(Sr,La)TiO_3$ alloyed with 20% of Cr has been explained by an enhanced coherent motion of the conduction electrons due to ferromagnetically aligned spins [49].

In the case of the n-type interface, the temperature dependence of the sheet resistance helps to further understand the nature of the scattering. The temperature dependence of the sheet resistance is found to be logarithmic over one

decade ($\sim 5\text{--}50\text{K}$, see Fig. 3.1b). The sheet resistance can be described by $R_s = a \ln(T/T_{eff}) + bT^2 + cT^5$, where $T_{eff} \sim 70\text{K}$ is an effective crossover temperature scale, and where the T^2 and T^5 terms are suggestive of electron–electron and electron–phonon scattering, relevant at higher temperatures. Saturation of the logarithmic term is observed below $\sim 5\text{K}$. Additionally, we observe a voltage-induced resistance suppression at low temperatures, as shown in the inset of Figure 3.1b, in which a four-point differential resistance measurement is shown at the temperatures indicated in Figure 3.1b.

An explanation, although still suggestive at the moment, for the observed logarithmic temperature dependence of the sheet resistance is the Kondo effect [187], which describes the interplay between localized magnetic moments and mobile charge carriers [187, 193, 194]. T_{eff} can then be interpreted as the Kondo temperature. The Kondo temperature in this definition depends on other temperature-independent scatter terms, which in the present case, however, are small, as can be seen from the depth of the minimum in Figure 3.1b. The energy scale $k_B T_{eff}$, where k_B is the Boltzmann constant, is of the same order of magnitude as the observed energy scale $g\mu_B H$ over which magnetoresistance effects occur, where g is the gyromagnetic factor and $g\mu_B$ is the Bohr magneton. The suppression of the Kondo effect at finite bias voltage in single-impurity (quantum dot) systems [194, 195] arises from the fact that the Kondo resonance is pinned to the Fermi level and that an excursion of the conduction electrons from the Fermi level (owing to a finite bias) decreases the Kondo scattering. For an ensemble of impurities, it is much more difficult to apply a well-defined bias voltage, and in the present case, the voltage drop per unit cell (in our case of the order of microvolts) is only very small. Therefore, the interpretation of our experimental observations in terms of the Kondo effect is, as said, still speculative.

Magnetoresistance in spin-scattering models in general is proportional to the square of the global magnetization [192], $[R_s(H) - R_s(0)]/R_s(0) \propto -M^2(H)$, which allows to extract a measure of $M(H)$ from the magnetoresistance data of Figure 3.2a. The derived magnetization is shown in Figure 3.2b and is linear at low magnetic fields, and saturating at high fields. The kink at small fields is an artifact of the model that does not take into account the small positive contribution to the magnetoresistance as visible in Figure 3.2a. The nature of the positive contribution needs to be further investigated, but could be related to two-band conduction effects². The low-field susceptibility $\chi = dM/dH$, for the different temperatures is plotted in the inset of Figure 3.2b, from which a Curie-Weiss dependence $\chi = C/(T + \theta)$ is found, where C is a constant and θ is an offset temperature, characteristic for antiferromagnetic coupling at an energy scale of $k_B \theta = 40\mu\text{eV}$. The competition between this energy scale and a possible Kondo singlet ground state depends on the development of the exchange interactions as function of temperature and density of states [196]. A locally antiferromagnetic interaction between mobile and localized spins could in principle cause a ferromagnetic alignment of the localized spins, as in the Ruderman-Kittel-Kasuya-Yosida model of itinerant ferromagnetism [186].

The explanation for the temperature dependence of R_s and the negative magnetoresistance in n-type $\text{SrTiO}_3/\text{LaAlO}_3$ conducting interfaces in terms of the

²See Supplementary Information of [19].

Figure 3.2: Large negative magnetoresistance. **a**, Sheet resistance R_s of an n-type $\text{SrTiO}_3/\text{LaAlO}_3$ conducting interface, grown at 1.0×10^{-3} mbar, under applied magnetic field perpendicular to the interface at 0.3 K, 1.3 K and 4.2 K. The magnetic field sweep direction is indicated by arrows. **b**, Magnetization in units of $g\mu_B/\pi$ as function of the applied field, as inferred from a quadratic dependence of the magnetoresistance in **a** on magnetization. The susceptibility is derived from the linear slope at low fields. Inset: low-field inverse susceptibility as function of temperature, fitted by the Curie–Weiss law $\chi = C/(T + \theta)$ with $\theta = 0.5 \text{ K}$.

magnetic scattering centres requires the presence of magnetic moments. Magnetic effects from carrier doping or oxygen vacancies in $\text{Sr}_x\text{La}_{1-x}\text{TiO}_3$ systems have been sought for, but have never been observed [49]. Although very low impurity concentrations are known to give rise to the Kondo effect, for the observed strong $R_s(T)$ minimum and large magnetoresistance of 30%, orders of magnitude more impurities (on the order of 10%, as determined from comparable experimental studies [49, 50]) are required than the upper limit that was determined from the X-ray photoelectron spectroscopy analysis on our samples (maximally 0.1%). The necessary magnetic moments can only arise from the polar discontinuity, as schematically illustrated in Figure 3.1c. The interface between two non-magnetic materials has itself become magnetic.

Our present finding of a large magnetoresistance at the interface between TiO_2 -terminated SrTiO_3 and LaAlO_3 also sheds light on the influence of oxygen vacancies in related interface structures. With the present observation of magnetism, we have shown that the polar discontinuity is in fact present and that the interface conductivity cannot solely be attributed to oxygen vacancies in the considered range of deposition pressures.

The conducting oxide interface thus forms an intriguing system for studying fundamental magnetic interactions in solid-state systems and possibly opens up the way for carrier-controlled ferromagnetism in all-oxide devices.

3.2 Hysteresis due to magnetocaloric effect

Hysteresis in magnetoresistance measurements was observed at sub-Kelvin temperatures, the magnetoresistance within the hysteresis loop was shown to have a slow relaxation rate and thus being strongly dependent on magnetic field sweep rate, as described in [19] and shown in figure 3.3. In our original publication it was suggested that this hysteresis was resulting from magnetic remanence even though the shape was described as puzzling and could not be fully explained by such an overshoot of the signal. The relaxation rate appeared to decrease monotonically with temperature and field [73]. Figure 3.4a shows the resistance as a function of time, t , in a constant field of 0.8 T. Here, the field is perpendicular to the substrate, but the effect is independent of the field orientation. A relaxation rate can be defined as $R_0^{-1} \frac{dR}{d \ln t}$, where R_0 is the resistance value at the start of the relaxation. The measured relaxation data can be fitted well with this logarithmic term and the extracted relaxation rates are presented in Fig. 3.4b.

Figure 3.3: Hysteresis. a, Sheet resistance at 0.3 K of an n-type $\text{SrTiO}_3/\text{LaAlO}_3$ conducting interface, grown at 1.0×10^{-3} mbar. Arrows indicate the direction of the measurements (at a rate of 30 mT/s). b, Relative sheet resistance saturation at a constant magnetic field of 4 T, as indicated in a.

From new insights it has since become clear that this consideration, concerning a hysteresis artefact in R_s as a result of magnetic ordering, is no longer valid [197, 198]. A magnetocaloric effect, also referred to as adiabatic demagnetization, in the ceramic 20-pin leadless chip carrier from Spectrum Semiconductors became evident after careful further evaluation of the measurement set-up. This magnetocaloric effect in the chip carrier is the clear cause for the hysteresis loop, not any behaviour intrinsic to the $\text{LaAlO}_3/\text{SrTiO}_3$ interface itself. For these $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces grown at increased partial oxygen pressures, even a minor temperature change strongly impacts the resistivity at low temperatures,

Figure 3.4: (a) Time dependence of resistance after the magnetic field sweep is interrupted at 0.8 T (indicated by the vertical dotted line). The data are fitted by a logarithmic function (dashed line). (b) Relaxation rates obtained by fitting the time dependent resistance with a logarithmic fit. The lines are guides for the eye.

see figure 3.1b. Therefore a small heating or cooling of the sample holder due to spin alignment of magnetic impurities in the chip carrier can cause a notable change in the resistance of the sample. A temperature change of up to ~ 300 mK would explain the hysteresis loop shown in figure 3.3a. Interestingly this is notably higher than the ~ 60 mK reported on a similar sample and set-up [198]. As the interface is in very close contact to the coolant, effective heat transfer may vary due to a different position on chip carrier and explain the higher temperature impact value resulting in the more pronounced hysteresis loop at $\sim 10\%$ of R_s in the initial study [197] compared to more recent analysis $\sim 2\%$ of R_s [198]. It seems good to note therefore that the chip carrier itself may heat up and cool down considerably.

The above evaluation, of hysteresis resulting from a magnetocaloric effect, has been presented to Nature Materials [197] where it was decided that these represented new insights and as such did not require publication as a correspondence. While the PhD thesis of Veerendra K. Guduru elaborates on this topic as well [198], a publication with further details is planned to be published separately in the future.

The conclusion of the publication [19] regarding scattering of conduction electrons off localized magnetic moments still stands as the logarithmic temperature dependence and general shape of the large negative magnetoresistance are not influenced by the aforementioned magnetocaloric effect.

3.3 Reflection in retrospect

The results described in section 3.1 formed the first experimental confirmation of magnetic effects at $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces, indicative of the scattering of conduction electrons off localized magnetic moments. It followed theoretical prediction of ferromagnetic alignment of the induced electron spins within the Ti-3d conduction band for these types of interfaces [11, 13]. Being able to attribute such effects as intrinsic to the interface itself is important and from the onset there has been significant concern within the research field about the influence of oxygen vacancies and resulting non intrinsic charge carriers, potentially moving freely and deeply in the SrTiO_3 substrate, dominating measurements [18, 69, 115]. Therefore the first step was to study sample growth for a wide range of partial oxygen pressures to attain a higher oxidation state in order to reduce the influence of oxygen vacancies. This valid approach has since been more widely adopted while another approach, utilizing an additional annealing step in increased partial oxygen pressure after concluding layer growth at lower pressures, has been very popular as well. The conclusion in our original publication that magnetism can be induced was based on three considerations of which two are still standing. First, the logarithmic temperature dependence of R_s suggestive of a Kondo effect where localized magnetic moments and mobile charge carriers interact. Second, the large negative magnetoresistance with the derived low-field susceptibility following a Curie-Weiss dependence which describes its behaviour above the Curie point.

While non-magnetic origins such as weak localization [38] and spin-orbit coupling [87] have been suggested and the samples in those studies may yield partially similar behaviour, care must be taken as the growth process in those studies differs from the one described here and their samples are subsequently manipulated to a similar state by application of voltage. These studies specifically demonstrate a strong influence of magnetic field orientation, which is indeed indicative of orbital physics and may match with e.g. weak localization where interference of conduction channels reduces the probability of electron propagation. In contrast, the strong negative magnetoresistance described in this chapter is field direction independent which is indicative of spin physics.

By now, more evidence for localized magnetic moments at this interface has been reported [54, 58, 60, 63, 199]. While magnetic ordering would appear counter intuitive as it would be expected to disrupt the pairing mechanism required for superconductivity, remarkably both superconductivity and magnetic states may co-exist in a single sample [55–57] albeit at different locations in the sample, likely reflecting sample inhomogeneity.

The study discussed in this chapter contributed to the understanding of the influence of oxygen during sample growth and was the initiator for a flurry of work related to magnetic ordering in these interfaces. While not yet completely understood nor without debate, research is required to further our understanding of the origin, density and distribution of magnetic moments in these interfaces. Such an understanding would also improve our opportunities for engineering of magnetism at interfaces in the broader field of functional oxide heterostructures.

CHAPTER

4

Magnetoresistance oscillations at the $\text{SrTiO}_3/\text{LaAlO}_3$ interface

Low-temperature and high-field magnetotransport data on $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces, grown at relatively high oxygen partial pressures, are presented. Oscillations in the magnetoresistance are observed, showing an uncommon $\sqrt{B}$ periodicity, both in large-area unstructured samples as well as in a structured sample. Several explanations are considered in terms of a highly mobile two-dimensional electron gas. The current state of research into quantum oscillations in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces is evaluated.

This chapter is partially based on:

M. van Zalk, **J. Huijben**, A. J. M. Giesbers, M. Huijben, U. Zeitler, J. C. Maan, W. G. van der Wiel, G. Rijnders, D. H. A. Blank, H. Hilgenkamp, and A. Brinkman, *Magnetoresistance oscillations and relaxation effects at the SrTiO_3 - LaAlO_3 interface*, ArXiv cond-mat (2008)

The author of this PhD thesis has contributed to this publication by the fabrication of samples, the performed measurements and the discussion of results.

