ATOMIC-SCALE STUDIES OF STRUCTURE AND BONDING AT PEROVSKITE OXIDE HETEROINTERFACES

A Dissertation
Presented to the Faculty of the Graduate School
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by
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Perovskite oxides exhibit an almost universal range of ground states including insulator, semiconductor, metal, superconductor, ferromagnet, antiferromagnet, spin glass, ferroelectric, and piezoelectric. Many of these phenomena occur in materials that are lattice-matched within a few percent of one another, giving rise to the possibility of heteroepitaxial structures using perovskite oxides, accessing these multiple degrees of freedom. The existence of interfaces can, however, greatly affect the macroscopic properties of these heterostructures, leading on the one hand to exotic new phases stabilized at the interface or on the other hand to the degradation of bulk-like properties. Here scanning transmission electron microscopy (STEM) in combination with electron energy loss spectroscopy (EELS) is used to study interface phenomenon in perovskite-oxide heterostructures.

In STEM the self-focusing of the probe electron wavepacket by channeling along a zone axis in a crystalline material can strongly affect the annular dark field (ADF) image contrast. By exploiting these channeling effects, atomically thin, buried SrTiO$_3$ layers on Si were imaged in plan view, revealing a non-uniform coverage by epitaxial SrTiO$_3$ islands and 2x1 Sr-covered regions. The dewetting of thin SrTiO$_3$ films grown on Si(100) is caused by a phase-separation instability as predicted by density functional theory calculations. Improved coverage was obtained by choosing growth conditions away from equilibrium.
Atomically abrupt interfaces have been demonstrated for all-oxides heterostructures. However, for most systems there are intrinsic limitations to the abruptness of an interface. Polar discontinuities at oxide interfaces can cause atomic reconstruction. In LaVO$_3$/SrTiO$_3$ multilayers a second effect, preferential Sr surface segregation, is shown to dominate. The vanadate layers exhibit a growth asymmetry, with diffuse lower and atomically-abrupt upper interfaces. This suggests that segregation processes can set an upper limit to the obtainable interface sharpness in perovskite oxide heterostructures.

Starting with an abrupt interface between LaVO$_3$ and LaVO$_4$, spatially-resolved EELS is used to probe how the transition from V 3d$^2$ in LaVO$_3$ to V 3d$^0$ in LaVO$_4$ is made. Although no bulk phase of LaVO$_4$ with V 3d$^1$ configuration exists, a nanometer-wide region of V 3d$^1$ is found at the LaVO$_3$/LaVO$_4$ interface, rather than a mixture of V 3d$^0$ and V 3d$^2$. This two-dimensional sheet of 3d$^1$ electrons is an example for electronic reconstruction at a complex oxide interface, which can be used to induce and stabilize non-bulk-like valence states.

How does the presence of interfaces affect the physical properties of the complex oxide heterostructure? La$_{0.7}$Sr$_{0.3}$MnO$_3$ is a conducting ferromagnet at room temperature. However, in manganite/titanate tunnel junctions interface spin and charge modulations are thought to create an interfacial dead layer, thus fundamentally limiting the use of this material in small dimensions. Here, the degradation of the magnetic and transport properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayers is found to correlate with a higher degree of intermixing at the interfaces and the presence of extended cation defects in the La$_{0.7}$Sr$_{0.3}$MnO$_3$ layers. When these extrinsic defects are eliminated, metallic ferromagnetism at room temperature can be stabilized in ultrathin manganite layers.
BIOGRAPHICAL SKETCH

Lena Fitting Kourkoutis started her physics studies at the University of Rostock, Germany in 1998. After finishing her “Vordiplom” she continued her studies for one semester at the Technical University of Luleå, Sweden, followed by one year at the North Carolina State University in Raleigh (NCSU), USA. At NCSU she worked in R. J. Nemanich’s research group on the “Dynamics of Erbium Silicide and Germanium Nanostructure Formation on Silicon Surfaces” and was awarded her Diplom in physics from the University of Rostock after returning to Germany. In August of 2003 Lena moved to Ithaca and started her Ph.D work in the School of Applied and Engineering Physics at Cornell University. The M.Sc. was awarded in May 2006 and the Ph.D in August 2009.
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Over the last few years I have gotten very much used to routinely obtaining high quality STEM images of oxide heterostructures. However, it should not be forgotten that this success is based on several factors. (I) A stable, optimized microscope. Many thanks to John L. Grazul, Mick Thomas and Earl J. Kirkland who have maintained and tweaked the various microscopes on a day-to-day basis. (II) TEM sample preparation is the key. Shortly, after I arrived at Cornell, John L. Grazul introduced me to the “dirty secrets” of sample preparation - they are indispensable. (III) High quality specimens! I’ve been fortunate to collaborate with many experts in the field of oxide thin film growth, who have provided me with beautiful and interesting specimens. Here, I would like to mention the groups and people who have prepared the specimens used in this work. It was a pleasure working with Harold Y. Hwang and his students, post-docs and assistant professors: Takuya Higuchi, Yasuyuki Hikita, Yasushi Hotta, Naoyuki Nakagawa, Jong Hyun Song, Tomofumi Susaki. The samples studied in Chapter 6 and 7 were grown by Y. Hotta. J. H. Song has prepared the La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayers and performed the transport and magnetic measurements presented in Chapter 8. The SrTiO$_3$ bicrystal examined in Chapter 5 was prepared by Stefan Thiel and Andreas Schmehl in Jochen Mannhart’s
group. The SrTiO$_3$/Si samples (Chapter 3 and 4) were grown by Venugopalan Vaithyanathan in Darrell G. Schlom’s group. In addition I would like to acknowledge C. Stephen Hellberg, Hao Li, Melanie Parker and K. Anderson, who collaborated with us on the SrTiO$_3$/Si phase separation project.

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CHAPTER 1
INTRODUCTION

The structurally-related family of perovskite oxides exhibits an almost universal range of electronic properties. Insulating, semiconducting, metallic, superconducting, ferromagnetic, antiferromagnetic, ferroelectric, and piezoelectric oxides exist, many of which are lattice-matched within a few percent of each other, giving rise to the possibility of heteroepitaxial structures accessing these multiple degrees of freedom [1–3]. When joining two complex oxides at the atomic scale, exotic phases can be stabilized at the interface which can greatly affect the macroscopic properties of the material and presents a unique opportunity to create new artificial states between two materials [4–9]. Recent examples include interface ferromagnetism induced between two paramagnets [10] and conducting and even superconducting interfaces induced between two insulators [4, 5, 8]. The understanding of phenomena that occur at complex-oxide interfaces and their utilization for the atom-by-atom design of multifunctional oxide heterostructures is a central goal of this research.

The technique of choice is the scanning transmission electron microscopy (STEM) in combination with electron energy loss spectroscopy (EELS), which allows me to measure structural and chemical changes across buried interfaces, grain boundaries, domain walls, line and point defects at the atomic scale [4, 6, 8, 9, 11–13]. In STEM an atomically small (0.1-0.2 nm) electron beam is scanned across the sample and electrons that are scattered to high angles are collected on an annular dark field (ADF) detector to form a 2D ADF image. The contrast in ADF STEM is based on the scaling of the scattering cross section as roughly $Z^{1.7}$, where $Z$ is the atomic number. Hence, in a first approximation, heavier atoms (larger $Z$ number) appear brighter and can be distin-
Figure 1.1: ADF STEM image of a La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ superlattice with atomically sharp interfaces grown by pulsed laser deposition. The view is down the [100] zone axis of the SrTiO$_3$ substrate.

The Sr/La columns being the brightest spots. This is demonstrated in the ADF STEM image of a La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayer shown in Fig. 1.1 with the Sr/La columns being the brightest spots.

As an analytic technique spatially resolved EELS utilizes the small beam size in STEM (indicated by the green circle) to probe the electronic structure on an atomic scale. By stepping across the interface and individually recording EELS spectra at beam positions separated by only a few Ångströms, chemical and electronic structure changes can be explored with sub-nanometer spatial resolution. However, a good understanding of the EELS fine-structure is necessary and will be discussed in Chapter 2. First, however, I will motivate my work by giving a brief overview of perovskite oxides; their structure, growth and properties.
1.1 Perovskite Oxides

1.1.1 Structure

The structure of an ideal cubic perovskite oxide, ABO$_3$, is shown in Fig. 1.2 and consists of an array of corner-sharing BO$_6$ octahedra with a larger A cation at the body-center position. In an alternative representation (Fig. 1.2(b)) the layered nature of the structure becomes apparent. Along a <001> direction ABO$_3$ can be described by the stacking of AO and BO$_2$ layers, which is extensively used when discussing polar discontinuities at heterointerfaces (see section 1.1.4).

A wide range of physical properties are accessible by substitution of the A- or B-site cation, however, depending on the ionic radii of the cations this can result in distortions which lower the crystal symmetry. Typical distortions include tilting of the octahedra or cation displacement within the octahedra, which leads to ferroelectricity in BaTiO$_3$. The importance of the ionic radii for the stability of the perovskite structure was first pointed out by Goldschmidt in the 1920s, who introduced the tolerance factor $t$ describing the size mismatch of A-site and B-site cations in the structure:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)},$$

(1.1)

where $r_A$, $r_B$ and $r_O$ are the ionic radii of the A-site and B-site cations and the oxygen anion [14]. Note, that in this picture the covalent character of perovskite oxides is ignored. For perfect size match ($t=1$) the oxide is expected to crystallize in the cubic structure with a B-O-B bond angle $\theta = 180^\circ$. If the A-site ions are too small to fill the space in the network of BO$_6$ octahedra ($t<1$), the ABO$_3$ structure adjusts by tilting and rotation of the octahedra to reduce the excess space around the A-site resulting in $\theta < 180^\circ$. Since $t$ can change with external parameters
such as temperature and pressure, structural phase transitions are expected as these parameters are varied. The ability of the perovskite structure to adjust to $t<1$ allows for extensive A-site and B-site cation substitution. Additionally, the structure can accommodate large concentrations of both oxygen and cation vacancies.

Of particular interest for this work are perovskite oxides in which B is a transition metal ion, typically with a formal valence of 3+ or 4+, and A is either a trivalent rare-earth or a divalent alkaline-earth ion.

### 1.1.2 Growth of oxide thin films

As shown in the previous section, perovskite oxides share similar crystal structures and only small variations in the lattice constants which opens up the possibility of creating heteroepitaxial structures where new electronic phases at the
interface can emerge. In order to explore these effects, it is, however, necessary to be able to grow these materials in well defined thin layers. Advances in growth techniques, in particular molecular beam epitaxy (MBE) and pulsed laser deposition (PLD), have allowed high quality materials with complex structures, such as quantum wells and superlattices to be fabricated, sometimes with atomic-layer precision [4, 15]. Using reflection high-energy electron diffraction (RHEED) the growth of these oxide heterostructures can be monitored and controlled with sub-unit-cell control.

In PLD a pulsed, high-power ultraviolet laser is focused onto a solid target and the energetically ablated material is deposited onto a heated substrate. In order to control the growth on an atomic level, growth conditions are chosen to ensure slow controlled deposition in a layer-by-layer fashion [3]. If the deposition parameters such as substrate temperature, oxygen partial pressure, laser fluence and repetition rate are optimized the cation stoichiometry of the target can be preserved during the deposition process. However, if not optimized, variations in the cation stoichiometry are expected and can cause significant changes in the physical properties of the film. In Chapter 8, we will show how the laser spot size affects the La$_{0.7}$Sr$_{0.3}$MnO$_3$ cation stoichiometry and thereby the magnetic and transport properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayers. Stoichiometry in oxygen is usually controlled by tuning the oxygen partial pressure (PO$_2$) in the growth chamber. This has been demonstrated in SrTiO$_{3-\delta}$/SrTiO$_3$ multilayers, which were grown by simply varying PO$_2$ and showed oxygen doping profiles with sub-nanometer abruptness [16].

In oxide-MBE the constituent elements are evaporated in the form of molecular beams and deposited in the presence of molecular oxygen (or with additional ozone) on a heated substrate. Typically, the molecular beam are obtained
by thermal evaporation of high purity elemental sources. By carefully tuning the shutter times and/or the deposition rates for each element the stoichiometry of the film can be controlled and atomically sharp interfaces can be obtained. The precise control over composition allows the effect of slight deviations in the film composition on the film structure to be studied, as we have done in the case of SrTiO$_3$ [17]. A series of Sr$_{1+x}$TiO$_{3+\delta}$ films was grown on SrTiO$_3$ substrates, where the Sr content ranged from Sr-rich to Sr-poor (-0.2 < x < 0.2). Here the Sr/Ti ratio was set by precisely shuttering the two molecular beams. ADF STEM images of the five Sr$_{1+x}$TiO$_{3+\delta}$ films in order of increasing x are shown in Fig. 1.3. Large variations in the film microstructure can be seen when comparing Sr-rich to Sr-poor SrTiO$_3$. In the former case, excess SrO is incorporated as Ruddlesden-Popper planar faults (Fig. 1.3(d, e)) and Sr-poor films have a more disordered structure due to missing Sr throughout the film (Fig. 1.3(a, b)). For the stoichiometric film (x=0), the film and the substrate are nearly indistinguishable (Fig. 1.3(c)), which clearly demonstrate the ability to grown high-quality films using MBE.
1.1.3 Physical Properties

Perovskite oxides show a rich variety of electronic phases including insulating, semiconducting, metallic, superconducting, ferromagnetic, antiferromagnetic, ferroelectric, and piezoelectric phases, as already mentioned in the introduction. For complex transition-metal oxides the diversity of phases is a result of the strong coupling between the spin, charge and orbital degrees of freedom. Competition and/or cooperation among the correlated-electron phases gives rise to phenomena such as high-temperature superconductivity and colossal magnetoresistance, which has driven the continued interest in complex oxides [18]. In this brief section, we will demonstrate the variety of states that are available in oxides using the prototypical correlated electron system La$_{1-x}$Ca$_x$MnO$_3$ (Fig. 1.6).