4.1 Introduction

At the time of the measurements described in this chapter, the discovery of conducting interfaces between the insulating perovskites SrTiO₃ and LaAlO₃ [10] had only just started to generate the intensive research that continues to this day. The conduction arising from a charge redistribution was primarily considered to occur at the interface in order to counteract an otherwise diverging electric potential in a polar material. Up until that point, oxide interface samples were shown to exhibit metallicity [10, 17, 20, 43], superconductivity below 200 mK [36] and magnetic effects [19]. The large variety of transport properties was ascribed to three structural aspects: the presence of oxygen vacancies [18, 69, 115], lattice deformations (including cation disorder) and the electronic interface reconstruction itself. The relative contributions being largely determined by the growth conditions [120].

Two-dimensional (2D) electron gases in semiconductor heterostructures have had an important impact on our fundamental understanding of electronic transport. Oxide 2D electron systems are particularly interesting because of the richness of electronic phases that the oxides provide. In 2008, two-dimensionality and the quantum Hall effect had just been demonstrated for ZnO/Mg_xZn_{1-x}O heterostructures [200]. For the LaAlO₃/SrTiO₃ interface, support for the 2D character of the metallicity was provided by the substrate termination dependence of the conductivity [10], the interlayer spacing dependence of coupled interfaces [17], the abrupt onset of conductivity above a critical LaAlO₃ thickness [20], conducting atomic force microscopy across cleaved samples [43] and the Kosterlitz-Thouless nature of the superconducting phase transition [36].

Quantum oscillations and high electron mobilities exceeding $10^4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ were presented in the seminal LaAlO₃/SrTiO₃ paper from the outset, yet these results required oxygen partial pressures lower than 10^{-5} mbar during deposition and the oscillations clearly indicated three-dimensional behaviour in rotating magnetic field [10]. In a way these results were not wholly different from the first measurements on a three-dimensional Shubnikov-de Haas effect in niobium and reduction doped SrTiO₃, with mobilities similarly exceeding $10^4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, a result dating back to 1967 [201]. Indeed, before long the high mobilities and oscillations insensitive to magnetic field rotation were reproduced and attributed to oxygen vacancy doping from the low oxygen partial pressures during deposition [69]. In contrast, as is the case with samples post-annealed in oxygen, for LaAlO₃ deposited on SrTiO₃ at relatively high oxygen pressures of $\sim 10^{-3}$ mbar, electronic reconstruction is expected to be the dominant cause of the transport properties [120]. In these samples, a low-temperature upturn in the interface resistance and a negative magnetoresistance have been observed [19], see Chapter 3.

It was an intriguing open question whether the 2D nature of the interface electron gas would result in quantum oscillations, how it would interplay with the previously shown magnetic effects and whether this could give rise to novel transport phenomena. In order to shed light on these questions, transport measurements on LaAlO₃/SrTiO₃ interfaces at 50 mK in magnetic fields, B , up to 30 T were performed.

Figure 4.1: Magnetoresistance as a function of applied magnetic field at 50 mK, showing both hysteresis due to the magnetocaloric effect in the sample holder and oscillations. The numbered arrows denote the sweep direction. The inset shows the behaviour around zero field. The sharp peak at zero field is observed both in the upsweep as in the downsweep.

4.2 Experiment

All samples are grown by pulsed laser deposition, as described in Ref. [19]. One of the samples is structured in order to improve uniformity over the probed surface. The structures are defined by Ar^+ etching, while keeping the etched surface insulating by optimizing the etch time and a short anneal in oxygen. Thin gold contact pads, defined by lift-off, are deposited to yield low contact resistances. The samples are electrically connected by wire bonding to the gold contact pads and, for the unstructured sample, to the edges of the sample. Measurements were conducted in a dilution refrigerator with a base temperature of 40 mK in magnetic fields up to 30 T. Resistance measurements were performed using a standard low-frequency lock-in technique. Heating effects due to the measurement currents were excluded by using a measurement current of less than 5 nA, below which the resistance was current-independent.

4.3 Results

Figure 4.1 shows a typical magnetoresistance curve at 50 mK. Clearly visible are hysteresis due to the magnetocaloric effect in the sample holder, see also Chapter 3, and oscillatory behaviour. Sweeping the magnetic field from zero upwards, the resistance oscillates in field. In the downsweep, the resistance smoothly increases. Only when the background is subtracted a small reminiscent of the oscillations can

Figure 4.2: Magnetoresistance oscillations for different sweep rates at 50 mK. In the main graph, the curves are offset by 5 kΩ per curve. Minima (maxima) positions are designated by open (closed) triangles and drop lines. The lower graph shows the derivative of the curve measured with a sweep rate of 120 mT/sec. The inset shows the complete series of field sweeps, plotted without offset.

be found on the down-sweep too. The overall magnetoresistance $[R(B) - R_0]/R_0$ increases with lower temperatures up to values of -70% (-91% for the structured sample).

In Fig. 4.2 magnetic field sweeps are shown for different sweep rates with the field oriented under an angle of 30° with respect to the sample surface. At higher sweep rates, the hysteresis loop, due to the magnetocaloric effect in the sample holder, opens further and resistance oscillations become more visible. However, the minima and maxima positions shift only weakly with increasing sweep rate, excluding time-dependent oscillatory phenomena. Furthermore, the resistance values in zero field and in high field do not vary in subsequent field sweeps. The amplitude of the oscillations is on the order of the resistance quantum, $h/e^2 = 25.8$ kΩ.

The periodicity of oscillations is uncommon and their behaviour appears to be elucidated by plotting minima and maxima positions versus $\sqrt{B}$, see Fig. 4.3.

Figure 4.3: Resistance minima and maxima versus $\sqrt{B}$. The minima and maxima positions show a square root behaviour in magnetic field. The maxima (minima) positions are plotted at (half) integer values, indicated by filled (open) symbols. The circles correspond to the perpendicular orientation of the field, the angle between field and sample is 30° for the triangles.

A striking square root periodicity is found. Here, it is assumed that the second minimum and the third maximum in Fig. 4.2 are hidden in the steep resistance decrease around 0.7 T. For perpendicular fields low sweep rate data are available. We can extract resistance oscillations by subtracting a smooth background curve. For comparison, these data points are added to Fig. 4.3. It must be noted that the resistance of the sample has almost doubled between the two experiments, due to aging effects, so the directional dependent measurements have to be interpreted with great care.

The oscillatory behaviour with the $\sqrt{B}$ periodicity was reproduced on a $20 \times 20\text{-}\mu\text{m}^2$ structured sample, see Fig. 4.4. Here, oscillations are observed up to the highest field of 30 T, both in increasing as well as in decreasing fields, even for sweep rates as low as 25 mT/sec. Subsequent sweeps reproduce well, although after a timescale of days changes occur in the relative amplitude of the oscillations accompanied by small shifts in the minima and maxima positions.

4.4 Discussion

Many oscillatory phenomena measured in magnetic fields are connected to Landau levels, the observable formation of which being dependent on two conditions. First, the thermal energy must be much smaller than the energy level separation and the energy level separation in turn must be lower than the Fermi energy, E_F , such that these levels will not become blurred and the passing of E_F may be resolved:

Figure 4.4: (a) Magnetic field dependence of the resistance of a structured sample. Minima are denoted by triangles and dashed lines. (b) Also for structured samples, a square root dependence is found for the periodicity of the oscillations.

$$k_B T \ll \hbar \omega_c < E_F \quad (4.1)$$

Second, broadening of Landau levels due to scattering should be much smaller than their energy level separation, which may be expressed in terms of the scattering time τ :

$$\omega_c \tau \gg 1 \quad (4.2)$$

These conditions may be rewritten by substituting for the cyclotron frequency $\omega_c = eB/m^*$, where e is the electron charge and m^* the electron band mass, and using the approximation $\tau = m^* \mu / e$, where μ is the electron mobility:

$$k_B T \ll \hbar e B / m^* < E_F \quad (4.3)$$

$$\mu B \gg 1 \quad (4.4)$$

Assuming the electron band mass to be roughly equal to the rest mass electron of an electron, this means that temperature should be on the order of 1 K and the magnetic field on the order of 1 T when electron mobility is on the order of $10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Further reduction of temperature and increase of magnetic field may allow more levels to be resolved with greater clarity.

While these conditions appear to be met in $\text{LaAlO}_3/\text{SrTiO}_3$ studies as referenced in the introduction, they cannot be fulfilled on first sight in our samples, given their low mobility [19]. However, pronounced resistance anisotropies are observed in our samples, which can be linked to the orientation of the substrate steps. In a sample with multiple structures, the anisotropy occurs in all structures individually, indicating that the anisotropy arises from the steps, rather than from an inhomogeneity over the sample. The maximum resistance ratio measured for two perpendicular orientations implies that the resistance perpendicular to the steps is at least 10 times larger than the resistance in parallel to the steps. The step edge resistance might either arise from the discontinuity of the interface, acting as a scattering center or tunnel barrier, or from residual insulating [10] SrO terminated regions between the TiO_2 terminated terraces, which are too narrow to be observed by atomic force microscopy. If scattering occurs predominantly on the substrate step edges, a highly mobile electron gas between the steps is an intriguing possibility.

In conventional 2D electron gases, the formation of edge channels gives rise to zero longitudinal resistance and the quantum Hall effect. Whenever a Landau level crosses the Fermi energy, states connecting two adjacent edges become available and the zero resistance breaks down. This gives rise to $1/B$ periodic Shubnikov-de Haas oscillations. In principle, a confining potential modifies this picture, giving rise to a widening of the Landau level spacing in energy for low fields [202]. However, for larger fields, one should recover the $1/B$ periodicity, which is not the case for our samples. The absence of $1/B$ oscillations might be explained by local variations in the Fermi energy. Within this picture, there will always be positions on the sample where a Landau level crosses the Fermi energy, and zero longitudinal resistances will no longer occur. However, edge channels of deeper lying Landau levels can still be formed. The radii of the skipping orbits are not determined by the Fermi energy, but by the field alone:

$$r_n = \hbar k_n / eB = \sqrt{2(n + 1/2)\hbar / eB} \quad (4.5)$$

With k_n being the wave vector for Landau level n . The variations in carrier density will only cause small shifts of the skipping orbits towards or away from the edges. Within an edge channel the chemical potential is constant, and thus the formation of edge channels is expected to modify the potential distribution over the sample strongly.

Although the exact physical character is unknown, the substrate steps may provide some barrier on which edge states can be formed. In our system, the

probability for electrons to cross the edges and move into the next terrace is larger than zero. It is known that the barrier transparency can be greatly enhanced by the formation of edge channels [203]. A scaling of the transparency, for example with the incident angle of the electron, seems not unlikely, giving rise to a commensurability condition $m \times 2r_n = W$, where m is some integer and W the width of the terraces. The condition that an orbit should at least fit once between two adjacent edges is fulfilled for $m = 1$.

We can qualitatively construct the expected oscillatory resistance behaviour by making a summation of conductance peaks belonging to n and m . Assuming that variations in the terrace width form the main broadening mechanism, the peak width can be obtained from $\Delta B = \frac{dB}{dW} \Delta W$. We add a minimum peak width arising from other broadening mechanisms. The influence of this for higher fields is negligible. The height of the peak is found by applying normalization. A typical result is given in Fig. 4.5 where a terrace width $W = 124$ nm is used, which is the average terrace width of the structured sample as measured by atomic force microscopy and x-ray diffraction. The slopes $\Delta N / \Delta \sqrt{B}$ that can be determined this way correspond well to the experimentally obtained values for the different samples.

In the scope of this interpretation, the fact that the first clear minimum in both the unstructured and structured samples can be seen from field values of 1 T sets a minimum to the mobility between the substrate steps of 10^4 cm²V⁻¹s⁻¹, given condition 4.4. While the unstructured sample appears to have a visible minimum for $n = 1$ at the lower value of 0.1 T, care must be taken as other effects may be playing a role.

Even though the $\sqrt{B}$ dependence is striking, it can not be ruled out that the periodicity is a coincidental result of other effects at play. The sweep rate dependent measurements in Fig. 4.2 seem to show a connection between sweep rate and oscillations. Upon increasing the temperature, the oscillations disappear at a rather low temperature having only been observed at a base temperature of 50 mK, whereas the hysteresis due to heating effects vanishes only above 300 mK. While quantum oscillations due to the magnetocaloric effect directly are a possibility [204, 205], in such a case a $1/B$ periodicity of oscillations and a sign reversal of the temperature change and thus oscillation amplitude for up and down sweeps of the magnetic field would be expected. Another effect could be universal conductance fluctuations, these are aperiodic in nature and have amplitude e^2/h [206]. The existence of such fluctuations has been demonstrated in mesoscopic LaAlO₃/SrTiO₃ interfaces [207].