The parent compounds, LaMnO$_3$ and CaMnO$_3$, were studied in some detail by Wollan and Koehler [19] more than 50 years ago and were shown to be antiferromagnetic insulators in the ground state. Both end members as well as the compounds in the La$_{1-x}$Ca$_x$MnO$_3$ series are 3d-electron systems, in which the degeneracy of the 3d-electron levels is partially lifted due to the octahedral crystal field potential which is created by the surrounding O$^{2-}$ ions. This splitting into two levels of t$_{2g}$ ($d_{xy}$, $d_{xz}$, $d_{yz}$) and e$_g$ ($d_{z^2}$, $d_{x^2−y^2}$) symmetry is schematically shown in Fig. 1.4. In O$_h$ symmetry, the e$_g$ orbitals point toward the O$^{2−}$ ions while the t$_{2g}$ point in between, which results in a higher energy of the (antibonding) e$_g$ states. Exchange splitting further pushes the t$_{2g}$ and e$_g$ minority-spin levels above the majority-spin states, which causes LaMnO$_3$ with a Mn 3d$^4$ configuration to be dominated by the partially filled e$_g$ band ($t_{2g}^3 e_g^1$). The insulating behavior of LaMnO$_3$ is due to local deformations of the MnO$_6$ octahedron (Jahn-Teller effect) which further splits the doubly degenerate e$_g$ level.
The 3d electrons therefore become localized in this Mott insulating state below the Jahn-Teller distortion temperature 758K and spin-/orbital-ordering emerges at lower temperatures (Fig. 1.5) [20]. Below 140K the antiferromagnetic ordering in LaMnO$_3$ is A-type with ferromagnetic coupling in the orthorhombic basal plane ($ab$) and antiferromagnetic coupling along the c-axis, as shown in Fig. 1.5 [18].

Due to the almost identical ionic size of Ca and La a solid solution La$_{1-x}$Ca$_x$MnO$_3$ forms in the entire range of Ca concentration and the effect of doping on the physical properties of the system can be explored. By doping Ca$^{2+}$ into La$^{3+}$ sites the Mn 3d band filling (concentration of Mn$^{4+}$) can be controlled. As $x$ increases and Ca is doped into LaMnO$_3$ hole carriers are introduced into the Jahn-Teller split e$_g$ band, while low doping of La in CaMnO$_3$ induces electrons into the empty e$_g$ band. However, as shown in the La$_{1-x}$Ca$_x$MnO$_3$ phase diagram (Fig. 1.6), La$_{1-x}$Ca$_x$MnO$_3$ remains insulating for low (0.0<$x$<0.2) Ca doping levels even with ferromagnetic or canted ferromagnetic coupling, which is attributed to phase segregation effects in the low-hole doping regime [20].
Figure 1.5: Sketch of the $e_g$ orbital and spin ordering in LaMnO$_3$ (reproduced from [21]).

Similarly, insulating behavior is found for high ($x > 0.875$) Ca doping levels, possibly with canted-antiferromagnetic coupling.

For intermediate doping levels, $0.2 \leq x \leq 0.5$ a paramagnetic insulating-to-ferromagnetic metallic transition occurs upon cooling, with a maximum in the Curie temperature $T_c$ at a doping level of $x = 3/8$. This ferromagnetic metallic regime is typically viewed in the framework of double exchange where hopping of $e_g$ electrons between Mn$^{3+}$ and Mn$^{4+}$ through an oxygen ion produces ferromagnetic coupling [23, 24]. For higher doping levels, $x \geq 0.5$, charge carriers were believed to localize in a periodic arrangement (i.e. Mn$^{3+}$ and Mn$^{4+}$ are found on different crystal sites) below the charge-ordering temperature $T_{CO}$. However, doubts about the validity of the ionic picture of charge ordering has been supported by recent experimental results [25–28], which show much smaller differences in the Mn charge on different sites.

In addition to the wide variety of phases in correlated-electron systems, giant responses to external fields have been observed in the transition region from one phase to another [18]. One widely studied example is the colossal magnetoresistance (CMR) in manganites [29, 30] which has stimulated intense research
1.1.4 Electronic properties of interfaces

With the advances in heteroepitaxy of complex oxides it is now possible to fabricate interface between two oxides with atomic precision (see section 1.1.2). The
presence of such interfaces, however, can result in the degradation of bulk-like properties, which is detrimental for device applications. In manganite tunnel junctions, for example, the degradation of the ferromagnetic ordering at the interface is believed to limit the obtainable magnetoresistance [31], which will be discussed in more detail in Chapter 8. Carrier depletion has been found to limit the superconducting critical current at cuprate grain boundaries [32]. In these examples, atomic scale doping of the interface was found to significantly improve device performance.

Interfaces between two oxides can on the other hand also generate novel electronic phases that are not accessible in bulk, which presents a unique synthetic opportunity to create new artificial states. Interface ferromagnetism induced between two paramagnets [10], and conducting and even superconducting interfaces induced between two insulators [4, 5, 8] are recent examples. Here, we will briefly review the cases, starting with the LaTiO$_3$/SrTiO$_3$ interface.

SrTiO$_3$ is a band insulator with empty 3d bands. As La$^{3+}$ is substituted for Sr$^{2+}$ one electron is introduced per unit cell. LaTiO$_3$, however, is also an insulator (Mott insulator) due to strong electron correlations which opens up a Mott-Hubbard gap despite the high carrier concentration of one electron per site. Atomically-abrupt multilayers and interfaces between LaTiO$_3$ and SrTiO$_3$ were grown by PLD and ADF STEM images are shown in Fig. 1.7 [4, 33]. While the growth can be controlled down to the atomic level and La dopants can be restricted to a single unit cell thick layer, the charge distribution of the extra electron associated with LaTiO$_3$ spreads out beyond the chemical distribution of La (Fig. 1.7 (c)) in order to minimized the free energy of the electrons [4]. A length scale of 1 nm is found for the crossover from Ti$^{4+}$ to Ti$^{3+}$ at the single
interface. The broad charge distribution causes Ti to exist in a range of mixed valence states. The interface between the Mott insulator LaTiO$_3$ and the band insulator SrTiO$_3$ is therefore metallic.

An additional mechanism that can generate carriers but can also lead to atomic reconstruction is the formation of a polar discontinuity at an interface [34–36]. One interface that has recently been extensively studied is that between the two insulators LaAlO$_3$ and SrTiO$_3$. The polar discontinuity arises because in the [001] direction SrTiO$_3$ is comprised of a sequence of charge neutral [SrO] and [TiO$_2$] sheets, while in LaAlO$_3$ the [LaO]$^+$ and [AlO$_2$]$^-$ sheets are charged (in this simplified picture any covalency effects are ignored). For both possible
Figure 1.8: Polar catastrophe illustrated for the (a) n- and (b) p-type interfaces between LaAlO$_3$ and SrTiO$_3$. For the unreconstructed interfaces the alternating net charges ($\rho$) of the (001) planes in LaAlO$_3$ produce an electric field ($E$) which leads to an electric potential ($V$) that diverges with thickness. The polar catastrophe can be avoided if (c) at the n-type interface 1/2 electron per unit cell is added to the last Ti layer and (d) at the p-type interface 1/2 electron per unit cell is removed from the SrO plane in the form of oxygen vacancies. (reproduced from [33])

stacking sequences, AlO$_2$/LaO/TiO$_2$ or AlO$_2$/SrO/TiO$_2$, the polar discontinuity causes a large electric potential build-up across the LaAlO$_3$ layer which can be removed by moving carriers to or from the interface as shown in Fig. 1.8. The AlO$_2$/LaO/TiO$_2$ interface electronically reconstructs adding 1/2 electron per unit cell to the last Ti layer which is possible due to the mixed-valence character of Ti and a 2 dimensional electron gas (2DEG) is formed at that interface. The AlO$_2$/LaO/TiO$_2$ (n-type) interface is therefore metallic while the AlO$_2$/SrO/TiO$_2$ (p-type) is insulating [5]. However, the thickness of the LaAlO$_3$
layer has to exceed 3 unit cell before the n-type interface becomes conducting [37]. This is in agreement with the polar discontinuity picture where the LaAlO$_3$ layer is expected to reach a critical thickness before the electric potential build-up causes the interface to reconstruct. For the n-type LaVO$_3$/SrTiO$_3$ interface a similar critical thickness of 5 unit cells is found [38]. Recent work has now shown that the 2DEG generated at the n-type LaAlO$_3$/SrTiO$_3$ interface becomes superconducting below $\sim$200mK [8], promising an exciting future for novel phenomenon at oxide interfaces.

### 1.2 Thesis Outline

Starting with the primary techniques used in this work, Chapter 2 gives a brief overview of electron energy loss spectroscopy (EELS) performed in the scanning transmission electron microscope (STEM), focusing in particular on core-level EELS. The signal in this range is closely related to the local density of states partitioned by site, element and angular momentum, however, the effect of the core-hole created during the excitation process needs to be taken into account. In this light, trends in the near edge fine-structure of the Ti-L$_{2,3}$ and the O-K edges for perovskite oxides will be discussed and extensively used throughout this thesis.

In Chapter 3 self-focusing of an electron wavepacket by channeling in a crystal is experimentally demonstrated. This effect can be exploited to image atomically thin buried layers through the substrate by carefully tuning the thickness of the sample, so that the electron probe intensity is maximized when reaching the buried layer. In Chapter 4 this technique is successfully used to image thin SrTiO$_3$ layers grown on Si(001) in plan-view. Typically, such thin layers are
studied in cross-section in order to determine the interface structure between the substrate and the film. However, in the cross-section geometry one typically averages over 30-50 atoms in projection, which can hamper the direct determination of the interface structure if the layer islands and the sample thickness exceed the average size of a single island. This is, in fact, the case for the SrTiO$_3$/Si systems, were plan-view STEM reveals that the thin SrTiO$_3$ layer is not uniform but islands. This de-wetting is caused by a phase-separation instability, as predicted by density functional theory calculations.

In the remaining chapters of this thesis annular dark field STEM imaging and spatially resolved EELS are used to study defects and interfaces in all-oxide systems. In Chapter 5 a low-angle twist boundary in SrTiO$_3$ and its dislocation network is studied. Spatially resolved EELS on the cores of one set of dislocations running parallel to the beam direction suggests Sr-deficient cores. The second set of dislocations, orthogonal to the latter, is imaged by its strain field using low-angle annular dark field (LAADF) imaging. Further, the effect of small crystal tilts on the channeling of the electron beam is analyzed.

As discussed in Section 1.1.4 the presence of an interface between two oxides can greatly affect the properties of the heterostructure, resulting in the degradation of bulk-like properties or the generation of novel electronic phases. Interfaces in oxides have therefore attracted much attention. Here, three systems are discussed.

In LaVO$_3$/SrTiO$_3$ heterostructures (Chapter 6) the interface profiles are shown to be asymmetrical with diffuse lower and atomically-abrupt upper vanadate interfaces. As possible driving forces for the observed growth asymmetry the polar discontinuities at the two interfaces and preferential Sr surface segregation during the growth are discussed. The results suggest that segrega-
tion processes, which play an important role in the growth of traditional III-V semiconductor heterointerfaces, can also set an upper limit to the obtainable interface sharpness in perovskite oxide heterostructures.

For the abrupt interface between LaVO$_3$ and LaVO$_4$ following question is asked in Chapter 7. How is the transition from V 3d$^2$ LaVO$_3$ to V 3d$^0$ LaVO$_4$ made? The results show that although no bulk phase of LaVO$_x$ with V 3d$^1$ configuration exists, a nanometer-wide region of V 3d$^1$ is found at the LaVO$_3$/LaVO$_4$ interface. This is an example for electronic reconstruction at a complex oxide interface, which here leads to the stabilization of the non-bulk-like charge state, 3d$^1$ V.

Finally, in Chapter 8 the microstructure of La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayers is studied and related to changes in the physical properties of the system. Here spatially resolved EELS is performed on an aberration corrected microscope which allows two-dimensional chemical maps to be recorded at the atomic-scale. Spectrum imaging shows enhanced interdiffusion and extended defects that are introduced to accommodate for the cation offstoichiometry in the La$_{0.7}$Sr$_{0.3}$MnO$_3$ layers. When these extrinsic defects are eliminated by optimizing the interface structure and the stoichiometry of the La$_{0.7}$Sr$_{0.3}$MnO$_3$, the properties of the system can be improved beyond previous expectations.
CHAPTER 2
CORE-LEVEL ELECTRON ENERGY LOSS SPECTROSCOPY OF
PEROVSKITE OXIDES

2.1 Introduction

In electron energy-loss spectroscopy (EELS) the energy distribution of electrons which have interacted with a specimen and have undergone inelastic scattering is measured. If the incident electrons have an energy on the order of one hundred eV and are reflected from the surface of the specimen, the technique is referred to as high-resolution electron energy-loss spectroscopy (HREELS) which is an inherently surface sensitive technique due to the short electron mean free path of just a few monolayers. Using HREELS an energy resolution as low as a few meV is obtainable which allows vibrational modes as well as electronic excitations of surfaces to be measured [39].

In a transmission electron microscope (TEM) the energy of the incident electrons is typically in the range of 100-300 keV which significantly increases the mean free path and allows the electron to completely pass through specimens up to about a micron thick. The contribution to the energy-loss spectrum due to the surface is therefore strongly reduced and bulk properties of a material can be measured. If performed in a STEM, the electron probe can further be focused down to a narrow spot of 0.1 - 1 nm and EELS spectra can be obtained with high spatial resolution. In the following chapters, spatially resolved EELS is extensively used to determine the electronic properties of perovskite interfaces and of individual defects.

For thin specimens the most intense feature in a typical EELS spectrum is the
Figure 2.1: Using the example of SiO$_2$ the main features of an EELS spectrum are shown. Past the zero-loss peak the low loss region is dominated by valence electron excitations. Core-level ionization edges occur at higher energy losses (reproduced from [40]).

zero-loss peak at 0 eV (Fig. 2.1), which is due to elastic and quasi-elastic scattering of the incident electron by the atomic nuclei. Phonon scattering, which involves an energy transfer of the order of $k_B T$ ($\sim 25$ meV at T=300 K), is usually not resolvable from the incident beam in TEM-EELS and treated as "quasi-elastic".