Perhaps the most promising scenario is a combination of multiple Shubnikov-de Haas oscillations deriving from 2D conduction subbands with different carrier effective masses. This effect has been successfully demonstrated in high resolution Shubnikov-de Haas oscillations in LaAlO₃/SrTiO₃ interfaces capped with a single monolayer of SrCuO₂ and two monolayers of SrTiO₃ [97]. In both these scenarios, up and down sweeps yield the same result and rotation of the magnetic field away from a perpendicular orientation would diminish the oscillations accordingly. As the measurements described in this chapter lack sufficient fidelity, fitting contributions from multiple subbands and further in depth analysis would require additional measurements.

Figure 4.5: (a) Result of the edge-state model as described in the text. The inset shows a schematic representation of the edge states at the substrate step edges. Oscillations arise from the commensurability of the edge states between two adjacent semi-transparent step edges. (b) For a terrace width corresponding to that of the structured sample, the period of the oscillations and the $\sqrt{B}$ behaviour is reproduced reasonably well.

4.5 Outlook

At the time of the measurements described here, Shubnikov-de Haas oscillations of three dimensional nature had been demonstrated in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures dominated by oxygen vacancy based carrier doping. As the carriers are delocalized throughout the pristine SrTiO_3 substrate, resulting mobilities are high and on the order of $\sim 10^4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Samples with a significantly lower contribution of carriers originating from oxygen vacancies had been demonstrated to be two dimensionally confined to the interface, yet these exhibited significantly lower mobilities which placed them firmly outside of the condition regime capable of demonstrating quantum oscillations. Shortly thereafter, Shubnikov-de Haas oscillations with clear two dimensional signature were demonstrated in delta doped thin films of SrTiO_3 , exhibiting mobilities of $10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [208].

In LaAlO₃/SrTiO₃ heterostructures, Shubnikov-de Haas oscillations with two-dimensional signature at a single frequency were demonstrated by two groups consecutively in a short time span [41, 70]. This was achieved by improving growth conditions and employing earlier work on mobility modulation by electric field effect [209]. The combination allowed improved mobilities reaching up to $5 \times 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, satisfying required conditions for quantum oscillations. Both studies suggested equally that at best half of the carriers appeared to contribute to these oscillations.

Another approach toward increased mobilities is through interface engineering, e.g. by other deposition techniques with potentially improved defect control [145], or by the incorporation of functional layers. A striking example of this latter approach has been achieved by adding a capping layer, composed of a single SrCuO₂ monolayer with several monolayers of SrTiO₃, to the LaAlO₃/SrTiO₃ heterostructure. It was suggested that enhanced oxygen surface exchange reduces impurity scattering, resulting in vastly improved mobilities reaching values of $5 \times 10^4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [96]. Samples of this kind have been used to resolve additional Shubnikov-de Haas frequencies, originating from four two-dimensional subbands, demonstrating a higher percentage of carriers contributing to quantum transport [97]. While marked improvements such as these have been made in recent years, the quantum Hall effect at crystalline 2DEG SrTiO₃/LaAlO₃ based interfaces has remained elusive to this day.

Moving away from wholly crystalline layers, the quantum Hall effect has been recently demonstrated using modulation-doped amorphous LaAlO₃/SrTiO₃ heterostructures [72]. Suggested to arise from spatially separating 2DEG carriers in the topmost layer of the SrTiO₃ substrate from ionized donors in the nearby amorphous LaAlO₃, mobilities are shown to exceed $10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [99].

The LaAlO₃/SrTiO₃ interfaces in the samples presented in this chapter are markedly different in nature from the typical interfaces being investigated, demonstrating Kondo-like scattering at low temperatures and negative magnetoresistance regardless of magnetic field orientation [199]. While these samples show intriguing oscillations in magnetic field, the origin is currently unclear although possible interpretations of the unconventional periodicity have been suggested. Carefully revisiting the measurements would be required for further analysis of the potential origins of oscillations in these samples, potentially revealing novel electron correlation effects.

CHAPTER

5

Polar-discontinuity-retaining A -site intermixing and vacancies at $\text{SrTiO}_3/\text{LaAlO}_3$ interfaces

The atomic intermixing between LaAlO_3 overlayer and SrTiO_3 substrate is studied in order to understand its relation with the doping mechanism. The result shows a vacancy-rich A -site composition of neutrally charged $\text{Sr}_{1-1.5x}\text{La}_x\text{O}$ layers, the formation of which already starts at the onset of deposition. The measured A -site compositions do not take away the polar instability, which thus still requires a change from the nominal structure and/or composition at the B -sites. Evidence is given for such a mechanism starting at a thickness of 3 unit cells. [In collaboration with the research group of prof. Stierle, Universität Hamburg, measurements performed at the ANKA Synchrotron Radiation Source at Karlsruhe Institute of Technology]

This chapter includes the following publication:

V. Vonk, **J. Huijben**, D. Kukuruznyak, A. Stierle, H. Hilgenkamp, A. Brinkman, and S. Harkema, *Polar-discontinuity-retaining A -site intermixing and vacancies at $\text{SrTiO}_3/\text{LaAlO}_3$ interfaces*, Phys. Rev. B **85** (2012)

The author of this PhD thesis has contributed to this publication by the fabrication of samples, the performed measurements and the discussion of results.

5.1 Publication

Our anomalous surface x-ray diffraction study of the interface between SrTiO₃-(001) substrates and thin polar films of LaAlO₃ shows La/Sr interdiffusion leading to neutrally charged Sr_{1-1.5x}La_xO layers. From a thickness of two unit cells, the LaAlO₃ film's interior retains its polar stacking sequence, which is compensated by a cationic compositional change of the substrate's terminating TiO₂-layer. While such valence-retaining intermixing does not resolve the polar catastrophe, it may be a general feature at oxide interfaces influencing the electronic and magnetic properties.

5.1.1 Introduction

Interfaces between perovskite-related materials disclose unanticipated physical properties. Whereas these compounds, with general formula ABO_3 , are of great interest for their richness in bulk properties, over the past years it has been identified that surfaces and interfaces add another dimension to their phase diagrams. One of the most intriguing examples is SrTiO₃(001) and its interface with LaAlO₃. This interface possesses a two-dimensional electron gas (2DEG), which shows conduction [10], superconductivity [36], and even magnetic effects [19, 54], properties that are absent in the bulk of both wide-band-gap insulating compounds. Interestingly, the 2DEG is absent in LaAlO₃ films thinner than four unit cells [20], unless it is capped by SrTiO₃ [17].

The nominal interface is characterized by a transition from a non-polar (STO) to a polar (LAO) crystal structure, which introduces a diverging electrostatic energy. In the so-called electronic reconstruction scenario, it is proposed that valence changes of the interfacial titanium from 4+ to 3+ can annihilate the polar instability and form a 2DEG [14]. It has also been proposed that new conducting phases could form, either by oxygen vacancies [18, 69, 115] or by atomic intermixing [116], the latter of which has been confirmed with a variety of techniques [131]. It remains unclear how these scenarios can be reconciled with the thickness-dependent insulator-conductor transition [20], since doping in these cases is expected for any film thickness. Several papers address this problem thereby focussing on electronic reconstruction [122, 155] or oxygen vacancies [160, 210].

Transport measurements reveal interfacial carrier concentrations much lower than what is predicted by electronic reconstruction [17], whereas spectroscopic studies indicate both localized and itinerant Ti 3d states [135]. Others report the absence of band-bending and band offsets [148] which would be expected within the electronic reconstruction scenario.

In order to understand the atomic intermixing and its relation with the doping mechanism, we make use of anomalous surface x-ray diffraction (SXRD), focussing in particular on the cationic composition at the *A*-sites. The most important result is that La doping of the substrate leads to a vacancy-rich *A*-site composition of Sr_{1-1.5x}La_x, the formation of which already starts at the onset of deposition. The uncovered *A*-site compositions do not take away the polar instability, which thus still requires a change from the nominal structure and/or composition at the *B*-sites. Our data show evidence for such a mechanism starting at a thickness of

three unit cells.

5.1.2 Experiment and results

Sample preparation

Thin films of LaAlO_3 with thicknesses of 1-5 unit cell layers (named 1-5UC hereafter) were grown on single TiO_2 -terminated $\text{SrTiO}_3(001)$ substrates (Crystec) by pulsed laser deposition (PLD) at an oxygen pressure of 3×10^{-5} mbar. This intermediate pressure is high enough to avoid bulk substrate conductivity by oxygen vacancies and allows for comparison with other studies.

Single TiO_2 -terminated SrTiO_3 substrates were obtained by a well-established wet chemical etching procedure [211]. During the deposition of the thin films, use of reflection high-energy electron diffraction (RHEED) enabled unit cell thickness control by counting intensity oscillations. The oxygen partial pressure during deposition was kept at 3×10^{-5} mbar, while the substrate temperature was 1043 K. During cool-down to room-temperature, the oxygen pressure was increased to 400mbar and each sample was kept at 873K for 1 hour in order to maximize oxidation. After growth the surfaces of the films are characterized by Atomic Force Microscopy (AFM), which shows a terrace-step structure. Typical step-heights are 4 Å, which is an indication that the substrate's step-height is maintained after overgrowth by LaAlO_3 .

Data collection and fitting including anomalous CTR's

Crystal truncation rod (CTR) data sets on the various samples were obtained at the MPI-MF beamline at the Ångström Quelle Karlsruhe (ANKA), Germany [212]. The CTR data were integrated and corrected [213], resulting in sets of structure factors. For samples 1UC and 5UC further data were collected at an x-ray energy of 6.28 keV probing the La-L_1 absorption edge. Structure refinement for these samples was carried out using the anomalous and non-anomalous data simultaneously, which prevents large correlations between the occupancies of Sr and La at the A -sites¹. This unwanted effect is due to the similarity in the atomic scattering factors (f_a) of Sr and La ($|f_{\text{La}} - 1.5f_{\text{Sr}}| \leq 2$, for $0 < \sin(\theta)/\lambda < 1$). For example, the scattering by a site occupancy of $\text{La}_x\text{Sr}_{1-1.5x}$ is indistinguishable from an A -site fully occupied by Sr. Only by including data taken at the absorption edge of one of the two elements, thereby altering f_a , a unique solution for the site occupancies can be found. In order to rule out the effect of enlarged thermal diffuse scattering, for sample 1UC data were taken at 90K as well. Refinement of the low temperature data did not reveal any anomaly compared to room temperature, and essentially the same composition and atomic positions were found.

Results of data reduction and fitting using space group $P4\text{mm}$ are listed in Table 5.1. Exemplary CTRs for samples 1-5UC are shown in Figure 5.1. A modified version of the program *ROD* [215] is used to fit structural models to the CTR data [214]. The Supplementary Information of [151] lists the refined structural parameters for all samples.

¹For the anomalous data, the La atomic scattering factor is corrected by $f' = -10.8$ and $f'' = 14.3$. See ref. [214] for details about the data analysis.

Figure 5.1: Crystal truncation rod data (dots) and fits (lines). Shown are the (2,0) rods for samples 1UC (left) to 5UC (right). Fits to the non-anomalous data are red (upper) and anomalous blue (lower). For sample 1UC the 90K data are dash-dotted.

X-ray reflectivity

X-ray reflectivity (XRR) curves, see Fig. 5.2, taken at 10.0keV and 6.28keV of sample 5UC show a striking difference indicative for La interdiffusion. The apparent thickness as 'seen' by the x-ray beam is different for the two x-ray energies, although they are taken from the same sample. Since the difference between the two curves is determined only by the anomalous scattering of La, it must follow that the difference between the two fitted thicknesses ($t_{6.28} = 27 \text{ \AA}$ and $t_{10.0} = 19 \text{ \AA}$) of $8(2) \text{ \AA}$ is the La interdiffusion depth.

In the XRR regime, the derivative $d\rho'/dz$ of the scattering density ρ' is probed. Far away from resonances the scattering density is equal to the electron density ρ . Close to resonances, the scattering density can be obtained by correcting ρ with f' and f'' , which account for the dispersion and absorption. Our results indicate that at 10.0 keV, there is hardly any difference in density between the SrTiO₃ substrate and the interdiffusion region, whereas at the La L₁-edge the contrast

Sample	data points	unique points	R_{merge}	p	χ^2 ^a
1UC	192+532	80+107	0.172+0.165	19	0.92
1UC (90K)	80	80	-	19	1.8
2UC	642	149	0.157	23	0.60
3UC	835	196	0.192	20	0.91
4UC	707	201	0.099	27	2.0
5UC	1225+532	228+107	0.08+0.234	37	2.7

Table 5.1: Results of the data collections and structure refinements of the various samples. Listed are the total number of data points and unique points after merging using space group P4mm. CTR's were measured at 10.00keV. For samples 1UC and 5UC the second values give the number of data points collected at the La-L₁ absorption edge. The value R_{merge} indicates the agreement between different symmetry equivalent points. Structural models with p parameters are fitted to all the data resulting in a single χ^2 value.

^a $\chi^2 = \frac{1}{N-p} \sum_{hkl} \frac{(|F_{obs}| - s_E |F_{calc}|)^2}{\sigma(F_{obs})^2}$, with N the number of measurements, p the number of parameters, F the structure factor and s_E the scale factor for the particular x-ray energy.

Figure 5.2: X-ray reflectivity curves of the nominally 5 unit cell thin film, taken at two different x-ray energies. Open circles show the data points taken at $E=6.28\text{keV}$ (blue, upper) and $E=10.0\text{keV}$ (red, lower) and their corresponding fits (solid lines). The inset shows schematically the structure of the film whereby the colors indicate the effective scattering density ρ' that is probed at each x-ray energy. The Interface (IF) has a significantly different ρ' at the La-L₁ edge.

between the substrate and the interdiffusion region is substantial. The fit to the 10.0keV data shows some deviation around $Q=0.2$. This is an indication that the real interdiffusion profile is not very accurately described by the used error function. Nevertheless, the period of the thickness oscillations is well reproduced, and it is not expected that more complicated interdiffusion profiles will change that.

Thickness-dependent composition

Figure 5.3 shows the A -site electron occupation Z_A in the different films obtained from fits to the CTR data whereby $Z_A = \theta_{\text{Sr}}Z_{\text{Sr}} + \theta_{\text{La}}Z_{\text{La}}$, with occupancies θ , $Z_{\text{Sr}} = 38$ and $Z_{\text{La}} = 57$. It is important to note that a value of Z_A close to 57 means that the site is (almost) completely occupied by La, and that no Sr can be present. From a thickness of 3 unit cells, atomic layers with A -sites almost fully occupied by La occur. The results also show that the A -sites in the outermost film layers are all close to $Z_A = 38$, the same value as in the substrate.

The A -site electron occupation summed over all layers within one film, ΣZ_A , is plotted in Fig. 5.3. A linear relation as a function of film thickness is found, of which the slope is $54(2) \text{ \#e}/(\text{unit cell layer})$ and the offset $-20(7) \text{ \#e}$. From the slope it can be concluded that, as expected, with the growth of each unit cell LaAlO_3 one complete layer of La atoms ($57\text{ \#e}$) is deposited. The negative offset means that some of the heavier La disappears from the film and is partially replaced by the lighter Sr. This exchange of Sr and La starts already with growth of the first unit cell layer and seems not to change anymore with increasing film thickness. The A -site compositions summed over all film layers in samples 1UC and 5UC are $\text{La}_{0.2}\text{Sr}_{0.7}$ and $\text{La}_{4.1}\text{Sr}_{0.3}$, respectively. We estimate that the error in

Figure 5.3: Electron weight at the various *A*-sites ($Z_A = \theta_{\text{Sr}} Z_{\text{Sr}} + \theta_{\text{La}} Z_{\text{La}}$). Shown are the results for all the thicknesses of 1 to 5 unit cells; *A*-sites in the substrate are in red (bright), those in the film are black (dark). The levels of $Z_{\text{Sr}} = 38$ and $Z_{\text{La}} = 57$ are indicated for comparison. Errors are 5-10% of the values.

Figure 5.4: Sum of the total electron weight at the *A*-sites (ΣZ_A) as a function of the film thickness. The solid line is a linear fit as described in the text.

the total composition per element will be around $\sqrt{n}0.1$, where n is the number of unit cell layers. See Supplementary Information of [151] for the details of the data reduction, analysis, and atomic positions. This means that we find a significant La deficiency with respect to the films' nominal compositions. Furthermore, we find that a fraction of the La that disappears from the film stays within two SrTiO_3 unit cells from the interface region, and the rest diffuses much deeper into the substrate. This exchange of Sr and La results in a film and near-interface region containing an appreciable amount of vacancies, which can only be explained by segregation and accumulation of bulk SrTiO_3 *A*-site vacancies.

Strain and relaxation

Figure 5.5 shows the average distances between the *A*-sites, d_{AA} , along the growth direction for each film. Values for the distance across the nominal interface with SrTiO_3 , d_{AA}^0 , are shown separately in Fig. 5.5. We find an exponential relation for d_{AA} as a function of thickness with a characteristic decay of 2.7(2) unit cells and a thick film limit of 3.68(7) Å. The characteristic thickness coincides roughly with the reported insulator-conductor transition [20]. The thick film limit is very close to the expected *c*-axis lattice parameter of 3.71 Å for a LaAlO_3 film fully strained to SrTiO_3 , as explained below. The values of d_{AA}^0 are significantly larger than d_{AA} and level off at 3.92(2) Å from a thickness of 3 unit cells. This enlarged distance can not be caused by strain, but is an indication that the interfacial atomic configuration differs from the substrate and film. Nominally the TiO_2 layer is flanked by a SrO and a LaO layer, whereas within the film (compositionally) equal *A*-site layers are expected. Such symmetry breaking has been found to result in enlarged AO-BO₂ distances in bulk $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$ [216].

The heterointerface marks the transition between two intrinsically different crystal symmetries: $\text{Pm}\bar{3}\text{m}$ in the substrate and $\text{R}\bar{3}\text{c}$ in the film, whereby thin

Figure 5.5: (left) Averaged distances between A -sites (d_{AA}) as a function of the film thickness (lower black dots). The values for d_{AA} follow an exponential decay (black solid line) to 3.68(7) Å for thick films (black dash-dotted line) as described in the text. Also shown are the values for the distance across the interface of the substrate and film d_{AA}^0 (middle blue dots). Values of d_{AA}^0 level off to 3.92(2) Å (dashed line). The diamonds (black, upper) give the refined occupancies θ of the interfacial Ti atoms. (right) Schematic atomic model for an n unit cell thin LaAlO_3 film and its nominal interface (IF) with SrTiO_3 .

films are expected to adapt to the substrate. The cations in bulk LaAlO_3 occupy atomic positions on a bcc-based lattice, just as in the perfect perovskite structure. The rhombohedral crystal structure is determined merely by small deviations of the oxygen positions from cubic symmetry by tilts. Around 821K LaAlO_3 shows a phase transition to cubic [169]. If the LaAlO_3 film were completely relaxed and adopted its own bulk symmetry, owing to the oxygen tilt system, very weak reflections should be present in addition to the main perovskite peaks. For none of the films investigated here we have found such reflections, and the data were merged using spacegroup $P4mm$ with a single perovskite cell. Also the low temperature measurements at 90K of sample 1UC showed no additional reflections. It could still be that the extra reflections are present, but too weak to be detected. There were also no signs for in-plane lattice relaxation, which would be expected above the critical thickness for the formation of misfit dislocations. Therefore, we assume the films here to be pseudomorphic, also with respect to the oxygen octahedra network.

The out-of-plane film lattice parameter shows to exponentially approach the non-bulk value of 3.68(7) Å with increasing film thickness. This thick film limit c -axis corresponds to the value expected for the film's pseudomorphic state. Taking a Poisson ratio of $\nu = 0.26$ [217] and in-plane tensile strain $\epsilon = +0.030$ for the LaAlO_3 film results in an expected strained c -axis of 3.71 Å.

5.1.3 Discussion

It has been found in other studies that indeed La can diffuse deeply into the SrTiO₃ [131]. We find significant amounts of La in the first two SrTiO₃ substrate unit cell layers, which means that probably the La level in deeper layers is below the sensitivity of SXRD. Cationic diffusion in La-doped SrTiO₃ has been discussed to be an *A*-site vacancy mediated hopping mechanism, which increases with La doping levels [218]. It has also been suggested that for La-doped SrTiO₃ there exist two charge compensating mechanisms, electronic (Ti valence changes) and ionic (expulsion of Sr), which depend on the oxygen partial pressure [219]. Heating under oxidative conditions of La-doped SrTiO₃ leads to SrO outgrowth on the surface, and should result in a substrate composition Sr_{1-1.5x}La_xTiO₃[220]. Here we indeed find this composition, but only in a thin region close to the interface. It is very likely that this thickness depends on temperature and oxygen pressure. Including surface Sr islands in the fit models yielded insignificant coverages, which means that the amount of Sr is below the detection limit, or that Sr does not order epitaxially on top of the films.

In an earlier paper, we reported on the SrTiO₃/LaAlO₃ interface structure during PLD of the first unit cell layer [153]. Also there it was found that the occupancy of the atoms in the overlayer was close to 0.5, and this was interpreted as an incomplete unit cell layer. In fact, this is completely in line with the present results, only the less-than-unity occupancies should be interpreted as being atomic vacancies in stead of island coverages². The earlier in-situ SXRD measurements corroborate the present study's outcome that *A*-site interdiffusion appears with deposition of the very first layer.

Diffusion of La into the substrate leads to a non-polar structure in the form of (Sr_{1-1.5x}La_x)²⁺O²⁻ layers. The LaAlO₃ film does contain a polar stacking which requires that compensating charges of $\pm 0.5e$ exist on both its interfaces [14]. First, we focus on the films' terminating unit cell layers, i.e. at their free surfaces. Our data indicate that these contain neutrally charged AO layers. It is most likely that also the outermost BO₂ layers and oxygen atoms together form a charge neutral film termination. It is unlikely that a charged layer would follow the neutral AO layer and terminate the crystal. A compensating charge of $-0.5e$ should therefore be formed on the second last BO₂ layer, which is possible in the form of oxygen vacancies. Indeed, refinement of the oxygen occupancies in this layer results in values close to the expected 7/8. Next we consider the film-substrate interface where La/Sr intermixing takes place. In principle, intermixing does not take away the diverging electrostatic energy, but would merely smear out the potential build-up at that particular interface [14]. An off-set of $\pm 0.5e$ is still necessary. Since our data indicate that this off-set is not dictated by the interfacial AO layers, it must appear on the nearby BO₂ layers. Oxygen vacancies in this layer would cause a positive charge whereas a negative charge is required. For the purpose of investigating the composition of the substrate's terminating BO₂ layer, its Ti occupancy is refined. The results in Fig. 5.5 show that from a thickness of 3 unit cells the Ti occupancy drops to about 0.85. This decreased scattering power is

²For x-ray scattering these two are indistinguishable as long as the island size is smaller than the x-ray coherence length.

Figure 5.6: Schematic view along the (100) direction of the final atomic structures of samples 1UC (left) to 5UC (right). The dotted line indicates the nominal interface. The A -sites with an occupancy $\text{Sr}_{1-1.5x}\text{La}_x$ are drawn by the largest spheres. The change at the interfacial Ti site from a film thickness of 3 unit cells is indicated by an enlarged darker sphere.

either due to the appearance of B -site vacancies or due to intermixing with the lighter element Al. Assuming vacancies, a composition of $\text{Ti}_{0.85}\text{O}_2$ would result in a charge of $-0.6e$ for this layer. In case of Ti/Al intermixing, the scattering power of $\text{Ti}_{0.85}\text{O}_2$ is almost indistinguishable from that of a composition $\text{Ti}_{0.5}\text{Al}_{0.5}\text{O}_2$, which would have a charge of $-0.5e$. Both scenarios would provide the required $-0.5e$ charge and compensate the film's electrostatic energy build up.

The picture of the thin film atomic structure that emerges from our study is schematically shown in Fig. 5.6. Deposition of LaAlO_3 on SrTiO_3 leads immediately to La/Sr intermixing, thereby forming charge neutral $\text{La}_x\text{Sr}_{1-1.5x}\text{O}$ layers and a non-conducting phase. This charge neutral layer is found in the substrate but also in the topmost AO layer of the films. From a thickness of 2 unit cells La-rich layers are formed and with that a polar film stacking. From a thickness of 3 unit cells, we find a compositional change at the substrate's terminating B -sites, which annihilates the diverging electrostatic energy. These results show that the expected potential built-up over the interface of 1-5 unit cell thin films is for a large part structurally compensated. However, these results can not rule out that electronic reconstruction, be it in much weaker form, is the mechanism responsible for the 2DEG formation.

Vacancies play a role in LaAlO_3 surface reconstructions [221], SrTiO_3 grain boundaries [222], and could be responsible for inhomogeneities by clustering [146]. They also contribute to the strain state [223], and could therefore play a role in strain relaxation at oxide heterointerfaces. The vacancy-mediated valence-retaining intermixing found here would provide a pathway for strain relaxation over typical diffusion lengths without altering the typical ionic nature on either side of the interface. This might be a general feature at oxide heterointerfaces.

5.1.4 Conclusion

We have investigated by anomalous SXRD the SrTiO₃/LaAlO₃ atomic interface structure for 1 up to 5 unit cell thin films. All the films investigated show La deficiency and contain many atomic vacancies. Irrespective of the thickness, all the substrates are doped with La, thereby forming charge neutral Sr_{1-1.5x}La_xO layers. From a film thickness of 2 unit cells, a polar LaAlO₃ stacking sequence can be identified. The resulting electrostatic energy build up is partly compensated by a compositional change at the *B*-sites in the substrate's terminating TiO₂ layer.