Coulomb interactions between the incident electron and the atomic electrons causes inelastic scattering and gives rise to the features in the EELS spectrum past the zero-loss peak. In the low-loss region, i.e. up to an energy loss of $\sim 50$ eV, inelastic scattering by conduction or valence electrons dominates. A plasmon, which is the collective excitation of outer-shell electrons, is generated by the electric field of the incident electron. As the fast electron moves through a material the nearby electrons are displaced due to Coulomb repulsion creat-
ing a net positive potential behind the moving electron [39]. The work done in displacing the electron gas in the sample gives rise to the characteristic plasmon loss peak in the low-loss region of the EELS spectrum. Depending on the sample, interface plasmons (for samples with internal interface such as heterostructures) and surface plasmons, which dominate for thin specimens, can also be generated. In addition to the collective excitations, valence interband transitions and radiative losses such as Čerenkov radiation give rise to features in the low-loss region. A drawback for spatially resolved EELS is that the low-loss signal is not localized at the atomic level [41, 42]. For atomic resolution studies one therefore has to use core-loss edges.

Core-level ionization edges occur within a range of ~50 eV to several thousand eV and involve the excitation of electrons from a core orbital to unoccupied states above the Fermi level. In an EELS spectrum these ionization edges are superimposed on a background due to the high-energy tails of valence electron excitations and ionization edges of lower binding energy. This background contribution can easily be removed for quantitative analysis [41]. Since the core-electron binding energies are specific for each element and type of subshell, it is possible to obtain information about the elemental composition of a sample. Furthermore, the fine-structure of an ionization edge can give information on bonding, coordination and interatomic distances. The extended fine structure, starting at 40-50 eV above the edge onset, is due to scattering from neighboring atoms and reflects the short range order of a material. In this work, we will however focus on the energy loss near-edge structure (ELNES) within the first 30-40 eV of the edge onset.

As will be discussed in the following section, the observed intensity for a core-level excitation is, to a first approximation, proportional to the local den-
sity of states partitioned by site, element and angular momentum. The core hole which is created during the excitation process can, however, strongly modify the ELNES. Using the Ti-L\textsubscript{2,3} edges, we will demonstrate how near-edge fine structure “fingerprints” of various titanates can be used to track the Ti valence in a material. Finally, trends in the O-K ELNES for transition metal oxides will be discussed, since oxygen is the common element for all oxides and a good understanding of the O-K ELNES is therefore desirable.

In this introduction we have only provided a brief overview of conventional EELS. For details of the technique the reader is referred to an excellent book by R. F. Egerton [41] and a number of review articles [39, 43–45].

2.2 Theory of core-level electron energy loss spectroscopy

A quantum-mechanical theory of inelastic collisions of fast charged particles with atoms was first established by H. Bethe in 1930 [46]. In this treatment, which is based on the first Born approximation (lowest order in the interaction $V$ between the particle and the atom), the differential cross section for a fast but non-relativistic incident electron is given by

$$
\frac{d^2\sigma}{dE d\Omega} = \frac{m_e^2}{4\pi^2\hbar^2} \frac{k'}{k} \sum_{i,f} \left| \int e^{i\vec{q} \cdot \vec{r}} \Psi_f^*(\vec{r}_1, \ldots, \vec{r}_Z) V \Psi_i(\vec{r}_1, \ldots, \vec{r}_Z) d\vec{r}_1 \cdots d\vec{r}_Z d\vec{r} \right|^2 \delta(E-(E_f-E_i)),
$$

(2.1)

where $m_e$ is the electron mass, $\vec{k}_i$ and $\vec{k}_f$ are the initial and the final wavevectors of the incident electron and $\vec{q}$ is the scattering vector. The position of the incident electron relative to the center of the atom is $\vec{r}$ and the eigenfunctions $\Psi$ are given in coordinates of the bound electrons $\vec{r}_j$. 

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The interaction Hamiltonian is the Coulomb potential

\[ V = -\sum_{j=1}^{Z} \frac{e^2}{|\vec{r} - \vec{r}_j|} + \frac{Z_N e^2}{|\vec{r}|}, \]  

(2.2)

where \( Z_N e \) is the charge of the nucleus. The nuclear contribution to Eq. (2.1) is zero due to the orthogonality of the eigenfunctions. By first performing the integrating over \( \vec{r} \) using Bethe’s integral [46],

\[
\int \frac{e^{i\vec{q} \cdot \vec{r}}}{|\vec{r} - \vec{r}_j|} d\vec{r} = \frac{4\pi}{q^2} e^{i\vec{q} \cdot \vec{r}_j},
\]

(2.3)

the differential cross section can therefore be rewritten as

\[
\frac{d^2\sigma}{dE d\Omega} = \frac{4}{a_0^2 q^4} \frac{k'}{k} \sum_{i,f} |\rho_{f,i}|^2 \delta(E - E_f + E_i),
\]

(2.4)

where \( a_0 \) is the Bohr radius and \( \rho_{f,i} \) are the transition matrix elements given by

\[
\rho_{f,i} = \left\langle \Psi_f \left| \sum_{j=1}^{Z} e^{i\vec{q} \cdot \vec{r}_j} \right| \Psi_i \right\rangle = \int \Psi_f^* \sum_{j=1}^{Z} e^{i\vec{q} \cdot \vec{r}_j} \Psi_i \prod_{j=1}^{Z} d\vec{r}_j.
\]

(2.5)

For small momentum transfer, i.e. the scattering is restricted to very small angles, the exponential in the transition matrix can be expanded in a power series. The first non-zero term will be for dipole transitions and high order terms can be neglected if \( |\vec{q} \cdot \vec{r}| \ll 1 \). The differential cross section using the dipole approximation then simplifies to

\[
\frac{d^2\sigma}{dE d\Omega} = \frac{4\gamma^2}{a_0^2 q^4} \frac{k'}{k} \sum_{i,f} \left| \left\langle \Psi_f \left| \sum_{j=1}^{Z} (i\vec{q} \cdot \vec{r}_j) \right| \Psi_i \right\rangle \right|^2 \delta(E - E_f + E_i),
\]

(2.6)

where we have now included a relativistic correction factor \( \gamma \) to account for relativistic effects [47].

In the simplest model for core-level transitions only single-particle transitions are considered and many-body effect are ignored [48]. Consequently, the differential cross section for transitions from an initial core state \( |i\rangle \) to final state \( |f\rangle \) is

\[
\frac{d^2\sigma}{dE d\Omega} \propto \sum_{i,f} \left| \left\langle f \left| \vec{r} \right| i \right\rangle \right|^2 \delta(E - E_f + E_i).
\]

(2.7)
Here, we further assumed that the specimen is isotropic or polycrystalline, which allows us to average over all orientations [45, 49]. The dipole selection rule limits the transitions from a core state with orbital angular momentum $l$ to final states with angular momentum ($l \pm 1$). For core-level transitions the initial state is sufficiently localized that Eq. (2.7) can be recognized as the local density of states (LDOS), where the final states are projected onto a localized basis. In this picture, the differential cross section can therefore be factorized into atom-like matrix terms $M_l(E)$ and the local angular-momentum-resolved density of states $\rho_l(E)$ [50].

$$\frac{d^2\sigma}{dEd\Omega} \propto |M_{l+1}|^2 \rho_{l+1} + |M_{l-1}|^2 \rho_{l-1}, \quad (2.8)$$

where the matrix elements $M_{l\pm 1} = \langle f_{l\pm 1}|r|i_l \rangle$ vary slowly with energy, giving rise to the characteristic envelope of a core-level edge, while the near-edge fine structure is due to the density of states term [44, 45, 50]. Note, however, that for anisotropic materials, where the scattering vector has a definite direction and the averaging over all directions is not performed, the DOS may be insufficient to describe the ELNES and mixing of contributions from different orbital is possible [51].

The near-edge fine structure of a core-level EELS edge can therefore, to a first approximation, be interpreted as the local density of empty states above the Fermi level, partitioned by angular momentum, by element (since the energy is measured with respect to the unique binding energy of the core state) and by site (if the EELS measurement is performed with a localized probe in a STEM). However, many-body effects, multiple scattering and broadening of the LDOS due to the finite lifetime of the core-hole and the excited final state have to be taken into account to fully understand the features of a core-level edge.
2.3 \( L_{2,3} \) edges in 3d transition metal oxides

For \( L_{2,3} \) edges transitions from an initial 2p state to final states of both s- and d-character are allowed according to the dipole selection rule. The radial overlap of the initial 2p and the 3d states is, however, significantly larger than the overlap of the 2p and 4s states. Additionally, the density of states of the 4s band is considerably lower than that of the 3d band [43, 52]. For 3d transition metals the \( L_{2,3} \) edges are therefore dominated by 2p\( \rightarrow \)3d transitions.

In the single particle description, discussed in section 2.2, the \( L_{2,3} \) ELNES should be closely related to the LDOS of the unoccupied 3d states. However, comparison of the calculated d-projected-LDOS and \( L_{2,3} \) EELS spectra of transition metal oxides show poor agreement [52]. This discrepancy is due to the strong overlap of the wavefunctions of the 2p hole and the 3d electrons, which results in large multiplet effects due to Coulomb and exchange interactions (these interactions are large compared to the dispersion of the 3d bands) [53]. Since the 3d electrons are relatively tightly bound and the d bands are quite narrow, the \( L_{2,3} \) edges in transition metal oxides can successfully be simulated using an approach based on atomic physics multiplet theory where solid-state effects are introduced as a perturbation [54]. This approach is valid for systems where the intra-atomic interactions are larger than the hybridization effects. An extensive review of multiplet effects is given by de Groot [53].

For \( L_{2,3} \) edges all interactions are dominated by the spin-orbit interaction in the 2p shell, which gives rise to the well separated \( L_3 \) (2p\(^{3/2}\)\( \rightarrow \)3d) and \( L_2 \) (2p\(^{1/2}\)\( \rightarrow \)3d) edges. Since the final 3d states are very narrow bands, sharp lines are visible at the edge threshold which are also referred to as “white lines” after being first discovered in x-ray absorption spectroscopy recorded on photo-
graphic film [55]. Corresponding to the \((2j + 1)\) degeneracy of the initial core state, the statistical white line branching ratio (L\(_3\)-to-L\(_2\) intensity ratio) is 2:1. However, large variations from the statistical value are observed across the 3d transition row [52, 56, 57]. In SrTiO\(_3\), for example, the Ti-L\(_{2,3}\) edge (Fig. 2.2) shows an apparent reversal of the branching ratio, with a more intense L\(_2\) edge. This redistribution of intensity is due to multiplet effects and 3d spin-orbit coupling (for systems with partially filled 3d bands) [58]. A 2:1 ratio is only expected when the Coulomb and the exchange interactions of the 2p hole and the 3d electrons are small compared to the core-hole spin orbit interaction [59].

In multiplet calculations of the ELNES solid-state effects are introduced as a perturbation. The most prominent effect of the solid is the crystal field, which breaks the symmetry around the excited atom. The atomic spectrum (spherical symmetry), which is obtained from atomic multiplet calculations, therefore needs to be projected onto the appropriate symmetry group. For simple perovskite oxides the transition metal is octahedrally coordinated by 6 oxygen atoms, i.e. \(O_h\) symmetry, which splits the degenerate 3d final states into two levels of \(t_{2g}\) (\(d_{xy},\ d_{xz},\ d_{yz}\)) and \(e_g\) (\(d_{x^2−y^2},\ d_{z^2}\)) symmetry. In \(O_h\) symmetry, the \(e_g\) orbitals point to the ligands while the \(t_{2g}\) point in between, which results in stronger bonding of the \(e_g\) orbitals to the ligands and therefore a higher energy of the (antibonding) \(e_g\) states. Each of the two L\(_{2,3}\) edges are therefore split into the lower-lying \(t_{2g}\) and higher-lying \(e_g\) levels. De Groot et al. [60] have pointed out that the splitting within the L\(_3\) (and the L\(_2\) edges) are related to, but not equal to the crystal field splitting. Even for small crystal fields, an energy splitting immediately appears, because other final states which were not accessible in spherical symmetry are now mixed in.

Direct comparison of atomic multiplet calculations (projected in the appro-
appropriate crystal field) and the experimentally measured L\textsubscript{2,3} edges would only work if the material is completely ionic. Transition metal oxides, however, have partially covalent character, which results in modification of the near-edge fine structure. This effect of the non-negligible hybridization of the transition metal with the ligand atoms, oxygen in our case, can be taken into account in the multiplet calculations by reducing the effective Coulomb and exchange parameters (Slater integrals) from their atomic values [53, 61]. The intra-atomic interactions are thereby reduced due to solid-state effects.

The Ti-L\textsubscript{2,3} edges for various oxides and for Ti metal are shown in Fig. 2.2(a). For SrTiO\textsubscript{3} where the Ti atom is octahedrally coordinated, the combination of spin-orbit splitting and crystal field splitting gives rise to the expected 4 strong peaks and multiplet calculations of Ti\textsuperscript{4+}, i.e. 3d\textsuperscript{0}, in perfect O\textsubscript{h} symmetry shows good agreement with the experimental results [60]. A more complex multiplet structure is expected if the site-symmetry of the transition metal is reduced, e.g. from octahedral to tetragonal or if the occupancy of the 3d band in the ground state is increased from d\textsuperscript{0} resulting in a larger number of final states as in LaTiO\textsubscript{3} where the formal valence of Ti is 3+ (3d\textsuperscript{1} ground state configuration) [43, 62]. The transition metal L\textsubscript{2,3} ELNES is therefore sensitive to the valency of the transition metal ion and its coordination.