5.2 Reflection in retrospect

The results described in Section 5.1 confirmed the presence of significant cation intermixing, which had initially been reported based on electron energy loss spectroscopy (EELS) [14], and demonstrated the presence of atomic deficiencies in LaAlO₃/SrTiO₃ interfaces. We aimed to find the structural composition of LaAlO₃-/SrTiO₃ interfaces for a series of samples of increasing film thickness and study whether a structural transition could be found matching the robust conductivity onset at the critical thickness of the LaAlO₃ overlayer [20]. The initial samples were synthesized, mostly following the approach described in Chapter 2, at the University of Twente in August 2007. In order to reduce potential oxygen vacancies further and allow closer comparison to samples of other research groups, an extra post growth annealing step was applied. This however means that these structures are not necessarily fully representative of the structures in the other, transport related, studies presented in this dissertation. The samples were subsequently measured at the ANKA Synchrotron Radiation Source, starting in August 2007. Usage of highly accurate measurement techniques, such as SXRD, are important as minor structural changes may be sufficient to trigger significant changes to the physical properties of the materials under investigation. Shortly after we started our measurements, an interesting article was published which used a similar SXRD approach on a single sample with a 5 unit cell LaAlO₃ overlayer [116]. Considerable intermixing, distortions and the formation of metallic La_{1-x}Sr_xTiO₃ were shown, to which the existence of the conductivity in LaAlO₃/SrTiO₃ interfaces was ascribed. As the article entailed a single sample above the critical thickness for conductivity, possible structural transitions around such a critical thickness could not yet be studied.

Our work described here is in agreement with the results from various research groups regarding the demonstration of considerable, polar discontinuity retaining, A-site intermixing [14, 116, 131, 147, 155, 156]. In contrast, there are some deviations regarding potential cation vacancies in charge neutral layers of Sr_{1-1.5x}La_xTiO₃ and from B site compositional changes, by intermixing or deficiencies, in the substrate's terminating TiO₂ layer. In order to draw some attention to further interesting information available in our data set ³, an extra figure has been drafted. Figure 5.7a shows the atomic structure of the 5 unit cell sample, this time with the average charge distribution ρ added to the right of the stack. This charge distribution has been derived from the occupancies, shown in Figure

³see supplemental information from [151] for the refined data

Figure 5.7: Additional information from the structural refinements for the 5 unit cell sample. (a) Atomic structure to the left, charge distribution ρ to the right. (b) Occupancy per atom for each AO or BO₂ layer. The 0 position is located at the interface, between TiO₂ and LaO layers. (c) Electrostatic potential build up in an unreconstructed "catastrophe" interface or minimized potential "ideal" interface [14]. The last AlO₂ and the topmost oxygen layer are omitted here as they should be considered with caution, because of the low scattering power and correlation with surface roughness [151, 155].

5.7b. The resulting sum of the potential is shown in Figure 5.7c, together with the polar "catastrophe" of an unreconstructed interface and an "ideal" reconstructed interface with electronically and structurally minimized potential [14]. Interestingly, derived directly from our data set using the average values, there seems to be little electrostatic potential build up present. This means that no Ti³⁺ fractions could be estimated from potential minimization considerations, as any Ti³⁺ would diverge the curve further away from 0. It must be said however that there is considerable uncertainty in the occupancy values, care must be taken when interpreting these results. Additionally, the La deficient occupancies shown in Figure 5.7b would appear to satisfy the condition that only Al-rich LaAlO₃ results in interface conductivity [141].

One of the original aims of the study was to relate structural transitions to the conductivity transition from 3 to 4 unit cells. Unfortunately, this relation could not be found from our data set while a considerable structural mitigation, of the electrostatic potential build up from the polar discontinuity, appears present for all samples. Clearly, this can not be the entire story as typical transport measurements demonstrate a robust critical thickness of the LaAlO₃ overlayer [20], which is even reproduced at the exact same critical thickness on similar systems

[121]. There may be several possible causes for this discrepancy related to the experimental set-up and sample. First, the LaAlO₃/SrTiO₃ interfaces may not be considered fully homogeneous over the entire sample surface, notable example here is the potential coexistence of magnetism and superconductivity [55–57], while e.g. defect clustering may play a role as well. The SXRD beam would average these different regions if their scale is on the order of the beam size or smaller. A second averaging effect could be time averaging of metastable distortion states switching between various conformations. A further cause could be from the highly energetic X-ray source SXRD employs, from which photodoping resulting in band bending could play a role. This could preclude the necessity of a critical thickness arising altogether, though it has been suggested that this influence would be minimal [132]. Even so, a structural transition accompanying the electrical transition at the critical thickness, has since been shown in the abrupt transition of rumpling in AO and BO₂ planes [156].

A single study may not provide the final answer regarding the structure-property relation in these complex samples, as there is tremendous sensitivity to variation and it currently appears impossible to engineer a perfect, abruptly defined, heterostructure. Sample preparation details, measurement techniques and analysis approaches vary strongly between research groups, while approaches that yield the best physical properties may potentially result in badly defined structural systems. That said, when approached with multiple research groups, it could be worthwhile to establish ideal growth and testing protocols beforehand and combine results from multiple analysis techniques such as SXRD and EELS. Highly interesting would be the thickness evolution of the structural composition in currently considered ideal, for instance highest mobility, n-type LaAlO₃/SrTiO₃ samples. A comparison with the structural composition of p-type samples would surely be worthwhile too.

CHAPTER

6

Local probing of coupled interfaces by variable-temperature scanning tunnelling spectroscopy

Bilayers on SrTiO₃ substrates are studied in order to understand the coupling between subnanometer spaced conducting interfaces. This is achieved by scanning tunnelling microscopy (STM) and spectroscopy (STS) experiments on STO-capped LAO layers on STO(001) substrates, revealing the individual interface (2DEG) and surface (2DHG) conducting sheets including their temperature dependent coupling. [In collaboration with the research group of prof. Zandvliet, University of Twente]

This chapter includes the following publication:

M. Huijben, D. Kockmann, **J. Huijben**, J. E. Kleibeuker, A. van Houselt, G. Koster, D. H. A. Blank, H. Hilgenkamp, G. Rijnders, A. Brinkman, and H. J. W. Zandvliet, *Local probing of coupled interfaces between two-dimensional electron and hole gases in oxide heterostructures by variable-temperature scanning tunneling spectroscopy*, Phys. Rev. B **86** (2012)

The author of this PhD thesis has contributed to this publication by the fabrication of samples, the performed measurements and the discussion of results.

6.1 Publication

The electronic structure of epitaxial oxide heterostructure containing two spatially separated 2D conducting sheets, one electron-like (2DEG) and the other hole-like (2DHG), has been investigated using variable temperature scanning tunneling spectroscopy. Heterostructures of $\text{LaAlO}_3/\text{SrTiO}_3$ bilayers on (001)-oriented SrTiO_3 (STO) substrates provide the unique possibility to study the coupling between sub-nanometer spaced conducting interfaces. The band gap increases dramatically at low temperatures due to a blocking of the transition from the conduction band of the STO substrate to the top of the valence band of the STO capping layer. This prevents the replenishment of the depleted electrons in the capping layer from the underlying 2DEG and enables charging of the 2DHG by applying a negative sample bias voltage within the band gap region. At low temperatures the 2DHG can be probed separately with the proposed experimental geometry, although the 2DEG is located less than 1 nm below.

6.1.1 Introduction

Following the discovery [10] of novel two-dimensional electron gas/liquid behaviour occurring at interfaces between insulating oxides, such as SrTiO_3 (STO) and LaAlO_3 (LAO), many studies have revealed the rich phenomenology of these conducting states [19, 36, 120] and the potential for novel device structures on length scales smaller than attainable with standard semiconductors [224, 225]. A key ingredient underlying the conductivity appears to be the polar discontinuity across the interface between the polar LAO and the non-polar STO. This is conceived to result in an electrostatic potential build-up in the LAO, causing a transfer of electrons from the surface, across the LAO layer, into the STO conduction band. In addition to this electronic reconstruction induced doping, also extrinsic sources are found to contribute to the interface behaviour, such as oxygen- and cation-vacancies [18, 19, 69, 115] or cation intermixing [116, 131, 146].

For LAO films grown on TiO_2 -terminated STO substrates an insulator to metal transition was found when the LAO film exceeds a thickness of 3 unit cells [20]. This is in line with the understanding that a critical LAO thickness is needed to acquire a sufficiently strong potential build up to drive the charge transfer. Remarkably however, when a STO capping layer is grown on top of the LAO film, metallic behaviour is seen already for single LAO unit cell thickness [17]. This was interpreted as the result of a surface dipole effect in the STO [226], contributing to the potential build up [94]. A tantalizing consequence following from this is the occurrence of a two-dimensional hole gas (2DHG) at the STO surface formed by oxygen $2p$ -states from which electrons have been transferred to the two-dimensional electron gas (2DEG) at the STO-LAO interface underneath. This would imply a parallel configuration of a two-dimensional electron conductor and a two-dimensional hole conductor at a distance of only about 2 perovskite unit cells (uc), which is less than 1.0 nm. Such a situation is reminiscent to coupled 2DEG/2DHG systems in semiconductor heterostructures, in that case at typical distances of several 100's of nm, in which for example exciton formation and their potential Bose-Einstein Condensation are studied. [227, 228]. Key to the occur-

rence of excitons in such bilayer 2D systems is minimizing the separation distance to achieve strong Coulomb interaction, while maintaining a small probability of recombination by their spatial separation.

Evidence for the occurrence of parallel conducting sheets (2DEG and 2DHG) in STO(001)/LAO/STO heterostructures was provided by magnetotransport studies and ultraviolet photoelectron spectroscopy [94], which demonstrated macroscopically the presence of electrons as well as holes. However, the spatial separation of conducting sheets with exclusively electrons or holes as carriers could not be determined yet. Here, we report on the local characterization of the electronic structure of closely coupled 2DEG and 2DHG interfaces by scanning tunnelling microscopy (STM) and spectroscopy (STS) experiments on STO-capped LAO layers on STO(001) substrates, revealing the individual interface (2DEG) and surface (2DHG) conducting sheets including their temperature dependent coupling.

6.1.2 Experiment

Unit cell controlled growth process

The epitaxial STO(001)/(2 unit cell LAO)/(1 unit cell STO) heterostructures used for these studies were fabricated by pulsed laser deposition with reflection high-energy electron diffraction (RHEED) control of the growth process [180]. Preparation by a combined HF-etching/anneal treatment [173] is expected to result in atomically smooth TiO_2 -terminated SrTiO_3 (100) substrates, which enables unit cell controlled growth of individual oxide layers. All substrates had vicinal angles of $\sim 0.1^\circ$. Single crystal STO(001) and LAO(001) targets were ablated at a laser fluence of $\sim 1.3 \text{ J/cm}^2$ and a repetition rate of 1 Hz. The substrate was held at 850°C during deposition of both layers, while an oxygen pressure of $2 \times 10^{-3} \text{ mbar}$ was used. RHEED analysis demonstrates the preservation of the (1x1) surface reconstruction from the initial TiO_2 -terminated STO (100) substrate [185] surface to the final surface of the STO top layer.

To demonstrate the high level of control and reproducibility of the growth procedure, RHEED intensity analysis is shown in Fig. 6.1 of the growth of two SrTiO_3 (001)/(2 uc LaAlO_3)/(1 uc SrTiO_3) heterostructures. Identical characteristics were observed in the RHEED analysis displaying the reproducibility of RHEED-assisted pulsed laser deposition. The deposition of LaAlO_3 was stopped exactly in the second maximum of the RHEED intensity, indicating the growth of two unit cells. The deposition of the SrTiO_3 toplayer was interrupted after a single unit cell. However, one extra laser pulse, more than required for the maximum of the RHEED intensity oscillation, was given to be certain that the SrTiO_3 toplayer was fully closed. This can be observed in Figure 6.1 where the intensity after the last laser pulse is slightly lower than the intensity of the maximum.

After growth, the heterostructures were slowly cooled to room temperature in the oxygen deposition pressure at a rate of $10^\circ\text{C}/\text{min}$. As a counter electrode for the STM/STS experiments aluminum wirebonds have been used, forming a shared contact to both interfaces separated a few mm from the investigated area, see Fig. 6.1. We note that for such thin stacks, contacting the conducting interfaces/surfaces separately is experimentally very challenging. Subsequently, the heterostructures were transferred through air to an ultra high vacuum variable

Figure 6.1: RHEED intensity analysis during epitaxial growth of two $\text{SrTiO}_3(001)/(2 \text{ uc LaAlO}_3)/(1 \text{ uc SrTiO}_3)$ heterostructures by RHEED-assisted pulsed laser deposition showing identical characteristics.

temperature cryostat for scanning tunneling microscopy (STM) and spectroscopy (STS) analysis without any intermediate heating or etching procedure.