A useful concept in ELNES is that of coordination “fingerprints” where the general form of the ELNES is predominantly sensitive to the nearest neighbor coordination [43]. This is most likely to occur on cations with strong contractions of the valence electrons. It implies that a detailed understanding of the DOS of complex materials is not necessary in order to interpret the ELNES for a specific edge. The detailed shape of the multiplet can instead be used to determine the valence of a transition metal ion, which is demonstrated in Fig. 2.2(a)
where only small variations in the Ti-L_{2,3} edge fine-structure are visible for the tetravalent Ti in SrTiO_{3}, EuTiO_{3}, CaTiO_{3} and La_{2}Ti_{2}O_{7}. The small changes in the Ti-L_{2,3} edge fine-structure of these oxides could be due to changes in the local Ti site symmetry or due to variations in the covalency of the compounds [53, 60, 63]. In Fig. 2.2(b) fingerprints for Ti^{4+} and Ti^{3+} are shown. As the Ti valence (or the number of 3d electrons) decreases the Ti-L_{2,3} edges shift to lower energies which is caused by changes in the electrostatic energy at the Ti site and the fine-structure changes due to the presence of a larger number of final states. Shifts of the L_{2,3} edges to higher energies and changes in the fine-structure with
Additional fine-structure features are resolved if an electron monochromator is used which results in a reduction of the instrumental energy resolution from $\sim 0.6$ eV to $\sim 0.2$ eV.

Careful inspection of the Ti-L$_{2,3}$ edge for SrTiO$_3$ also shows that the L$_2$ edge is broader than the L$_3$ edge. This broadening is due to the presence of an additional decay channel (Coster-Kronig Auger decay process), which results in a shorter lifetime of the $p_{1/2}$ states [66]. The spectra shown in Fig. 2.2 were recorded with an energy resolution of 0.5-0.6 eV. However, in order to study intrinsic broadening effects the instrumental energy resolution has to be improved which is now possible by using electron monochromators. This improvement in resolution is demonstrated in Fig. 2.3 for the Ti-L$_{2,3}$ edges in SrTiO$_3$ and for Sc-L$_{2,3}$ in GdScO$_3$. Each of the main multiplet lines has its own characteristic broadening, which is due to an additional decay channel for the L$_2$ edge, as mentioned above, and solid-state broadening effects (vibrational and disper-
sional broadening) [60]. At an energy resolution of \( \sim 0.2 \) eV (as determined from
the FWHM of the zero loss peak) we also observe two additional pre-peaks,
which are indicated by arrows in Fig. 2.3(a) for the Ti-L\(_{2,3}\) edges. These small
leading peaks have been reproduced in multiplet calculations and are due to
multiplet effects [60]. Their position is controlled by the Coulomb and exchange
parameters [60] and can therefore give some information about the importance
of solid state effects in the material.

2.4 Trends in the O-K edges

The O-K ELNES is sensitive to the local electronic structure and in particular to
the chemical bond formed between the oxygens and the their neighbors. Start-
ing again with the dipole selection rule, transitions from the 1s core state to un-
occupied states of p symmetry are allowed and are closely related to the ELNES
of the O-K edge. For CuO it has been shown that up to \( \sim 15 \) eV above edge on-
set, the O-K edge is dominated by transitions to states of O 2p (not 3p) character
[67]. The O-K edge is therefore typically described by O 1s\( \rightarrow \)2p transitions. In
a pure ionic picture, however, O\(^2-\) has a 1s\(^2\)2s\(^2\)2p\(^6\) configuration and the 1s\( \rightarrow \)2p
channel should be closed. But transition metal oxides are not fully ionic, but
show a considerable covalent contribution. This covalency reduces the number
of filled states with O 2p character and the channel for 1s\( \rightarrow \)2p transitions opens
up. The strength of the O-K edge signal close to the edge threshold therefore
reflects the degree of covalency in the compound.

As discussed before, a core-hole is created during the excitation process that
can have significant effects on the ELNES. At the O-K edge, however, the O
1s core hole is generally well screened by the O 2p valence electrons [68], and
Figure 2.4: O-K edge EELS for SrTiO$_3$. The peaks in the spectrum are associated with O 2p orbitals hybridized with Ti 3d ($A_1$ and $A_2$), Sr 4d (B) and higher-energy metal states such as Sr 5p and Ti 4sp (C, D).

has only small effects on the spectral shape. The O-K ELNES can therefore be interpreted on the basis of partial DOS calculations. This is in contrast to the previously discussed transition metal L$_{2,3}$ edges, which are dominated by multiplet effects due to the strong correlations between the 2p core hole and the 3d electrons.

For 3d transition metal oxides it is generally accepted that the O-K threshold structure arises from covalent mixing of transition metal 3d and O 2p states, which introduces O p character in unoccupied states of predominantly transition metal character [65, 69–71]. Depending on the filling of the 3d bands and the local symmetry, the threshold structure may consist of one or several peaks which can be interpreted in terms of crystal field and exchange splitting [65, 70].

Fig. 2.5 shows a series of O-K edges for various oxides, which will be used to demonstrate some of the trends in the O-K ELNES of perovskite oxides. Starting with the well studied SrTiO$_3$ (separately shown in Fig. 2.4), the bottom of the conduction band (and the first 5 eV of the O-K edge) is dominated by the
empty Ti 3d states that are split into the $t_{2g}$ and $e_g$ subbands in the octahedral crystal field. The weak $\pi$ hybridization of the Ti-3d $t_{2g}$ with the O 2p orbitals results in the formation of a narrow band and a sharp peak $A_1$ at the edge onset. The band corresponding to the stronger $\sigma$ hybridization of Ti-3d $e_g$ with O 2p orbitals is broader and is visible in the O-K edge as a much smaller second peak $A_2$ [72]. Due to the strong dependence on hybridization effects, the O-K ELNES is sensitive to changes in the local transition metal geometry. This has been shown in both anatase and rutile, where the distortions of the octahedra allow cation-cation and anion-anion interactions, with the net result of similar band widths of the $t_{2g}$ and $e_g$ bands [72].

When comparing the O-K edge of SrTiO$_3$ with that of LaTiO$_3$ large changes in the ELNES are visible (Fig. 2.5). As La is substituted for Sr the Ti valence changes from 4+ to 3+, doping one electron per site into the empty Ti 3d band, i.e. 3d$^0$ to 3d$^1$ configuration. This decreases the number of unoccupied 3d states which is reflected in the O-K edge as a reduction in the intensity of the first peak. As another electron is added to the 3d band for LaVO$_3$ (3d$^2$) the first peak decrease further. Finally, in La$_2$Ti$_2$O$_7$ a strong first peak is observed again, in accordance with a Ti valence of 4+. These trends show that the first $\sim$5 eV beyond edge onset reflect the filling of the transition metal 3d bands and therefore the transition metal valence.

When comparing the O-K edges of SrTiO$_3$ and LaTiO$_3$ changes are not only found in the fine-structure at edge onset. Additionally, there is a large shift in the position of the second main peak. For SrTiO$_3$ this peak (peak B in Fig. 2.4) has been related to bands of Sr 4d states hybridized with O 2p. The O-K ELNES therefore not only contains information about the valency of the transition metal ion, but also about the A-site cation. As Sr is replaced by La in LaTiO$_3$ the sec-
Figure 2.5: Trends in the O-K edge for a series of perovskite oxides. The features in the first ~5 eV beyond edge onset reflect the filling of the transition metal 3d bands and therefore the transition metal valence. The second main peak is dominated by the A-site cation and shifts to lower energies as Sr is substituted by La (right dotted line).

The second peak shifts to lower energies reflecting now bands of mainly La 5d weight. This shift in the position of the second peak upon La for Sr substitution is shown in Fig. 2.5 for a series of compounds and demonstrates that the second peak is dominated by the A-site cation. Note, however, that the position of the second main peak cannot be directly correlated with the position of the A-site cation d bands due to the potential overlap with the Ti 3d-e_g band [73], for which a larger dispersion is expected due to the stronger σ interactions with the ligands as mentioned above. Compared to SrTiO_3 this overlap is larger in the case of
LaTiO$_3$, since the La 5d bands are shifted to lower energies. Finally, the third and forth main peaks in SrTiO$_3$ (peaks C and D in Fig. 2.4) are attributed to bands of higher-energy metal states such as Sr 5p and Ti 4sp, respectively [72].

In Fig. 2.6 a collection of O-K edges for various oxides is given and will serve as a reference. Similar arguments as in the case of the titanates can also be made to explain the differences in the O-K ELNES of the two manganites LaMnO$_3$ and SrMnO$_3$ shown in Fig. 2.6. Again, the second main peak (5-10 eV above edge onset), which is attributed to mainly Sr 4d/ La 5d bands, shifts to lower energies as Sr is replaced by La. The Mn valence change from 4+ to 3+ results in the reduction of the spectral weight at edge onset, in accordance with this region of the O-K edge being dominated by the Mn-3d bands. The observed O-K pre-peak structure is in agreement with previous results by Kurata et al. [65], who have extensively studied manganese oxides and interpreted the pre-peak structure with support of a molecular-orbital picture. For Mn$^{4+}$, a d$^3$ system, exchange splitting in addition to the crystal field splitting has to be taken into account [70]. The intense first O-K peak in SrMnO$_3$ can then be attributed to transitions to majority-spin e$_g$ and minority-spin t$_{2g}$ bands, which have similar energy positions due to the nearly identical values of exchange and crystal field splitting [65, 70]. The second weaker peak is due to transitions to minority e$_g$ states.

Compared to the O-K edge of SrTiO$_3$ the edge onset of SrMnO$_3$ shifts to lower energies, which suggests that the Mn-3d states are located below the Ti-3d bands in SrTiO$_3$. Similarly, it has previously been shown that an additional shoulder at the O-K edge onset of Ba$_3$Ti$_2$MnO$_9$ compared to BaTiO$_3$ can be attributed to transitions to Mn 3d states [61].

For NdNiO$_3$ compared to LaNiO$_3$, and for DyScO$_3$ compared to GdScO$_3$
Figure 2.6: O-K edge EELS of various perovskite oxides.
only small changes in the O-K ELNES are observed (Fig. 2.6), because the 3d configuration does not change (d\(^7\) for both nickelates and d\(^0\) for both scandates). The small change in the position of the second peak is due to the substitution of the A-site cation.

Finally, it should be pointed out that the presence of oxygen vacancies in the material will damp out the O-K ELNES [16, 74], which has to be taken into account when interpreting changes in the O-K fine-structure at perovskite oxide interfaces or around defects.

### 2.5 Conclusions

In this chapter we have presented a brief overview of core-level EELS as studied in a STEM, with particular emphasis on the information contained in the electron loss near-edge structure (ELNES). Following Bethe’s treatment of inelastic scattering it was shown that, to a first approximation, the ELNES can be interpreted as the local density of empty states above the Fermi level, partitioned by angular momentum, by element and by site. The effect of the core-hole that is created during the excitation process has to be taken into account, however, and can strongly modify the ELNES. This is in particular important for the transition metal L\(_{2,3}\) edges, which are dominated by atomic multiplet effects due to the strong correlations between the 2p core hole and the 3d electrons with, however, strong sensitivity to the symmetry of the surrounding crystal field. The L\(_{2,3}\) ELNES is therefore a powerful probe of the valency and the coordination of the transition metal ion.

For the O-K edge the 1s core hole has only small effects on the spectral shape and the ELNES can therefore be interpreted on the basis of partial DOS calcu-
lations. The O-K ELNES for transition metal oxides can be divided into three regions. The features within the first \(\sim 5\) eV above edge onset are dominated by transition metal 3d states (hybridized with O 2p) and are therefore sensitive to the valency of the transition metal ion. The peaks 5-10 eV above edge onset are attributed to A-site cation d bands and at higher energies the ELNES is dominated by bands of higher-energy metal states. The O-K ELNES therefore contains information about both the transition metal ion as well as the A-site cation and a good understanding of the fine structure is necessary in order to interpret changes at perovskite oxide interfaces or around defect, as will be discussed in the following chapters.

Core-level EELS in a STEM is a powerfully technique for studying interatomic bonding at high spatial resolution. With current advances in instrumentation smaller probe sizes (<1Å) and higher beam currents are achievable, which makes 2 dimensional chemical imaging of composition and bonding at the atomic scale possible [75] (Chapter 8).
CHAPTER 3
DIRECT MEASUREMENT OF ELECTRON CHANNELING IN A CRYSTAL USING SCANNING TRANSMISSION ELECTRON MICROSCOPY

Self-focusing of a high-energy electron wave packet by channeling along a zone axis in crystalline silicon is directly measured by scanning transmission electron microscopy using thin SrTiO$_3$ islands grown on Si(100) as test objects. As the electron probe propagates down a silicon atom column it is progressively focused onto the column. At 12 nm the channeling signal reaches its maximum and the probe is narrowed down to 0.5 Å, resulting in a fourfold increase in the ADF intensity of the SrTiO$_3$ islands for 12 nm thick samples. This enhancement in the visibility of the SrTiO$_3$ layers is lost if the sample is flipped up-side-down and the channeling occurs only after the probe scatters off the SrTiO$_3$ layer. The experimental results show good agreement with multislice simulations. We find that while electron channeling enhances the visibility of on-column atoms, it suppresses the contribution from off-column atoms. It can therefore be used as a filter to selectively image the atoms that are the most aligned with the atomic columns of the substrate.

3.1 Introduction

Annular dark field (ADF) imaging in a scanning transmission electron microscope (STEM) has proven to be a powerful technique for characterizing buried structures, such as thin films, isolated vacancies and defects in a crystal [4, 16, 76, 77]. Because the scattering contrast in high-angle annular dark field (HAADF) imaging is strongly dependent on the atomic number Z, it is often referred to as Z-contrast imaging [78, 79]. In zone-oriented crystals, how-
ever, electron channeling causes the probe wavefunction to be focused on the atomic columns and can strongly affect the ADF image contrast. Theoretical studies of electron channeling in crystals have shown that the probe intensity at the exit surface of a crystal can strongly be enhanced [80–82], thus leading to increased visibility of an adatom [81] or of dopant atoms [83]. Electron channeling through the substrate can also be used to image thin, buried layers, which will be shown in Chapter 4 for the case of SrTiO$_3$ grown on Si(100) [12].

While experimentally, electron channeling has successfully been exploited to image buried structures, the channeling signal has so far not been measured directly, but rather simulations have been used to predict its evolution with crystal thickness.

Here, we directly measure channeling enhancement in Si(100) by using the ultrathin, buried SrTiO$_3$ islands as test objects to track the evolution of the differential ADF signal and find good agreement with simulations.

In the following sections the experimental and theoretical methods are outlined, the results of multislice simulations of electron channeling in Si(100) are presented and compared with the experimental results. Finally, the visibility of a single Sr atom on Si(100) is shown to strongly depend on its position compared to the atomic columns of the substrate and the resulting implications for imaging buried layers are discussed.
3.2 Methods

3.2.1 Experimental Techniques

The SrTiO$_3$/Si sample was prepared by molecular-beam epitaxy using following growth sequence. First, a 1/2 monolayer (ML) Sr template [84–87] is deposited on a (2x1) reconstructed clean Si (001) surface at 700°C. After cooling to close to room temperature, 3 MLs of epitaxial SrO followed by 2 MLs of amorphous TiO$_2$ are deposited in high oxygen partial pressures and then heated up in vacuum until the TiO$_2$ reacts (a topotactic reaction) with the underlying SrO to form SrTiO$_3$ [85, 88]. Finally, the film was capped with amorphous Si (a-Si) to prevent damage of thin SrTiO$_3$ layer during the TEM sample preparation. In addition, a second sample was prepared as above, but with the Sr template increased to 1 ML.

Plan-view TEM samples were prepared by polishing the Si substrate at a 2° wedge angle followed by low-energy, low-angle ion milling of the back side (substrate side) in a Fischione Model 1010 ion mill. To minimize any water exposure, an alcohol based lubricant (Allied Blue Lube) was used during sample cutting and polishing. A sketch of the specimen wedge and its orientation relative to the direction of the incident beam is shown in Fig. 3.1. If the sample is oriented, so that the electron beam propagates through the crystalline Si (c-Si) layer before scattering off the SrTiO$_3$ layer (Fig. 3.1(a)), electron channeling can enhance the visibility of the thin, buried SrTiO$_3$ layer as will be shown in the following sections. If on the other hand the sample is flipped up-side-down, the a-Si layer constitutes the entrance surface and the electron beam reaches the SrTiO$_3$ layer before propagating through the c-Si substrate.
Figure 3.1: Sketch of two sample wedge orientations relative to the direction of the incident electron beam. (a) The sample is oriented so that the electron beam propagates through the crystalline Si (c-Si) layer first. The thickness of the c-Si substrate can be controlled by moving the beam along the sample wedge. (b) The sample is flipped up-side-down. Now, the electron beam scatters off the SrTiO$_3$ layer before propagating through the c-Si.

Annular dark field (ADF) imaging was performed in a 200 kV FEI Tecnai F20 SuperTWIN STEM with a convergence semi-angle of (9.5±0.5) mrad. By varying the inner detector angle from ~65 to ~22 mrad, the imaging conditions can be switch from high-angle annular dark field (HAADF) to low-angle annular dark field (LAADF).

### 3.2.2 Multislice Simulations

Electron channeling, convergent beam electron diffraction (CBED) and ADF-STEM imaging were simulated using the multislice method [79, 89–91], in which the specimen is divided into slices parallel to the optic axis of the microscope (typically a single slice corresponds to one atomic layer) separated by vacuum. For each slice the projected atomic potential and the transmission function, which ultimately produces a small phase shift in the electron wavefunction as it passes through the slice, are calculated. Starting with a probe wavefunction focused at a specific position on the specimen (in STEM), the wavefunction is
transmitted through the sample, slice by slice, with Fresnel diffraction between slices. After propagating though the entire thickness of the crystal the electron wavefunction is scattered onto the detector. The ADF intensity is computed by incoherently integrating the intensity of the diffracted wavefunction over the annular detector geometry. The multislice calculation is then repeated for each position of the incident focused electron probe.

Phonon scattering is modeled using the frozen-phonon approximation [92–94] which assumes that the electron/atom interaction occurs so rapidly that the atom appears stationary and is frozen in ”mid-vibration” [92]. Following the Einstein model for thermal vibrations the frequency of oscillation of each atom is taken to be constant and all the atomic displacements to be uncorrelated with each other. This results in a Gaussian probability distribution of the atomic displacements, where the standard deviation is the r.m.s. atomic displacement along each direction. Note that small displacements (i.e. sub-slice) along the optic axis (z-axis) are lost because only the projection of the atomic potentials along the z-axis is used to compute the slice transmission function. A single phonon configuration is then defined as the entire set of all random atomic displacements [92]. Finally, multislice calculations are performed for a series of phonon configurations and the results are averaged incoherently.

For comparison with experiment, the incident probe was modeled to match the conditions of a 200 kV FEI Tecnai F20 SuperTWIN STEM (spherical aberration coefficient ($C_s$) =1.2 mm, defocus ($\Delta f$) =450 Å, semi-angle of the probe forming aperture ($\alpha_{ap}$) =9.6 mrad). The evolution of the electron probe, initially placed on an atomic column at the center of a 32.58×32.58Å$^2$ (6×6 uc$^2$) Si supercell and then propagating through the sample, was calculated on a 1024×1024 pixel grid, allowing a maximum scattering angle of 263 mrad. Phonon scat-
tering was taken into account as described above averaging over 20 phonon configurations with an r.m.s. atomic displacement for silicon of about 0.078 Å [95].

After propagation through the sample the exit wavefunction is diffracted, forming a CBED pattern. To obtain high resolution CBED patterns (high sampling in reciprocal space), a large supercell of 108.6×108.6 Å² (20×20 uc²) was chosen. This results, for a 1024×1024 pixel² grid, in a maximum scattering angle of ∼79 mrad, which is rather small since it does not include any higher-order Laue zone (HOLZ) rings. For our purposes, however, all features (scattering angles <30 mrad) were sufficiently reproduced, which we have confirmed by performing one calculation for a 22 nm thick crystal on a 2048×2048 pixel² grid and increasing the maximum scattering angle to ∼158 mrad. Further care has to be taken when simulating CBED patterns with overlapping diffraction disks, as is the case for our imaging conditions. Phase information is included in the areas where diffraction disks overlap (interfere) and the contrast is therefore sensitive to the position of the electron probe if it is smaller than the unit cell size. Here, we have averaged CBED patterns for 36 positions in the unit cell. For each probe position the CBED patterns for 20 phonon configurations were averaged, i. e. the final CBED pattern at each thickness is an average over 720 individual CBED patterns. Finally, all simulated CBED patterns presented in this paper are displayed on the logarithmic scale to bring out the low-intensity features.

The channeling signal was determined by simulating the ADF intensity after each slice and taking the derivative with respect to the sample thickness. The atomic potentials and transmission functions were sampled on a 4096×4096 pixel² grid over 81.45×81.45 Å² (15×15 uc²), allowing a maximum scattering an-
gle of $\sim 420$ mrad and the signal was averaged over 20 phonon configurations. The ADF detector angles were set according to the experimental values, i.e. the inner detector angle is 65 mrad in HAADF and 22 mrad in LAADF and the outer angle is five times the inner angle.

The visibility of a single Sr atom on a Si crystal, discussed in section 3.3.3, was calculated using a $2048 \times 2048$ pixel$^2$ grid over $38.01 \times 38.01$ Å$^2$ ($7 \times 7$ uc$^2$), resulting in a maximum scattering angle of $\sim 450$ mrad.

For all presented multislice results, except for the CBED calculations, the total integrated intensity after propagation of the wavefunction through the entire sample thickness lost less than 1 % of the incident intensity.

3.3 Results and Discussion

3.3.1 Multislice Simulations of electron channeling in Si(100)

The channeling signal, which is the differential ADF intensity $dI/dz$ with $z$ being the sample thickness, for an electron probe propagating through a Si crystal along a $<001>$ axis is shown in Fig. 3.2. Within the first few nm $dI/dz$ computed on an atomic column increases rapidly, reaching its maximum at $\sim 10$ nm. The differential contribution to the ADF image intensity of an atom placed at the thickness of the channeling maximum is enhanced fourfold compared to that of an atom at the entrance surface of the crystal. The visibility of a thin, buried layer can therefore be maximized by selecting the thickness of the crystalline substrate to be close to the channeling maximum. Additionally, this effect is beneficial for ADF-STEM imaging of thin crystalline samples as it damps the
Figure 3.2: Channeling signal, $dl/dz$, determined by simulating the ADF intensity after each slice and taking the derivative with respect to the sample thickness $z$. The channeling signal was computed for two probe positions, the first one on the atomic column and the second one in-between atomic columns, propagating down Si$<001>$. Phonon scattering was taken into account using the frozen-phonon approximation and following the Einstein model for thermal vibrations, averaging over 20 phonon configurations.

The effect of channeling can easily be understood in the framework of the linear-imaging model for ADF-STEM, which is valid for large ADF detector angles and states that the differential contribution to the ADF signal of a layer of atoms at thickness $z$ is the convolution of the probe intensity $|\Psi(r_p, z)|^2$ and the object function $T(r, z)$ of that layer [96]. The final image intensity for a sample of thickness $t$ is given by

$$I(r_p) = \int_0^t |\Psi(r - r_p, z)|^2 \otimes T(r, z) dz, \quad (3.1)$$
where \( \otimes \) stands for convolution. So, the differential contribution to the ADF signal is

\[
\frac{dI}{dz}(r_p, z) = |\Psi(r - r_p, z)|^2 \otimes T(r, z).
\]

(3.2)

When defining \( T(r, z) \) as a set of delta functions at the atomic positions weighted by an atomic scattering strength, proportional to \( Z^{1.7} \) for ADF-STEM [79, 97], the channeling signal can be directly related to the probe intensity at thickness \( z \) via equ. 3.2 as \( dI/dz \propto |\Psi(0, z)|^2 \), i.e. it tracks the on-column probe intensity.

The evolution of the electron probe shape as it propagates through the Si crystal was simulated using multislice. Within the first 10 nm the incident 1.4 Å beam is focused down to 0.5 Å, as shown in Fig. 3.3. At the channeling maximum the probe intensity is therefore strongly enhanced [80–82], thus leading to increased visibility of an adatom [81] or a dopant atom at that thickness [83]. After passing the first channeling maximum, the probe then dechannels, spreading intensity away from the center atomic column, which causes the channeling signal to drop to a minimum at \( z \sim 30 \) nm. Some of the intensity then channels back to the atomic column, increasing \( dI/dz \) again. As the probe propagates further through the crystal, it continues to spread, resulting in an overall damping of the channeling signal.

Large changes in the channeling signal are observed as the probe is moved from an atomic column to in-between four atomic columns (Fig. 3.2). Here, the probe again channels over the first 10 nm after which it dechannels, resulting in a rapid decrease of \( dI/dz \), almost down to the initial value at the sample entrance surface. At that point some of the probe intensity has channeled onto the atomic columns, resulting in a local maximum in the on-column channeling signal. For direct comparison with experimental results, phonon scattering has to be taken into account, which results in damping of some channeling peaks and
3.3.2 Experimental results of electron channeling in Si(100)

The channeling signal at a specific thickness of the Si crystal can be directly determined from ADF images of the SrTiO$_3$/Si sample discussed in Chapter 4. The SrTiO$_3$ island in different areas of the wedge-shaped sample are used in this case
Figure 3.4: Plan-view imaging of thin SrTiO$_3$ layers grown on crystalline Si and capped with amorphous Si in increasingly thicker areas of the sample. The sample was oriented so that the electron probe first propagates through the Si substrate before reaching the SrTiO$_3$ layer. The thickness of the crystal was determined by matching the experimentally recorded convergent beam electron diffraction (CBED) patterns (left half of (a-f)) with simulated CBED patterns of crystalline Si at various thicknesses (right half of (a-f)). Low angle annular dark field imaging of the SrTiO$_3$ layer (g-l) reveal the change in the visibility of the SrTiO$_3$ islands with sample thickness.

as test objects to track the evolution of the channeling signal with the thickness of the Si substrate.

Figure 3.4 (g-l) shows plan-view LAADF STEM images of SrTiO$_3$ islands on Si(100) in successively thicker parts of the sample, i.e. the average height of the SrTiO$_3$ islands remains constant, but the thickness of the Si substrate increases. For all displayed ADF images the difference between the maximum and the minimum intensity is fixed in order to demonstrate the change in the visibility of the SrTiO$_3$ islands. The thickness of the Si substrate was determined for each image from CBED patterns recorded in the same area. By matching the experimental CBED patterns, shown in the left half of Fig. 3.4 (a-f), with simulated ones (right half of Fig. 3.4 (a-f)), the thickness of the Si substrate can be determined within $\pm 2$ uc.

The procedure of extracting the average increase in the ADF image intensity
due to the presence of the SrTiO$_3$ islands on the Si crystal from the experimental ADF images is demonstrated in Fig. 3.5. First, the background (Fig. 3.5(b)) of the original image (Fig. 3.5(a)) was removed using a singular value decomposition routine laid out by Voyles et al. [83]. The histogram of the resulting background subtracted image is then fitted by two Gaussians, one describing the regions of the sample that are covered by SrTiO$_3$ islands and the second describing the uncovered regions. The difference between the centers of the two Gaussians is the average increase of the ADF image intensity due to the presence of the SrTiO$_3$ on the Si substrate, and is therefore a measure of the channeling signal at the specific thickness of the Si crystal in that region.