STS spectrum recording procedure

The scanning tunneling microscopy and spectroscopy experiments, see Fig. 6.2, are performed with an Omicron ultra-high vacuum low temperature STM, which has a base pressure of 3×10^{-11} mbar. Therefore any contamination during the measurements can be safely disregarded. We have used electrochemically etched tungsten STM tips for all our experiments. The temperature was varied from 77 K to 300 K. The sample bias and initial tunneling current setpoints were always kept below 4 V and 4 nA, respectively. The $I(V)$ experiments are performed by presetting the sample bias and the tunneling current, and with this the tip-sample separation, at an initial value and subsequently measuring I as a function of V with the feedback disabled [229], i.e. with the tip-sample separation fixed.

The IV curves are averaged over the entire $30 \times 30 \text{ nm}^2$ scans. Each scan involves 100 IV traces, taken in a 10×10 grid. The variation from trace to trace is marginal. The STS measurements were recorded as follows. Before opening the feedback loop a delay of 200 microseconds was used. After opening the feedback loop, the voltage was kept constant at the set point and a delay of 50 microseconds was applied. At each voltage point the current was measured for 640 microseconds,

Figure 6.2: (a) Schematic representation of the experimental geometry. Two spatially separated 2D conducting sheets, one electron-like (2DEG) and the other hole-like (2DHG), are considered to be created at the interfaces in STO(001)/LAO/STO heterostructures. Temperature dependent scanning tunneling microscopy (STM) and spectroscopy (STS) are performed by monitoring the tunneling current I_t between the tip and the sample as a function V_s , voltage at the sample relative to the tip. (b) Surface topography image and (c) corresponding height profile recorded by STM at -1.0 V and 300K.

followed by a delay of 50 microseconds. After every change in bias voltage a delay of 80 microseconds was applied. Before closing the loop again a delay of 100 microseconds was applied and after closure of the feedback loop a delay of 50 microseconds was applied before continuing the scanning. So in total, including the normal scanning, this amounts to about 4 minutes for a 30 x 30 nm scan (200 x 200 points measurements with a 10 x 10 STS grid). The differential conductance dI/dV was extracted numerically from the $I(V)$ curve. In order to check the quality of our dI/dV data we have also measured the differential conductivity using a lock-in technique. The normalized differential conductance $(dI/dV)/(I/V)$ is known to resemble the Local Density of States (LDOS) of the surface [229, 230], whereby it should be noted that at the Fermi level (where $V=0$) the normalized differential conductance is always 1. As is clear from Fig. 6.3, the exact shape of the LDOS spectrum depends on the actual value of the setpoints.

6.1.3 Results

The low level of surface roughness of our samples was confirmed by scanning tunneling microscopy analysis of the surface (Fig. 1), exhibiting smooth terraces separated by clear unit cell height steps similar to the surface of the initial STO (001) substrate. It is noted that for the STO capping layer about 8% more PLD

Figure 6.3: IV curves and LDOS, $(dI/dV)/(I/V)$ of the STO(001)/2LAO/1STO heterostructure, recorded at 300 K (a,b) and 77 K (c,d).

pulses than required for a single unit cell were used to ensure the presence of a fully closed STO capping layer, which explains the presence of small clusters in the STM images. In Fig. 6.3 the scanning tunneling spectroscopy data of the STO(001)/2LAO/1STO heterostructure at 300 K and 77 K are shown. Different initial setpoints were chosen at both temperatures to provide a bias voltage larger than the band gap. The most remarkable features are the increase of the band-gap from about 1.0 eV at 300 K (Fig. 6.3 b) to approx. 2.3 eV at 77 K and the increasing asymmetry at low temperatures. At 77 K this band gap is predominantly in the energy range below the Fermi level, as is common for n-type conducting behaviour.

The typical tunneling currents in our experiments are significantly higher than observed for STM/STS studies on uncapped 4 u.c. LAO layers on STO, as reported

Figure 6.4: Schematic representation (a) and DFT calculation (b) of the band-structure of the STO(001)/2LAO/1STO heterostructure with band gaps at 300 K and 77 K. Data taken from ref. [94]

by Breitschaft et al. [231] and Ristic et al. [232]. This supports the conjecture that in our STO-capped system the surface is conducting as well. In addition, the observation of high tunneling currents at positive sample biases, for the room temperature scans, is in line with a predominant tunneling from a 2D hole gas, as predicted to be present at the STO surface.

Density Functional Theory (DFT) calculations of the bandstructure [94] of the STO(001)/2LAO/1STO heterostructure are shown in Fig. 6.4. The valence band maximum is defined by the O $2p$ states at the M-point in the STO surface layer, while Ti $3d$ states at the LAO-STO substrate interface mark the bottom of the conduction band, located at the Γ -point of the Brillouin zone. The indirect bandgap for this system was calculated to be ~ 0.3 eV, while the direct bandgap at the Γ -points was ~ 0.8 eV. It should be noted though that DFT calculations typically underestimate band gaps. The small band gap experimentally observed at 300 K suggests that at this temperature both the surface (M-point) as well as the interface states (Γ -point) are probed. At cryogenic temperatures however, the tunneling from the STM tip to the finite k -value STO surface states appears to be inhibited. This notion is supported by the fact that the surface imaging resolution, at normal bias voltages ($< \pm 2$ V) in the STM experiments at 77 K was found to be considerably inferior to that at 300 K.

To further investigate the temperature dependence of the composite 2DEG-2DHG system, IV curves were recorded at various temperatures in the range from 80 K to 180 K. For every temperature, 900 IV-scans were recorded on a 10×10 grid (30×30 nm) and subsequently averaged. The result is shown in Fig. 6.5 a. Each IV-scan was obtained from an initial set point voltage of -1 V, and took

Figure 6.5: (a) Temperature dependent IV curves of the STO(001)/2LAO-/1STO heterostructure recorded from 83 K to 180 K. (Set point voltage $V = -1.0$ V and tunnel current $I = 1$ nA). (b) Current offset at zero bias for various temperatures.

Figure 6.6: IV curves of the STO(001)/2LAO-/1STO heterostructure recorded at 77 K with tunnel current setpoints of 0.5 nA (a) and 1.0 nA (b).

Figure 6.7: IV curves of the STO(001)/2LAO/1STO heterostructure recorded subsequently at 77 K with variable tunnel current setpoints of 0.25 nA (1,2,3: first curve 1 was recorded, followed by curve 2 and 3, respectively), 0.50 nA, 0.75 nA and 1.0 nA and sample bias -1.0 V.

approximately 0.2 seconds. The most remarkable observation is the offset of the current at zero bias for temperatures below 180 K. This offset increases with decreasing temperature, see Fig. 6.5 b. This current offset is interpreted resulting from a negative charging of the sample during the hold time at -1 Volt, before the scan is carried out. During the IV-scan, this charging is countered by a positive current flow to the sample.

This suggests that for decreasing temperatures the depletion of electrons in the upward shifted O 2p band cannot be replenished from the underlying interface and hence the STO capping layer is positively charged with respect to the tip. Since no evidence for a Coulomb gap and a Coulomb staircase is observed in IV curves, the charging energy ($e^2/2C$) must be substantially larger than the thermal energy kT . [233, 234] The latter implies that the capacitance must be significantly larger than 10^{-17} F. Decreasing the sample bias set point and scanning voltage to a value below -2 V does not result into charging of the top layer (see Figs. 6.6 a-b). Thus electrons that tunnel from filled states which are located more than 2 eV below the Fermi level of the STO capping layer can be replenished by the underlying interface at the substrate. Prolonged scanning at a voltage in the band gap region leads to a gradual increase of the decharging current (see Fig. 6.7). Moreover, increasing the set-point current shifts the charging current to higher values, but the decharging current at zero bias remains unaltered as shown in Fig. 6.7.

6.1.4 Discussion

The structural phase transition in STO from a cubic to a tetragonal phase may play a role in the fact that the phonon-assisted tunneling to the surface states is hampered by stiffening of the phonons. This phase transition is driven by the condensation of a zone corner phonon which involves the rotation of the oxygen octahedra [235]. Moreover, it is known that this phase transition must be treated very differently in the near-surface region than in the bulk of the crystal. For instance the order parameter increases when the surface is approached from the interior of the crystal [236]. Salman et al. [237] found that the structural phase transition of STO occurs at a much higher temperature near the surface (150 K) as compared to the bulk (105 K), which would be in line with the observation of a reduced accessibility of the surface states below this temperature.

We have studied the electronic structure of the surface of the perovskite STO-(001)/2LAO/1STO system with variable temperature scanning tunneling spectroscopy. At 300 K a band gap of ~ 1.0 eV is measured, whereas at 77 K the band gap widened to ~ 2.3 eV. The significant decrease in the band gap with increasing temperature is ascribed to an increased replenishment of charge from the underlying 2DEG to the surface 2DHG. At low temperatures the 2DHG can be positively charged by applying a negative sample bias voltage within the band gap region. At low temperatures the 2DHG can now be probed separately with the proposed experimental geometry, although the 2DEG is located less than 1 nm below. These local observations demonstrate for the first time the presence of two spatially separated 2D conducting sheets, one electron-like (2DEG) and the other hole-like (2DHG), in epitaxial oxide heterostructures.

6.2 Reflection in retrospect

The results described in Section 6.1 revealed the spatial separation of individual interface (2DEG) and surface (2DHG) conducting sheets, including their temperature dependent coupling. This study followed up on previous work which demonstrated macroscopically the presence of electrons as well as holes in parallel conducting sheets in STO(001)/2LAO/1STO heterostructures [94]. The follow-up was initiated in order to study the electronic structure and possible coupling between sub-nanometer spaced conducting interfaces in further detail. The initial samples were synthesized following the approach described in Chapter 2, allowing for a single extra laser pulse at the end in order to fully close the topmost SrTiO₃ layer. The samples were subsequently transported through air to a variable temperature STM setup. While it is known that single LaAlO₃/SrTiO₃ interfaces are sensitive to surface adsorbates [101, 112], it was chosen not to apply an extra annealing step in oxygen in the STM chamber. As the SrTiO₃ capping layer in these bilayer based samples is expected to prevent structural and chemical reconstructions at the LaAlO₃ surface [17, 94] and the intention was to keep it in a state representative for other measurements.

Combining the spatial resolution of STM imaging with the electronic structure resolving capabilities of STS, allows the study of local electronic configurations at the surface of materials under investigation. This has been successfully applied for

single $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces in order to study topics such as: the potential well origin [231], orbital order [232], in-gap states [238], and superconducting gap behaviour [39]. Also, using cross-sectional STM and STS, the evolution of band alignments across $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures has been revealed [68].

The discussion of the results on $\text{STO}(001)/2\text{LAO}/1\text{STO}$ heterostructures in Section 6.1 is partly based on a theoretically derived layer-resolved density of states, showing a marked build-up of electric potential due to the polar discontinuity present. The resulting band structure was taken from [94] and is shown in Figure 6.4b. For single $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces such an electric field build-up per unit cell has been sought for but appeared either not measurable by XPS [130–134] or strongly reduced in STS and XRD measurements [68, 125, 126]. Even though the results in Section 6.1 are concerning an SrTiO_3 capped system, seeing that there is currently no clear experimental proof for such large potential build-ups, care must be taken when interpreting these results in relation to that specific band structure. This however does not necessarily void the conclusion on the existence of spatially separated interface 2DEG and 2DHG conducting sheets, including their temperature dependent coupling, in $\text{STO}(001)/2\text{LAO}/1\text{STO}$ heterostructures. Here, the SrTiO_3 capping may protect the underlying LaAlO_3 from structural reconstructions and influence of adsorbates, resulting in the potential build up as predicted. Another possibility would be that a similar valence band structure and offset is present due to other sources, possibly from reconstructions, intermixing or vacancies.

The behaviour of conductivity at $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces has been shown to be quite sensitive to surface effects such as adsorbates. Additionally, STM and STS are highly surface sensitive analysis techniques, something that the research group of prof. Zandvliet together with this author used to good effect, partly on the same set-up, in order to study: confined surface states [239], Ge dimer diffusion [240], and binding of CO molecules [241]. This sensitivity however makes it quite difficult to conclusively interpret the data.

Further measurements could prove worthwhile and as a suggestion it could be considered to extend the range of samples to allow for LaAlO_3 layers from 1 to 3 unit cells and SrTiO_3 capping layer from 1 to 2 unit cells. This would give further experimental insight on the evolution of the band structure based on modulated coupling between the individual conducting sheets. Furthermore, inspired by work on single interfaces [68], cross-sectional STM and STS on $\text{STO}(001)/2\text{LAO}/1\text{STO}$ heterostructures, mapping subnanometer spaced 2DEG and 2DHG, could prove quite revealing. Recently, spatially separated 2DEG and 2DHG conducting sheets in $\text{STO}(001)/\text{LAO}/\text{STO}$ heterostructures have been directly observed [242] while their electronic interaction at shorter separation distances remains to be explored.