After repeating the described procedure for each recorded image, the evolution of the ADF intensity of the SrTiO$_3$ islands, i.e. the channeling signal, with thickness can be determined. The open symbols in Fig. 3.6 show the experimentally determined channeling signal for the case that the crystalline substrate constitutes the entrance surface for the electron probe, which then channels in the crystal before reaching the SrTiO$_3$ layer. As expected from the multislice results (Fig. 3.2) the signal increases rapidly as the probe channels in the crystal, resulting in a fourfold increase in the differential ADF intensity from its initial value at zero thickness to its maximum at ~ 12 nm. It then damps out for larger thicknesses. When directly comparing with the prediction, it is important to point out that experimentally, the ADF intensity is averaged over all probe positions as the incident probe is scanned across the area. For comparison with the experiment the simulated channeling signal is therefore approximated by the average of the channeling signal from on the atomic column and from in-between four atomic columns (both shown in Fig. 3.2). This simulated channeling signal is shown in Fig. 3.6 as a solid line. Note that it is not the absolute intensities, but
Figure 3.5: Process of extracting the average ADF intensity of the SrTiO$_3$ islands from plan-view ADF images. (a) Original ADF image, (b) background of (a) determined using a singular value decomposition routine and (c) the background subtracted image. The average intensity from the SrTiO$_3$ islands is determined by fitting 2 Gaussians to the histogram of (c) and taking the difference between the centers of the two Gaussians.

only the qualitative behavior of the channeling signal that is compared. Within the uncertainty of the experiment the theory matches our data, which demonstrated that this is, to the best of our knowledge, the first time that the evolution of the electron channeling signal in a crystal has directly been measured.

As a reality check the sample was then flipped up-side-down, so that the electron probe enters through the 15 nm thick amorphous Si layer, then reaches the SrTiO$_3$ before propagating through the crystalline Si substrate. In this case, the probe does not undergo channeling before scattering off the SrTiO$_3$ layer. Since the thickness of the a-Si layer is fixed for all areas on the sample where
Figure 3.6: Comparison of the theoretical and the experimentally measured channeling signal in Si(100). For the experimental results the orientation of the sample is labeled by Substrate/STO, when the electron probe propagates through the substrate before scattering off the SrTiO$_3$ layer and by STO/Substrate when the sample is flipped up-side-down. The error bars reflect the uncertainty in the determination of the crystal thickness by matching the experimental CBED patterns with simulations and the standard deviation of the intensity of the SrTiO$_3$ islands determined for different parts of the ADF image by the procedure described in the text.

SrTiO$_3$ islands are observed, the contribution to the ADF intensity from the SrTiO$_3$ islands should remain constant. The solid symbols in Fig. 3.6 show the experimental results for this case and confirm this prediction. It is also worth pointing out that as the thickness of the crystalline Si approaches zero, the intensity of the SrTiO$_3$ islands is about the same for both sample orientations, as channeling in the Si substrate is eliminated.

The difference in the differential contribution to the ADF intensity for the two sample orientations demonstrates how the visibility of an SrTiO$_3$ island can be enhanced by exploiting electron channeling. Even for thicknesses larger than...
the optimum thickness, at which the channeling signal reaches its maximum, the intensity from the SrTiO$_3$ islands is enhanced when the sample is oriented so that the probe channels in the substrate first.

### 3.3.3 Electron channeling as a filter for on-column atoms

In the previous section we have experimentally shown that the visibility of a thin SrTiO$_3$ island can be enhanced by electron channeling in the substrate. As the probe channels onto the atomic column, its intensity and the differential contribution to the ADF signal increases. What happens, however, to an adatom that is displaced from the atomic column or is sitting in-between the atomic columns? In order to answer this question, we have calculated the visibility of a single Sr atom on Si(100) that is successively displaced from the atomic column. Here, the Sr visibility is defined as the fractional increase in the intensity due to the presence of the Sr atom.

Figure 3.7 shows the simulated Sr visibility as a Sr atom is displaced from the Si column along a $<100>_{Si}$ direction, as indicated in the sketch ($<110>_{Si}$ projection) in the top panel. Two cases were simulated, one where the thickness of the Si crystal corresponds to the channeling maximum (10 nm) and one for a thicker Si crystal (40 nm). In both cases, the Sr visibility strongly depends on the position of the Sr atom. As the Sr atom is displaced from the Si atomic column the visibility decreases and eventually drops below the detection limit. The point at which it falls below the detection limit depends not only on the sample thickness, but also on the imaging condition. For a 10 nm thick Si crystal a single Sr atom disappears after being displacement by only $\sim 0.5$ Å off the atomic column in HAADF imaging and by $\sim 0.7$ Å in LAADF. As the thickness of the Si
Figure 3.7: Visibility of a single Sr atom placed on a (a) 10 nm and (b) 40 nm thick Si substrate. As the Sr atom is moved off an atomic column the visibility decreases and drops below the detection limit when displaced by less than 1 Å. The visibility is calculated using a simple model (convolution of the incident probe intensity with the projected position of all the atoms in the sample weighted by $Z^{1.7}$) and multislice for two detector geometries corresponding to the LAADF and the HAADF signal. At a Si substrate thickness of 10 nm the Sr visibility for HAADF imaging closely follows the shape of the electron probe at that thickness.
crystal is increased to 40 nm the visibility decreases for all Sr positions and the Sr atoms remains visible only up to a displacement of $\sim 0.3 \text{ Å}$ in HAADF.

In order to understand the role of channeling, the multislice simulations are compared with a much simpler model, which does not take into account the evolution of the probe in the sample, but is simply the convolution of the incident probe intensity with the projected position of all the atoms in the sample weighted by $Z^{1.7}$. In this simple model, in which channeling is ignored, the visibility of an on-column Sr atom is reduced as expected. In addition we find that the visibility falls off more gradually with the displacement of the Sr atom. This suggests that electron channeling enhances the visibility of on-column atoms and filters out atoms that are sitting in-between the atomic columns. The rapid decrease in the visibility with Sr displacement can be understood by looking back at the evolution of the probe shape in the sample, discussed in section 3.3.1. As the probe channels in the crystal it narrows up and the intensity away from the atomic column decreases which in return results in a decrease in the visibility of an off-column atom. For HAADF imaging the Sr visibility therefore closely follows the probe shape after propagation through 10 nm of Si (Fig. 3.7(a)).

After displacing the Sr atom by 2.715 Å along a $\langle 100 \rangle_{\text{Si}}$ direction it is again aligned with a Si atomic column, however, now the Sr atom is much closer to the last Si atom in that column. In the simple model, only the projected positions of all the atoms in the sample matter and the visibility is, therefore, for both Sr positions the same. The multislice results show, however, that the reduction in the distance between the last Si atom in the column and the Sr adatom causes an increase in the Sr visibility. In LAADF imaging of a 10 nm thick Si crystal the visibility of a single Sr atom approaches 2.
Figure 3.8: Plan-view ADF-STEM images of a nominally 2.5 uc thick SrTiO$_3$ film grown on Si(100) using a 1 ML Sr template and capped with 15 nm of amorphous Si viewed along a substrate <001> zone axis. The sample is oriented so that (a) the Si substrate and (b) the a-Si layer constitutes the entrance surface. When electron channeling is used to enhance the visibility of the SrTiO$_3$ layer, the SrTiO$_3$ that is aligned with the Si columns is preferentially imaged and the apparent coverage decreases.

Finally, the multislice simulations also predict an increase in the visibility as the detector angles are changed from HAADF to LAADF imaging, which explains why we have used LAADF imaging conditions in the experimental setup.

The results discussed above imply that channeling in a crystal can be used not only to enhance the visibility of a thin layer, but also as a filter for imaging on-column atoms. If, on the other hand, one tries to also image off-column atoms, channeling is not desirable.

For the a-Si/SrTiO$_3$/Si sample one option is to flip the sample up-side-down, so that the a-Si constitutes the entrance surface. In that case, channeling occurs after the probe has scattered off the SrTiO$_3$ layer and, hence, all atoms in the thin SrTiO$_3$ layer are imaged. In Fig. 3.8 LAADF images of a a-Si/SrTiO$_3$/Si sample for the two orientations, Si substrate on top (Fig. 3.8(a)) and a-Si on top (Fig. 3.8(b)), are compared. For clarity, we have chosen a sample where
the thickness of the Sr template was increased to 1 ML, which results in a lower
density of SrTiO$_3$ islands when imaged using channeling in the Si substrate. Fig-
ure 3.8 clearly shows that the apparent coverage significantly increases, when
the sample is imaged in the “a-Si on the top” geometry. When imaged through
the Si substrate, the visibility of the SrTiO$_3$ islands is enhance due to channel-
ing in the crystal, but Sr atoms that are sitting off-column are filtered out. This
suggests that significant amount of SrTiO$_3$ is between the Si columns.

3.4 Summary and Conclusions

Electron channeling effects in the Si substrate have been exploited to image thin,
buried SrTiO$_3$ layers in plan-view ADF-STEM [12]. Here, we have used the
same sample to directly measured the electron channeling signal with thickness
of the Si substrate by tracking the increase in the ADF intensity due to the pres-
ence of thin SrTiO$_3$ islands. Multislice simulations of channeling in Si(100) agree
with the experimental results when phonon scattering is taken into account.

At a thickness of 12 nm the channeling signal reaches its maximum at which
the intensity of the SrTiO$_3$ islands has increased fourfold. This enhancement
in the visibility of the islands is lost when the sample is flipped up-side-down
and channeling occurs only after the electron probe has scattered off the SrTiO$_3$
layer. In that case, the contribution to the ADF intensity due to the presence of
a SrTiO$_3$ islands remains constant as the thickness of the substrate is increase by
moving to a thicker part of the wedge-shaped sample.

Using multislice we have further shown that while channeling results in an
increase in the visibility of on-column atoms, it suppresses the contrast from Sr
atoms sitting between the Si atomic columns. It therefore acts as a filter for on-
column atoms and should be avoided if atoms between the atomic columns of the substrate have to be imaged.
CHAPTER 4
IMAGING THE PHASE SEPARATION IN ATOMICALLY THIN, BURIED SrTiO$_3$ LAYERS BY ELECTRON CHANNELING

A phase-separation instability, resulting in the dewetting of thin SrTiO$_3$ films grown on Si(100) is shown by scanning transmission electron microscopy. Plan-view imaging of 1-nm thick, buried SrTiO$_3$ films was achieved by exploiting electron channeling through the substrate to focus the incident 0.2 nm beam down to a 0.04 nm diameter, revealing a non-uniform coverage by epitaxial SrTiO$_3$ islands and 2x1 Sr-covered regions. Density functional calculations, performed by C. S. Hellberg and K. E. Andersen (Naval Research Laboratory), predict the ground state is a coexistence of 2x1 Sr-reconstructed Si and Sr-deficient SrTiO$_3$, in correspondence with the observed islanding.

4.1 Introduction

Perovskite oxides exhibit a wide range of electronic and magnetic properties with potential device applications. In particular, SrTiO$_3$ can be used as a buffer layer for the growth of perovskite oxide heterostructures on Si. This opens up possibilities for the incorporation of novel materials into existing Si-based technology. The SrTiO$_3$/Si interface has been studied extensively [84, 85, 88, 98–105]; however, most experimental techniques rely on averaging, e.g., over large areas of the film or over the sample thickness. This also holds for electron microscopy which typically averages over 30-50 atoms in projection, depending on the sample thickness and the material. In this Chapter, we report the first experimental and theoretical evidence of phase separation in thin SrTiO$_3$ films on Si (100). Here, we minimize the effect of averaging by imaging thin (<1 nm) SrTiO$_3$ films
on Si in plan view, a result that is made possible by exploiting electron channeling in the silicon substrate to focus the incident 0.2 nm beam down to 0.05 nm, in much the same way as a fiber plate acts as an array of microlenses for light (see Chapter 3 for a detailed discussion on electron channeling in Si). This new imaging mode allows us to observe an apparent dewetting/islanding of the SrTiO$_3$ layer. At equilibrium, two phases coexist, corresponding to two different interface structures. This observation may be relevant for the successful growth of uniform SrTiO$_3$ films on Si, as it suggests that the growth has to be carried out away from equilibrium.

4.2 Methods

4.2.1 Sample Preparation

We used annular dark-field scanning transmission electron microscopy (ADF-STEM) to study the early stages of SrTiO$_3$ crystal growth on Si. The samples were prepared by molecular-beam epitaxy using two different growth sequences. Sequence I is identical to the one described in Chapter 3 (topotactic reaction on a 1/2 ML Sr template). To study the effect of the Sr template, two additional samples were prepared as in sequence I, but with the Sr template either omitted or increased to 1 ML. In the second growth sequence (sequence II), 1-2 MLs of Sr are initially deposited to promote the desorption of SiO$_2$ from Si [101]. A subsequent anneal at elevated temperatures (>700°C) results in a 1/2 ML Sr template on a clean (2x1) reconstructed Si (001) surface, similar to the surface obtained with sequence I. The SrTiO$_3$ growth is then started by co-
deposition of Sr and Ti at substrate temperatures of about 200-300°C and high oxygen partial pressures [84]. The low deposition temperature was chosen to study the behavior far from equilibrium. After the deposition of 2 epitaxial unit cells (uc) of SrTiO$_3$, the oxygen partial pressure is reduced and the substrate temperature increased to 500-700°C to improve the crystallinity of the film. Finally, all films were capped with amorphous Si (a-Si).

### 4.2.2 Experimental Techniques

For imaging we use high-angle ADF imaging, which is often referred to as Z-contrast imaging because the scattering contrast is strongly dependent on the atomic number [78, 79]. In zone-oriented crystals, however, channeling of the electron probe along the atomic columns strongly affects the ADF image contrast. Theoretical studies of electron channeling in crystals have shown that the probe intensity at the exit surface of a crystal can be strongly enhanced, [80, 81] thus leading to increased visibility of an adatom [81] or of dopant atoms [83]. Here we use this effect to enhance the visibility of the thin, buried SrTiO$_3$ layer by selecting the thickness of the crystalline substrate to be close to the channeling maximum, as discussed in detail in Chapter 3.

The ADF-STEM images were recorded on a monochromated 200 kV FEI Tecnai F20-ST STEM with a minimum probe size of $\sim$1.6 Å and a convergence semi-angle of (10±1) mrad. The inner detector angle for all cross-sectional images (Fig. 4.2(a-c), 4.7(b)) was 65 mrad. In order to increase signal to noise when imaging the SrTiO$_3$ films in plan-view the inner detector angle was reduced to 22 mrad. Further, to average out the scan noise in the high-magnification images
(except for Fig. 4.2(c), which was recorded in a radiation sensitive area), 5 to 12 successive images were cross-correlated and averaged. Finally, high-frequency noise was reduced by applying a smoothing filter to the images.