Afterword

Early 2004, Nature published the article "A high mobility electron gas at the $\text{LaAlO}_3/\text{SrTiO}_3$ heterointerface" by Akira Ohtomo and Harold Hwang. The article attracted a good deal of interest from the outset, jump started a research field and currently has more than 2250 citations, see Figure A1a. Of particular interest were the reported high electron mobilities, quantum oscillations and the promise of a charge state controlled by polar discontinuity. Nearly one and a half decade of research has since been committed to this topic, improving understanding of the phenomena in these materials and resulting in more than 850 publications specifically related to $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces, see Figure A1b. While the initial four years were relatively quiet in terms of the number of publications and citations, scientific impact was already high with the first demonstrations of critical thickness, field effect gating, superconductivity and magnetic effects. There has since been a steady increase in the number of publications and citations that extends to this day, showing a particularly marked increase in publication numbers in 2013. The work described in this thesis contributed to the field by demonstrating the first magnetic effects, unconventional oscillations, by studying the interfacial transition sharpness and by probing the interplay between spatially separated conducting sheets.

The $\text{LaAlO}_3/\text{SrTiO}_3$ interface is often referred to as a prime example and model system for interface based multifunctional oxide heterostructures. Indeed, the system is a host to many scientific curiosities worth researching such as superconductivity, magnetism, spin-orbit coupling and high electron mobility. As $\text{LaAlO}_3/\text{SrTiO}_3$ and related interfaces gained considerable momentum, research improved our understanding of oxide materials in general and oxide interface engineering in particular by refining experimental and theoretical tools. The knowledge and experience gained may prove to be very valuable in understanding and controlling the physics in other materials systems as well. However, while func-

Figure A1: Historical perspective of scientific attention: (a) Number of publications citing "A high mobility electron gas at the LaAlO₃/SrTiO₃ heterointerface" by Akira Ohtomo and Harold Hwang [10]. (b) Subset of publications specifically mentioning LaAlO₃/SrTiO₃ interfaces¹.

tional devices have been shown, the applicability of the LaAlO₃/SrTiO₃ interface in technology appears to be low for the time being as material properties at typical operating temperatures are not competitive to currently available technology. In order to aid the feasibility of eventual production, the inclusion of LaAlO₃/SrTiO₃ interfaces on industry standard silicon is being pursued but material properties suffer and generally there are issues limiting uniformity, stability and reproducibility. For systems comprised of complex components such as ternary LaAlO₃ and SrTiO₃ it may prove difficult to actually fulfil the role as promising material for oxide interface based electronics. For increased understanding and control over structural and electronic behaviour, further improvements to existing techniques are required regarding growth, characterisation and theoretical modelling. Due to the complex material constituents and electronic correlations, the effort may be considerable. Especially considering that any technological implementation needs to be highly promising in order to compete with conventional semiconductor materials which have gone through well over half a century of refinement backed by significant investments from academic and industrial parties.

When tackling complex issues it is worthwhile to invest in sustained collaboration and knowledge transfer between similar, but not necessarily like-minded, contributors. The oxide materials community has taken this to heart and ample opportunity for interaction is provided. There are annual meetings such as the International Workshop on Oxide Electronics and International School of Oxide Electronics or research networking programmes that allow grants for short visits or longer exchanges. Yet, scientific research is in the end geared for the individual success of research groups as funding is so closely tied to publication impact. Collaborations between different research groups is typically strong when skills are complementary and overlap between expertise is minimal. It may however be very valuable when groups with high overlap in expertise combine their efforts, in order to refine their skills, tools and results in unison with higher efficiency and

¹Based on Web of Science data, subset data derived from further filtering using: TOPIC = ((SrTiO₃-LaAlO₃) OR LaAlO₃/SrTiO₃ OR SrTiO₃/LaAlO₃) AND *interface*).

attention to detail. An additional benefit would be that after an initial discovery, other research groups may be able to correctly reproduce and verify results quicker which would allow increased acceptance of otherwise challenged results. For example in the case of $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces, there has been considerable debate as to which characteristics of the interface are intrinsic. This is intensified due to variations between samples from different research groups, which is not surprising as even within single samples there may be inhomogeneity. Details of growth and post processing, in so far as they are intended, are sometimes underexposed in publications which complicates the matter further.

Furthermore, mistakes and setbacks should be allowed more time in the spotlight in order to advance as a group with the most efficient use of time, energy and available funding. As an example, most applied research is highly dependent on input of materials such as substrates and targets from a small selection of specialized suppliers. For commercial companies this situation of dependence is common, yet typically a lot of effort is invested to try and circumvent the situation or at least mitigate the accompanying risks sufficiently. In oxide materials research there is currently no coordinated supplier quality check or communication pathway which means that all research groups will have to deal with non conformities in delivered goods separately. This results in loss of time and effort in order to find and correct the cause in the best scenario but when missed may even extend to wrong results and conclusions. An efficient approach to these situations is better performed as a larger group, guaranteeing knowledge transfer on the short and long term.

With further collaboration and knowledge transfer, the path forward should be open for many exciting discoveries and an improved chance of integration into functional devices.

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Summary

Complex oxides have phase diagrams of broad diversity, the increased interactions in their bulk resulting in spectacular phenomena, examples being colossal magnetoresistance, high transition temperature superconductivity, ferromagnetism and ferroelectricity. Additionally, the improved control over substrate surfaces and epitaxial deposition of complex oxides now allows the synthesis of abrupt interfaces, changing from one material to another over the distance of a single unit cell. In analogy to semiconductors where interfaces gave rise to novel interfacial states, there are tremendous opportunities in complex oxides to generate novel materials dictated by interfacial physics. A remarkable example was discovered by Akira Ohtomo and Harold Hwang in heterostructures composed of insulating perovskite constituents SrTiO_3 and LaAlO_3 , where the polar heterointerface was shown to result in an electron gas with high electron mobility and intriguing magnetoresistance oscillations. To further the understanding of behaviour and possible exploitation of this two dimensional electron gas at the interface between LaAlO_3 and SrTiO_3 , this thesis explores its synthesis, electronic properties and atomic structure.

The $\text{LaAlO}_3/\text{SrTiO}_3$ interface is often referred to as a prime example and model system for interface based multifunctional oxide heterostructures. Indeed, the system is a host to many scientific curiosities worth researching such as superconductivity, magnetism, spin-orbit coupling and high electron mobility. As a general overview of the exciting results obtained in recent years, the current state of research regarding $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces is described. As $\text{LaAlO}_3/\text{SrTiO}_3$ and related interfaces gained considerable momentum, research improved the understanding of oxide materials in general and oxide interface engineering in particular by refining experimental and theoretical tools.

In order to study the behaviour of well defined materials of high quality, it is important to establish control over their synthesis. As the interfacial states

are easily influenced, both by intended and unintended causes, great care must be taken while engineering these interfaces to understand and control the influences from charge transfer, defects, interdiffusion and distortions. This allows reproducible realization of samples and improves tunability for various competing factors driving their behaviour. A successful synthesis method for epitaxial $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces is described with examples for single interfaces, heterostructures and superlattices. Continued effort in understanding and improving the synthesis of these oxide materials systems will allow improved research into materials properties, functionality and may provide a route towards devices in viable applications.

While magnetic ordering would appear counter intuitive as it would be expected to disrupt the pairing mechanism required for superconductivity, it was theoretically predicted that magnetism can be induced at the interface between otherwise nonmagnetic SrTiO_3 and LaAlO_3 . To verify the existence of such induced magnetism and low dimensionality at the interface, transport properties on $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces have been studied down to 300 mK and in magnetic fields up to 30 T. In order to do so correctly and reduce unintended conduction channels, increased oxygen partial pressure during deposition is shown to play a pronounced role in the reduction of oxygen vacancy doping. For samples grown at relatively high oxygen partial pressures, a large negative magnetoresistance of the interface, together with a logarithmic temperature dependence of the sheet resistance is demonstrated. These effects are explained in terms of the scattering of conduction electrons off localized magnetic moments.

Two-dimensional electron gases in semiconductor heterostructures have had an important impact on the fundamental understanding of electronic transport. Oxide 2D electron systems are particularly interesting because of the richness of electronic phases that the oxides provide. A study was performed, in order to search for hallmarks of a two dimensional electron gas with high carrier mobilities, resulting in low-temperature and high-field magnetotransport data on $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces, grown at relatively high oxygen partial pressures. Oscillations in the magnetoresistance are observed, showing an uncommon $\sqrt{B}$ periodicity, both in large-area unstructured samples as well as in a structured sample. Several explanations are considered in terms of a highly mobile two-dimensional electron gas and considered in light of the current state of research into quantum oscillations in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces. As the $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces in the samples presented here are markedly different in nature from the typical interfaces being investigated, further analysis of the uncommon oscillations in these samples is required and could potentially reveal novel electron correlation effects.

The presence of significant cation intermixing at $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces was initially reported based on electron energy loss spectroscopy, it demonstrated the presence of atomic deficiencies in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces. In order to understand this atomic intermixing and its relation with the doping mechanism, anomalous surface X-ray diffraction was used. A vacancy-rich A-site composition of neutrally charged $\text{Sr}_{1-1.5x}\text{La}_x\text{O}$ layers is demonstrated to exist at the interface, the formation of which already starts at the onset of deposition. The measured A-site compositions do not take away the polar instability, which thus still requires a change from the nominal structure and/or composition at the B-sites. Evidence

is given for such a mechanism starting at a thickness of 3 unit cells. One of the original aims of the study was to relate structural transitions to the conductivity transition from 3 to 4 unit cells. Unfortunately, this relation could not be found from the data set while a considerable structural mitigation, of the electrostatic potential build up from the polar discontinuity, appears present for all samples.

Heterostructures of $\text{LaAlO}_3/\text{SrTiO}_3$ bilayers on (001)-oriented SrTiO_3 substrates provide the unique possibility to study the coupling between sub-nanometer spaced conducting interfaces. This is achieved by scanning tunnelling microscopy and spectroscopy experiments on SrTiO_3 -capped LaAlO_3 layers on $\text{SrTiO}_3(001)$ substrates, allowing local characterization of the electronic structure and revealing the individual interface and surface based conducting sheets including their temperature dependent coupling. The band gap is shown to increase dramatically at low temperatures due to a blocking of the transition from the conduction band of the SrTiO_3 substrate to the top of the valence band of the SrTiO_3 capping layer. This prevents the replenishment of the depleted electrons in the capping layer from the underlying two dimensional electron gas and enables charging of the two dimensional hole gas by applying a negative sample bias voltage within the band gap region.

In short, the work on $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces described in this thesis studied its synthesis, magnetic effects, unconventional oscillations, interfacial structure and the interplay between spatially separated conducting sheets.

Samenvatting

(Summary in Dutch)

Complexe oxides kennen een grote diversiteit in hun fasediagrammen, de oorzaak is te vinden in de toegenomen interacties in hun bulk hetgeen tot spectaculaire verschijnselen kan leiden. Voorbeelden daarvan zijn kolossale magnetoweerstand, hoge-Tc supergeleiding, ferromagnetisme en ferro-elektriciteit. Bovendien maakt de verbeterde beheersing van substraatoppervlakken en epitaxiale depositie van complexe oxides tegenwoordig de synthese van ‘abrupte’ grensvlakken mogelijk, die over de afstand van een enkele eenheidscel van materiaal veranderen. Naar analogie met halfgeleiders, waar de introductie van grensvlakken resulteerde in nieuwe toestanden, zijn er veel mogelijkheden om met complexe oxides nieuwe materialen te maken waarvan de eigenschappen bepaald worden door de fysica van het interface. Een bijzonder voorbeeld ontdekten Akira Ohtomo en Harold Hwang in heterostructuren die zijn opgebouwd uit de isolerende complexe oxides SrTiO_3 en LaAlO_3 . Zij toonden daarvoor aan dat het polaire grensvlak resulteert in een elektronengas met een hoge elektronenmobiliteit en intrigerende magnetoweerstand oscillaties. Voor een beter begrip en de mogelijke benutting van dit twee-dimensionale elektronengas op het grensvlak tussen LaAlO_3 en SrTiO_3 verkent dit proefschrift de synthese, elektronische eigenschappen en atomaire structuur van het grensvlak.

Het $\text{LaAlO}_3/\text{SrTiO}_3$ -grensvlak geldt als een uitstekend voorbeeld en modelsysteem voor grensvlak gebaseerde multifunctionele oxide-heterostructuren. Het systeem vertoont inderdaad veel wetenschappelijke bijzonderheden die de moeite van het onderzoeken waard zijn, zoals supergeleiding, magnetisme, spin-baankoppeling en hoge elektronenmobiliteit. Voor een algemeen overzicht van de interessante resultaten die in de afgelopen jaren zijn behaald, wordt de huidige stand van het onderzoek aan $\text{LaAlO}_3/\text{SrTiO}_3$ -grensvlakken beschreven. Omdat er veel onder-

zoek is gedaan aan deze en verwante systemen, is er meer begrip gekomen van oxide-materialen in het algemeen en van de realisatie van oxide-grensvlakken in het bijzonder, doordat experimentele en theoretische hulpmiddelen zijn verfijnd.

Om goed gedefinieerde materialen van hoge kwaliteit te kunnen bestuderen, is het nodig beheersing te krijgen over hun synthese. Omdat de toestand van het grensvlak makkelijk te beïnvloeden is door bedoelde en onbedoelde oorzaken, is zorgvuldigheid vereist bij de realisatie van deze grensvlakken, om de invloed van ladingsoverdracht, defecten, interdiffusie en kristalrooster vervormingen te kunnen begrijpen en beheersen. Een succesvolle synthesesmethode voor epitaxiale $\text{LaAlO}_3/\text{SrTiO}_3$ -grensvlakken wordt beschreven, met voorbeelden voor enkele grensvlakken, heterostructuren en superroosters. De voortdurende inzet om de synthese van deze oxide-materialen te begrijpen en verbeteren maakt het mogelijk om materiaaleigenschappen en nieuwe functionaliteit te onderzoeken. Dit opent wellicht een route naar devices voor interessante toepassingen.

Terwijl magnetische ordening contra-intuïtief lijkt omdat men zou verwachten dat dit het voor supergeleiding benodigde paringsmechanisme verstoort, was er een theoretische voorspelling dat magnetisme kan worden opgewekt op het grensvlak tussen de anderszins niet-magnetische materialen SrTiO_3 en LaAlO_3 . Om het bestaan van dergelijk geïnduceerd magnetisme op het interface te verifiëren, zijn de transporteigenschappen op $\text{LaAlO}_3/\text{SrTiO}_3$ -grensvlakken onderzocht bij temperaturen tot een minimum van 300 mK en in magnetische velden tot maximaal 30 T. Om dit correct uit te voeren en onbedoelde geleidingskanalen terug te dringen, is eerst aangetoond dat de partiële zuurstofdruk bij depositie een uitgesproken rol speelt in het verminderen van zuurstofgatendoping. Voor samples die zijn gegroeid bij een relatief hoge partiële zuurstofdruk is een hoge negatieve magnetoweerstand van het interface aangetoond, in samenhang met een logaritmische temperatuurafhankelijkheid van de laagweerstand. Deze effecten worden verklaard in termen van de verstrooiing van geleidingselektronen door gelokaliseerde magnetische momenten.

Twee-dimensionale elektronengassen in halfgeleider-heterostructuren hebben een grote invloed gehad op het fundamentele begrip van elektronentransport. 2D elektronensystemen in oxides zijn bijzonder interessant vanwege de rijkdom aan elektronische fases die de oxides bieden. Een studie is uitgevoerd naar de karakteristieken van een twee-dimensionaal elektronengas met hoge ladingsdragermobiliteiten. Dit heeft geresulteerd in magnetotransportdata bij lage temperaturen en hoge magnetische veldsterktes voor $\text{LaAlO}_3/\text{SrTiO}_3$ -grensvlakken die zijn gegroeid bij relatief hoge partiële zuurstofdruk. Er zijn oscillaties in de magnetoweerstand waargenomen die een ongebruikelijke $\sqrt{B}$ periodiciteit vertonen, zowel over grotere oppervlakken in ongestructureerde samples als in een gestructureerd sample met dimensies op micrometer schaal. Meerdere verklaringen zijn beschouwd in termen van een zeer mobiel twee-dimensionaal elektronengas en gewogen in het licht van de huidige stand van het onderzoek naar kwantumoscillaties in $\text{LaAlO}_3/\text{SrTiO}_3$ -grensvlakken. Omdat deze grensvlakken in de samples die hier zijn beschreven in karakter sterk verschillen van de typische grensvlakken die worden onderzocht, is een verdere analyse nodig van de ongewone oscillaties in deze samples. Die analyse kan wellicht nieuwe elektroncorrelatie-effecten opleveren.

De aanwezigheid van significante kation vermenging op $\text{LaAlO}_3/\text{SrTiO}_3$ -grens-

vlakken is eerder gerapporteerd op basis van elektronenergieverlies-spectroscopie; dit toonde de aanwezigheid van atomaire deficiënties in de grensvlakken aan. Om deze atomaire vermenging en het verband met het dopingmechanisme te begrijpen, is het grensvlak nader bestudeerd met anomalous surface X-ray diffractie. Het bestaan van een gaten-rijke *A*-site samenstelling van neutraal geladen $\text{Sr}_{1-1.5x}\text{La}_x\text{O}$ -lagen op het interface is aangetoond, waarvan de vorming al begint bij lagen van een enkele eenheidscel. De gemeten *A*-site samenstellingen nemen de polaire instabiliteit niet weg, die daarom nog steeds een verandering van de nominale structuur en/of samenstelling op de *B*-sites vereist. Het bewijs is geleverd voor een dergelijk mechanisme dat begint bij een dikte van drie eenheidscellen. Een van de oorspronkelijke doelen van de studie was structurele overgangen te relateren aan de geleidbaarheidstransitie van 3 naar 4 eenheidscellen. Helaas kon deze relatie niet uit de dataset worden afgeleid, terwijl in alle samples een aanzienlijke structurele compensatie aanwezig lijkt te zijn voor de elektrostatische potentiaal opgebouwd door de polaire discontinuïteit.

Heterostructuren van $\text{LaAlO}_3/\text{SrTiO}_3$ -bilagen op (001)-georiënteerde SrTiO_3 -substraten bieden de unieke mogelijkheid om de koppeling te bestuderen tussen geleidende grensvlakken die op subnanometer afstand van elkaar liggen. Dit wordt gedaan met scanning tunnelling microscopie en spectroscopische experimenten met SrTiO_3 -afgedekte LaAlO_3 -lagen op SrTiO_3 (001)-substraten. Dat maakt lokale karakterisering van de elektronische structuur mogelijk en toont de grensvlakken oppervlakgebaseerde geleidende lagen, inclusief hun temperatuurafhankelijke koppeling. Aangetoond is dat de band gap dramatisch toeneemt bij lage temperaturen als gevolg van het blokkeren van de transitie van de geleidingsband van het SrTiO_3 -substraat naar de top van de valentieband van de SrTiO_3 -afdeklaag. Dit voorkomt het aanvullen van elektronen in de afdeklaag vanuit het onderliggende twee-dimensionale elektronengas en maakt het opladen mogelijk van het twee-dimensionale gaten-gas door over het sample een negatieve bias-spanning aan te leggen in het band gap bereik.

Kortom, het in dit proefschrift beschreven werk aan $\text{LaAlO}_3/\text{SrTiO}_3$ -grensvlakken betreft de studie van hun synthese, magnetische effecten, bijzondere oscillaties, grensvlakstructuur en de wisselwerking tussen ruimtelijk gescheiden geleidende lagen.

Dankwoord

(Acknowledgements in Dutch)

Vele mensen hebben bijgedragen aan mijn promotie onderzoek en de totstandkoming van dit proefschrift. Het doet me deugd dat de uiteindelijke afronding ook ruimte geeft om eenieder te bedanken voor alle hulp en inspiratie, inbreng die zo essentieel is geweest voor het mogelijk maken van deze mooie ervaring.

In het bijzonder wil ik Hans bedanken voor het bieden van de mogelijkheid om te promoveren op een heel uitdagend onderwerp binnen een geweldige vakgroep. Je positieve maar kritische blik, inspiratievolle suggesties en flexibiliteit heb ik altijd zeer gewaardeerd en hebben in grote mate bijgedragen aan het proefschrift. Bedankt dat je ook de ruimte gaf om een promotie met start-up te combineren, het bedrijf heeft haar bestaan en huidige positie daar aan te danken.

Ik wil Alexander bedanken voor zijn aanstekelijke enthousiasme, goede discussies en essentiële inbreng binnen alle facetten van het onderzoek. Bedankt voor je goede suggesties en ondersteuning bij het schrijven van het proefschrift, heel fijn dat je ook promotor wil zijn.

Als leider van het Nanoelectronics programma wil ik Wilfred bedanken voor het bieden van een goed interdisciplinair platform te MESA+ Institute for Nanotechnology. Het bracht aanverwante onderzoeken nader tot elkaar, om zo van elkaar te leren en waar nodig hulp te bieden.

De ondersteuning vanuit technische en administratieve staf was top. Dick en Frank, natuurlijk dank voor de belangrijke technische ondersteuning en het draaiende houden van alle systemen in het lab. Maar vooral ook voor de sfeer bij lunch, uitjes of gewoon toevallige gesprekken. Ans en Inke, dank voor de vriendelijke administratieve ondersteuning en Ans in het bijzonder voor de subtiele hints in e-mail onderwerpen als iets mijn aandacht dreigde te ontsnappen.

Ik heb het plezier gehad om mijn tijd op de vakgroep te delen met vele andere studenten en promovendi, in het bijzonder dank voor Aico, Maarten, Joost, Kris en Kees. Ik kijk terug op goede gesprekken, onnavolgbare raps, pranks, motor uitjes, bergwandelingen en een hopelijk ondertussen verloren gegaan notitieboekje. Jongens, bedankt. Furthermore I'd like to thank Xiao Renshaw Wang for his enthusiastic contributions and our time together working behind the AFM. Good to see that you lead your own group now and even find the time to keep creating great artistic cover designs to boot.

Goede en constructieve samenwerking was er ook met de IMS vakgroep, het was fijn om onderzoek en conferenties te kunnen delen met o.a. Hans Boschker, Wolter, Gerwin en Josée. Dave, Guus, Gertjan en Mark, ik ben jullie zeer erkentelijk en begrijp dat jullie eerdere werk het mogelijk maakte dat ik dit onderzoek kon doen. Mark, dank voor alles. Bij de start was je aanwezig om met geduld en toewijding mij in te werken in het veld en de nodige processtappen aan te leren in het, voor mij nieuwe, PLD lab. Wat fijn dat ik ook bij jou aan kon kloppen voor advies met betrekking tot de uiteindelijk afronding.

Ik heb veel gehad aan de inbreng van anderen binnen en buiten de universiteit, vaak ondersteund door zeer specialistische meetapparatuur. Ik zou graag de groep willen bedanken die betrokken was bij het onderzoek te High Field Magnet Laboratory in Nijmegen en in het bijzonder het team aldaar: Jos, Uli en Jan Kees. Ook waren de experimenten met synchrotrons te Grenoble en Karlsruhe indrukwekkend, in het bijzonder wil ik Vedran en Sybolt bedanken voor de fijne samenwerking en inbreng op het gebied van Röntgen diffractie. Tijdens mijn afstuderen had ik het plezier om te mogen werken onder leiding van Harold en Arie in wat nu de PIN vakgroep is. Leuk was het om tijdens de promotie weer samen te kunnen werken en ik wil Daan, Arie en Harold bedanken voor hun expertise op gebied van STS en STM.

Ramon en Karel, fijn dat jullie mijn paranimfen willen zijn. Dank voor jullie vriendschap en hulp over de afgelopen jaren.

Pap en mam, bedankt voor het realiseren van de ideale omgeving om tot zo'n resultaat te komen. Pap bedankt voor een niet aflatende aandacht voor het behalen van immer betere resultaten. Mam bedankt voor het niet vergeten dat bepaalde resultaten soms al een compliment verdienen, het spijt me zo dat je dit niet meer met ons mee mag maken.

Dank aan Amy en Elena, om op gezette tijden mijn schrijfwerk in eenzame opsluiting te komen verlichten. De mooiste momenten tijdens het schrijven heb ik beleefd wanneer jullie mij gezelschap kwamen houden, door rustig erbij te komen zitten tekenen of juist door uitbundige dans sessies op te voeren.

Veel dank aan Anita. Jaren geleden adviseerde je me om niet te proberen zowel een promotie onderzoek als ook de prille fase van een start-up parallel te draaien, de tijd voor een bedrijf zou nog wel komen was je gedachte. Voor mij was die keuze niet eenvoudig en leek het momentum te groot om te laten lopen, daardoor betrok ik je in de nadelen van zo'n situatie met bijna onmogelijke werkweken. Bedankt voor je steun en hulp over de jaren en in het bijzonder het opvangen van huishouden en kinderen gedurende al die weekenden die uiteindelijk nodig waren om dit af te ronden. Ik kijk enorm uit naar de toekomst samen met ons gezinnetje!