4.2.3 Density functional theory calculations

First-principle density-functional theory (DFT) calculations for thin SrTiO$_3$ films on Si(100) were performed by C. S. Hellberg and K. E. Andersen (Center for Computational Materials Science, Naval Research Laboratory). For each film thickness, the free energy $F = E_{\text{DFT}} - \mu_{S_i}N_{S_i} - \mu_{T_i}N_{T_i} - \mu_{O}N_{O} - \mu_{S_i}N_{S_i}$ was computed for a range of candidate structures [98, 103, 106–109]. Here $E_{\text{DFT}}$ is the DFT energy, $\mu_X$ is the chemical potential of element X, and $N_X$ is the number of element X atoms. The calculations used the generalized-gradient approximation (GGA) [110] and projector-augmented wave potentials as implemented in VASP [111–113].

4.3 Results and Discussion

4.3.1 ADF-STEM imaging of thin, buried SrTiO$_3$ films on Si(100)

Figure 4.1 shows plan view ADF-STEM images of the nominal 2.5 uc thin, buried SrTiO$_3$ film grown using sequence I. Here, the sample was oriented so
Figure 4.1: Plan-view ADF-STEM image of a nominally 2.5 uc thick SrTiO$_3$ film grown on Si(100) and capped with 15 nm of a-Si, showing the formation of SrTiO$_3$ islands and non-uniform coverage. The SrTiO$_3$ formed at elevated temperatures in a topotactic reaction between 3 ML of epitaxial SrO and 2 ML of amorphous TiO$_2$, which were sequentially deposited on a 1/2 ML Sr template on Si(100) (sequence I).

that the crystalline substrate constituted the entrance surface and the thickness was chosen so that the contrast of the SrTiO$_3$ film was maximized. Using this setup the atomically thin SrTiO$_3$ layer can be imaged through the Si substrate. Surprisingly, the film is not uniform, but forms islands, which are visible as bright patches on dark background. The inset in Fig. 4.1 shows perovskite lattice spacings in the bright region, confirming that these patches are due to SrTiO$_3$.

Figure 4.2 shows cross-sectional ADF-STEM images of the nominal 2.5 uc thick SrTiO$_3$ films formed in topotactic reactions (sequence I) for various initial Sr template thicknesses. The average island height determined by cross-sectional STEM (Fig. 4.2) is 3.5 uc. This is consistent with non-uniform SrTiO$_3$
coverage, since the amount of SrTiO$_3$ deposited would correspond to a uniform film 2.5 uc thick. Figure 4.2(a) shows the SrTiO$_3$ film grown on a 1/2 ML Sr template viewed along Si[110]. The SrTiO$_3$ appears to grow in registry on the Si substrate; however, the intensity of the SrTiO$_3$ layer varies parallel to the interface, where, in the darker regions of the film the Ti sublattice is not resolved. These contrast variations in the cross-sectional images are expected, since for typical TEM sample thicknesses of 15-30 nm several islands plus the regions in between the islands are imaged in projection. Surface roughness effects due to sample preparation cannot account for the intensity variations, since the Si substrate does not show similar bright and dim regions parallel to the interface.

We also studied the effect of the initial Sr template on the coverage by plan view STEM for samples with the Sr template either omitted or increased to 1 ML Sr. Plan-view STEM images of these samples are shown in Fig. 4.3 and reveal a significant increase in the coverage from (12±4)% to (40±4)% when the 1/2 ML Sr template is added. A further increase of the initial Sr deposition from 1/2 to 1 ML, however, does not lead to a further improvement of the SrTiO$_3$ coverage. This suggests that for thin SrTiO$_3$ films formed in a topotactic reaction on Si the coverage is optimized by a 1/2 ML Sr template.

An interesting feature of the thin SrTiO$_3$ films grown on the 1 ML Sr template and without the Sr template is shown in the cross-sectional images in Fig. 4.2(b) and 4.2(c), respectively. In addition to the regions of 3.5 uc high SrTiO$_3$, there are patches that show a single layer of reconstructed Sr with double periodicity, even for the film without the Sr template layer. The cross-sectional images suggest that this layer occurs only in regions where the SrTiO$_3$ islands have not formed and hence is not covered by additional epitaxial SrTiO$_3$. Since these reconstructed-Sr patches are found for samples with and without a
Figure 4.2: Cross-sectional ADF-STEM images of a nominally 2.5 uc thick SrTiO$_3$ film grown on Si(100) and capped with 15 nm of a-Si. The films formed in a topotactic reaction (sequence I) on (a) a 1/2 ML Sr template, (b) a 1 ML Sr layer, and (c) on clean Si, respectively. The average island thickness of 3.5 uc is consistent with non-uniform SrTiO$_3$ coverage. The SrTiO$_3$/Si interfaces in (b) and (c) show patches of a second stable phase: 1 ML of reconstructed Sr with double periodicity.

Sr seed layer, they cannot be attributed to the Sr template, but must be inherent to the SrTiO$_3$/Si system. For the sample with a 1/2 ML Sr template this reconstructed layer was not observed directly, which might be explained by the relatively larger island size and hence the reduced size of the uncovered regions. Additionally, this layer of reconstructed Sr is very radiation sensitive and damages quickly under the electron beam.
Figure 4.3: Plan-view ADF-STEM images of nominally 2.5 uc thick SrTiO$_3$ films grown on Si(100) and capped with 15 nm of a-Si. The films formed in a topotactic reaction (sequence I) on (a,d) clean Si, (b,e) a 1/2 ML Sr template, and (c,f) a 1 ML Sr layer, respectively. The coverage decreases significantly if the 1/2 ML Sr template is omitted. An increase of the initial Sr deposition from 1/2 to 1 ML, however, does not lead to a further improvement of the SrTiO$_3$ coverage.

4.3.2 Prediction of phase separation from first-principle density-functional theory (DFT) calculations

In order to understand the formation of islands observed in Fig. 4.1 and the reconstructed Sr layer, first-principle DFT calculations were performed for SrTiO$_3$ film thicknesses from 0 to 6 ML, where the number of MLs corresponds to the number of TiO$_2$ layers in the structure. In this notation, 0 ML is the reconstructed Sr layer to simulate the experimental Sr-templated starting surface.

The energies of the most stable structures are shown in Fig. 4.4. At 0 ML, the
Figure 4.4: Calculated total energies of SrTiO$_3$ on Si(100) as a function of film thickness. For ease of visualization, the energies have been shifted by a linear function. The Maxwell construction, which is invariant to linear shifts, shows the ground state phase separates into thick and thin regions, where the thin phase is the 2x1 Sr reconstructed Si surface. Each structure is labeled by its electric polarization $P$ in units of electrons per 1x1 cell. The thinner films favor a high Sr concentration in the first layer, resulting in polarization $P$ as large as $P=1$. As the films grow thicker, the Sr concentrations in the first layer and the corresponding polarizations are reduced. The DFT calculations were performed by C. S. Hellberg and K. E. Andersen (NRL).
surface is 2x1 Sr reconstructed Si. At 1 ML, the favored structure has 1 ML of Sr at the interface and 0.5 ML Sr vacancies on the surface, resulting in an overall insulating system with a positively charged lower interface and negatively charged upper free surface. The surface/interface charge densities are $\pm e/a^2$ yielding a film polarization of $P = e/a^2$, where $a$ is the in-plane cell length and $e$ is the electron charge. When SrTiO$_3$ is lattice-matched to [001] Si, the cubic perovskite structure is distorted, and the SrTiO$_3$ can become ferroelectric [114], but the polarization in the favored 1 ML film is much larger than the equilibrium polarization of bulk SrTiO$_3$ lattice matched to Si. Figure 4.4 shows that as the SrTiO$_3$ becomes thicker, the structures with lower polarizations become progressively more stable. The reduced polarization requires a reduced compensating charge at the interface. In the simulation this is accomplished by reducing the interfacial Sr concentration. Experimentally, other mechanisms such as increased Si-oxidation could also play a role, especially if the growth kinetics inhibited diffusion of Sr away from the interface.

According to the Maxwell construction, the energy of each structure alone ($>0$ ML) is higher than the energy of a mixture of two phases: one at 0 ML and the other with a thicker film. Thus, any uniform film 1 ML or thicker is unstable with respect to a phase separation into SrTiO$_3$ islands and 2x1 Sr patches. Note, that the DFT energies have been shifted by a linear function so the energies at 0 ML (i.e., the 2x1 Sr surface) and 6 ML are at zero. This leaves the Maxwell construction unchanged. The 2x1 0 ML structure, shown in the top panel of Fig. 4.4, exhibits the same periodicity as the reconstructed Sr layer observed experimentally in Fig. 4.2(b) and (c).
Figure 4.5: (a) Ti-L$_{2,3}$ and (b) O-K EELS of a nominally 2.5 uc thick SrTiO$_3$ film grown on Si(100) compared to bulk SrTiO$_3$, suggesting large changes in the electronic structure.

4.3.3 Ti-L$_{2,3}$ and O-K electron energy loss spectroscopy of thin SrTiO$_3$ films grown on Si

The electronic structure of these thin SrTiO$_3$ films was studied using spatially resolved EELS. To minimize beam damage, Ti-L and O-K EELS spectra were recorded by scanning the electron probe over a line parallel to the interface. In Fig. 4.5 the Ti-L$_{2,3}$ and O-K edges from the center of a nominally 2.5 uc thick SrTiO$_3$ film are compared to reference spectra from bulk SrTiO$_3$. Large changes are observed in the near-edge fine-structure. The Ti-L edge (Fig. 4.5(a)) is shifted to lower energies, suggesting a reduction in the Ti valence compared to 4+ in bulk SrTiO$_3$ and the crystal field splitting is reduced resulting in two instead of four resolved peaks. O-K EELS of the thin SrTiO$_3$ film (Fig. 4.5(a)) shows a strongly reduced first peak, which is consistent with the filling of the empty Ti 3d $t_{2g}$ states as the Ti valence decreases. Ti-L and O-K EELS of the thin films are
Figure 4.6: (a, b) Ti-L and (c) O-K EELS of a nominally 5 uc thick SrTiO$_3$ film grown on Si(100) using sequence II. The inset in (a) is an ADF image from a different region of the film, where the two lines indicate where the EELS spectra were recorded.

thus significantly different from bulk SrTiO$_3$ suggesting the presence of defects such as vacancies in the thin film. This trend is qualitatively captured in the DFT results by missing interface atoms in the lower-energy structures.

If thin SrTiO$_3$ films show significantly different electronic properties compared to bulk, how thick do we need to go to obtain bulk like properties? In order to answer this question, we have prepared a nominally 5 uc thick SrTiO$_3$ film on Si using growth sequence II. In Fig. 4.6 the Ti-L and O-K EELS from
close to the interface and from the center of the SrTiO$_3$ film are compared. As we move from the interface to the center of the SrTiO$_3$ layer the Ti-L edge shifts to higher energies and the intensity of the first peak of the O-K edge increases, which is indicative of the center being more bulk like. However, even at $\sim$1 nm from the interface bulk SrTiO$_3$ properties have not yet been reached.

### 4.3.4 Improved coverage by low temperature epitaxy

The theoretical and topotactic experimental results show that at equilibrium a thin SrTiO$_3$ film grown on Si(100) phase separates. It may be possible to obtain a more uniform film when working away from equilibrium. For that purpose we have grown thin films using sequence II, where the growth is carried out at the lowest possible temperatures for epitaxy, followed by an anneal at elevated temperatures and low oxygen partial pressure [84]. Figure 4.7 shows plan-view and cross-sectional ADF-STEM images of a 2 uc thin SrTiO$_3$ film grown using sequence II. The Ti-sublattice in the SrTiO$_3$ film is clearly visible in the cross-sectional image (Fig. 4.7(b)) suggesting higher quality films. The coverage as determined from the plan-view images (Fig. 4.7(a)) is improved, but not complete. Hence, both growth sequences, low temperature SrTiO$_3$ epitaxy and SrTiO$_3$ formation by a topotactic reaction, result in non-uniform coverage, suggesting that this is inherent to the system.
Figure 4.7: (a) Plan-view and (b) cross-sectional ADF-STEM images of a nominally 2 uc thick SrTiO$_3$ film grown on Si(100) and capped with a-Si. The film was grown on a 1/2 ML Sr seed layer by Sr and Ti co-deposition at low temperature and high oxygen partial pressure followed by an anneal at high temperature and low oxygen partial pressure (sequence II). The SrTiO$_3$ film grown under these conditions shows improved coverage, but it is still not complete.

4.4 Summary and Conclusions

Here we have imaged thin, buried SrTiO$_3$ layers at atomic resolution in plan-view ADF STEM by exploiting electron channeling effects in the Si substrate. We have shown that thin SrTiO$_3$ on Si(100) will phase separate, resulting in a non-uniform coverage and the formation of SrTiO$_3$ islands, in agreement with first-principles density functional calculations. Improved coverage was obtained by
choosing growth conditions away from equilibrium. Spatially resolved EELS of these thin films show a significantly different electronic structure from bulk SrTiO$_3$ suggesting the presence of defects in the thin film. As the thickness of the film is increased to 5 uc, the center of the film becomes more bulk like, but still shows a reduced Ti valence.

Typically, ADF-STEM imaging of heterostructures can be used to analyze the interface structures. If a layer islands, however, and the average island size is smaller than the thickness of the TEM cross-section, the direct determination of the interface structure from cross-sectional images is not likely to be reliable, since we are probably averaging over several islands in projection.
CHAPTER 5
SUBTLETIES IN ADF IMAGING AND SPATIALLY RESOLVED EELS: A CASE STUDY OF LOW-ANGLE TWIST BOUNDARIES IN SrTiO₃

A screw dislocation network at the low-angle SrTiO₃/Nb: SrTiO₃ twist grain boundary has been analyzed by annular dark field (ADF) imaging and spatially resolved electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM). The cores of one set of dislocations running parallel to the beam direction appear dark in the ADF STEM images. EELS on the dislocation core reveals a reduced Sr/Ti ratio compared to the bulk suggesting Sr-deficient cores. The second set of dislocations, orthogonal to the latter, is imaged by its strain field using low-angle annular dark field (LAADF) imaging. Multislice image simulations suggest channeling of the electron probe on the atomic columns for small tilts, <1°, where the Sr columns act as beam guides. Only for larger tilts is the channeling effect strongly reduced and the fringe contrast approaches the value predicted by a purely incoherent imaging model. Ti-L₂,₃ EELS across the dislocation core shows an asymmetry between the EELS and the ADF signal which cannot be explained by the geometry or beam broadening. This asymmetry might be explained by an effective nonlocal potential representing inelastic scattering in EELS.

5.1 Introduction

Perovskite oxides have attracted significant attention due to a wide range of potential device applications for example as a dielectric material in capacitors, ferroelectrics, varistors and heterostructure substrates. In particular, SrTiO₃ with a simple cubic perovskite structure serves as a model system for the group of per-
ovskite oxides and has been studied extensively. It is well accepted that internal interfaces, such as grain boundaries, play an important role in determining the bulk properties of these materials. Segregation of charged defects at the grain boundary induces a compensating space charge in the surrounding depletion region [115], which can determine the macroscopic electrical properties.

Annular dark field (ADF) imaging and electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) has proven to be a powerful tool for the characterization of oxide interfaces [4], grain boundaries [76, 116–118] and dislocation cores [77, 119, 120]. Tilt-boundaries in SrTiO$_3$ have been heavily studied as a model system of edge dislocations in complex oxides [74, 76, 116–118, 121]. The stoichiometry of various tilt-grain boundaries has been analyzed and O deficient [74, 117, 118], Ti rich [118] and stoichiometric [76] cores have been found. No experimental results of the Sr concentration in the dislocation core were reported. As the grain misorientation in tilt-boundaries is confined to in-plane rotations when viewed along [001], this system was well-suited to atomic-scale imaging and spectroscopy. The out-of-plane rotation for twist boundaries has meant fewer high-resolution studies of screw dislocations have been made. Recently, screw dislocation cores in SrTiO$_3$ have been studied by Zhang et al. [120]. The results show a decrease of the O/Ti ratio and a reduced valence at the Ti-sites in the core region, attributed to oxygen-deficient dislocation cores. No significant change of the Sr/Ti ratio in the core region was detected.

Here, we have studied the structure and the chemical composition of screw dislocations at a low-angle twist grain boundary between SrTiO$_3$ and 0.1% Nb doped SrTiO$_3$. Similar to Zhang et al.’s [120] study of twist boundaries in pure SrTiO$_3$, we also find a decrease in the Ti valence at the dislocation cores. How-
Figure 5.1: Images of dislocation cores at [001] twist boundaries in SrTiO$_3$. (a) HRTEM image from Zhang et al. [120] showing a closed core structure. (b) HAADF image from this work showing an open core with a missing Sr-column. (c) A commercially-processed bicrystal where the dislocation cores have grown to open voids or pipes. The trend suggests the dislocation structure is very sensitive to the growth and annealing conditions.

ever, we also find a significant decrease of the Sr/Ti ratio and ultimately an open pipe or void structure, which suggests the structure of the screw dislocations is sensitive to the growth and annealing conditions (Fig. 5.1).

5.2 Experimental Techniques

The SrTiO$_3$/Nb(0.1%):SrTiO$_3$ bicrystal with a $\sim 2^\circ$ [100] twist grain boundary was produced by sintering [122]. The composition of the materials was selected according to their later usage as partially conducting substrates of oxide electronic devices. The structure of the twist-grain boundary and its strain field are studied by ADF imaging in a 200kV FEI Tecnai F20 SuperTWIN (ST) STEM with a minimum probe size of 1.6 Å [123] and a convergence semi-angle of $(9\pm1)$ mrad. By varying the detector angle, high-angle annular dark field (HAADF) as
well as LAADF imaging can be performed. The inner detector angles are 35 and 17 mrad, respectively. The chemical and electronic structures are probed on an atomic scale using spatially resolved EELS. The EELS measurement presented here were performed on a VG HB-501 100kV dedicated STEM (∼ 10 mrad), which is equipped with a parallel electron energy loss spectrometer and on the 200 kV FEI Tecnai F20-ST with a GIF Tridiem. The energy resolution as measured from the FWHM of the zero loss peak was 0.5 eV and 0.6 eV, respectively.

5.3 Results and Discussion

5.3.1 Structure of the dislocation core from HAADF STEM

Fig. 5.2 shows the HAADF STEM image of the low-angle twist grain boundary along the [100] zone axis. The relative tilt of the two crystals with respect to each other leads to strain at the twist grain boundary which is partially relieved by the formation of <100> screw dislocations. Two of these dislocations are visible as dark spots in the HAADF STEM image (Fig. 5.2).

HAADF imaging is often referred to as Z-contrast imaging because the scattering contrast is strongly dependent on atomic number [78, 79]. This would suggest Sr deficiency in the dark dislocation core, however, the left side of the bicrystal also shows reduced contrast which is rather due to the tilt of the left crystal off of the (100) zone axis. ADF STEM images of crystals are also sensitive to crystal orientation [81]. Channeling of the probe on the atom column for crystals oriented on zone axis leads to contrast enhancement in the ADF STEM image. As the crystal is tilted off axis, the channeling effect reduced and the
Figure 5.2: The HAADF image of screw dislocations at the low-angle (∼2°) twist grain boundary between SrTiO$_3$ and Nb:SrTiO$_3$. The right side of the bicrystal is oriented on the (100) zone axis.

c Contrast diminishes.

Fig. 5.3 demonstrates the effect of channeling for a thicker part of the sample. First, the bicrystal is oriented so that the left side is on the (100) zone axis, hence, in channeling condition and it appears bright compared to the right side (Fig. 5.3(a)). As the sample is rotated about an axis normal to the grain boundary the contrast reverses and the right side, which is now in channeling condition, appears bright (Fig. 5.3(b)). Hence, the reduced contrast on the left side of the bicrystal in Fig. 5.2 is due to its tilt off of the channeling condition.

Similarly, atomic disorder in the dislocation core could lead to a reduced contrast by dechanneling off of the atomic column [93, 124, 125]. Hence, the interpretation of HAADF STEM images as Z-contrast images is only a first approximation, where channeling and strain effects are not taken into account.
Figure 5.3: HAADF images of the low-angle twist grain boundary showing contrast enhancement due to channeling of the electron probe in zone oriented SrTiO$_3$. (a) The much brighter left side of the bicrystal is oriented on the (100) zone axis, whereas the right side is tilted $\sim 2^\circ$ off of the channeling condition. (b) The contrast is reversed by tilting the bicrystal, so that the right side is on axis, hence in channeling condition.

Careful image simulations are required to draw conclusions about the structure of interfaces, grain boundaries and in particular dislocation cores from ADF images.

### 5.3.2 ADF image simulations of tilted SrTiO$_3$ crystals using multislice and the incoherent imaging model

Using image simulations, we have further analyzed the effect of channeling on the fringe contrast as the SrTiO$_3$ crystal is tilted off of the (100) zone axis. Successively, a 23.43×23.43×195.25 Å SrTiO$_3$ crystal is rotated about the [100] axis in 1 mrad steps and an ADF line scan parallel to the rotation axis is simulated.
using multislice. The thickness of the SrTiO$_3$ crystal used in the simulation was chosen according to the estimated sample thickness of 10-30 nm. The position of the probe (200 kV, $C_s = 1.2$ mm, 10 mrad aperture, 450 Å defocus) is adjusted after each rotation so that it scans through two of the topmost Sr atoms at $x = 5.9$ and 9.8 Å. For comparison, the ADF intensity is simulated using a pure incoherent imaging model, which is the convolution of the electron probe wavefunction and the atomic potential weighted by $Z^{1.7}$. Fig. 5.4(a) and (b) show gray-scale maps of the ADF intensity as the crystal is tilted off of the (100) zone axis simulated using multislice and the incoherent imaging model, respectively. Initially, at 0° tilt, the probe is scanned across the Sr and O columns, as indicated by the solid line in Fig. 5.5(a) and the ADF intensity is peaked on the Sr columns in both simulations. The pure O columns are not resolved owing to the low scattering amplitude of the much lighter O at high angles. As the tilt angle $\theta$ increases, Ti atoms at the exit surface shift perpendicular to the scan direction and eventually move into the plane with the top Sr atoms over which the STEM probe is scanned (Fig. 5.5(b)). Hence, as the crystal is tilted not only the Sr (and O) but also the Ti atoms contribute to the scattered intensity.

For a 195 Å thick SrTiO$_3$ crystal the Ti atoms at the exit surface reach the scan line at a tilt $\theta = 0.57^\circ$, which leads to additional intensity between the Sr atoms in the incoherent imaging model. The multislice simulation (Fig. 5.4(a)), however, shows that only at tilts larger than 1° do the Ti-O column contribute significantly to the scattered intensity. This suggests that the probe channels along the Sr column even at non-zero tilts. For small tilts the Sr column therefore guides the probe and prevents significant probe intensity from reaching the Ti sites which in turn leads to reduced scattering from the Ti atoms. This effect of channeling
Figure 5.4: Gray scale map of the ADF intensity parallel to the rotation axis as the 195 Å thick SrTiO$_3$ crystal is tilted, simulated using (a) multislice and (b) the incoherent imaging model, respectively. The Sr atoms are at $x=5.86$ and 9.76 Å, the Ti atoms are at 7.81 Å. At 0° tilt the probe (200 kV, $C_s=1.2$ mm, 10 mrad aperture and 450 Å defocus) scans across the Sr-O and the pure O columns.

on the beam propagation is also reflected in the Ti fringe contrast,

$$\frac{(I_{Ti} - I_{\text{min}})}{(I_{Ti} + I_{\text{min}})},$$

shown in Fig. 5.6(c), where $I_{\text{min}}$ is the minimum ADF intensity. According to the incoherent imaging model, the Ti fringe contrast reaches its first maximum at $\theta \sim 0.8^\circ$, however it is zero for tilts up to $\sim 1^\circ$ in the multislice simulation.

The maximum and minimum ADF intensity as a function of are shown in Fig. 5.6(a). In the coherent imaging model the maximum ADF intensity, $I_{\text{max}}$,
Figure 5.5: (a) Top view of SrTiO$_3$ at 0° tilt, where the solid line indicates the position of the electron beam as it is scanned across the Sr-O and the pure O columns. (b) Side view of a SrTiO$_3$ crystal tilted by $\theta$ about an axis parallel to the scan line. Ti atoms at the exit surface shift perpendicular to the scan direction and move into the plane with the top Sr atoms over which the STEM probe is scanned.

shows oscillatory behavior corresponding to $\Delta\theta$ at which the Sr atoms at the exit surface are shifted by 1 unit cell in the y-direction. In multislice, $I_{\text{max}}$ initially decreases as the tilt increase up to 1.2°. For larger tilts $I_{\text{max}}$ increases again, however, with an increasing background, $I_{\text{min}}$, which is due to dechanneling of the cation column and scattering off the Ti atoms.

Similar to $I_{\text{max}}$, the Sr fringe contrast in the coherent imaging model shows an oscillatory behavior with tilt angle, Fig. 5.6(b). The fringe contrast first decreases from its maximum at $\theta = 0^\circ$ to its minimum of $\sim 30\%$ at $\theta = 0.8^\circ$. As the crystal is tilted further, the Sr fringe contrast oscillates around $\sim 0.38$, i.e. $\sim 50\%$.
Figure 5.6: (a) Maximum and minimum ADF intensity, (b) normalized Sr fringe contrast calculated using equation (1) and (c) Ti fringe contrast as a 195 Å thick SrTiO$_3$ crystal is tilted by $\theta$, extracted from the results of the multislice simulation and the results according to the incoherent imaging model, respectively, shown in Fig. 5.4.
of its initial value.

For small tilts up to 4 mrad the fringe contrast reduces by less than 5 % in both, the incoherent model and the multislice simulation. This is fortunate for STEM imaging in that the specimen can typically be aligned within 1 mrad of the zone axis. The Sr fringe contrast then falls off more slowly in the multislice simulation due to channeling of the probe on the atomic column. For larger tilts, $\theta > 1.3^\circ$, where the channeling effect is strongly reduced, the Sr fringe contrast decreases to $\sim 0.4$, approaching the value of the incoherent imaging model.

5.3.3 Imaging the strain field at the twist boundary

Fig. 5.7 shows HAADF and LAADF images of the low-angle twist grain boundary, where the right side of the bicrystal is oriented on the (100) zone axis. In HAADF (Fig. 5.7(a)) the crystal in channeling condition (right side) appears bright, as expected, whereas the in LAADF (Fig. 5.7(b), (c)) the contrast between the two sides is reduced and reversed showing a slightly brighter left side. The contrast reversal in LAADF results from the collection of a significant portion of the low order diffraction discs, which reach the LAADF detector as the crystal is tilted off the zone axis.

Channeling in a crystal is not only affected by crystal orientation but also by the presence of strain fields, which cause distortions of the atomic sites [125]. In strained regions the scattering distribution changes and the total intensity collected on the ADF detector can differ depending on the collection angles. This gives rise to additional contrast [125] in ADF STEM images.

The strain field at the SrTiO$_3$/Nb:SrTiO$_3$ grain boundary is visible as additional contrast variations in both the HAADF (Fig. 5.7(a)) and the LAADF
Figure 5.7: Strain fields at the low-angle twist grain boundary between SrTiO$_3$ and Nb:SrTiO$_3$. (a) High-angle annular dark field (HAADF) is strongly affected by the orientation of the crystal. The right side of the bicrystal is oriented “on axis”, hence in channeling condition and appears much brighter. The strain field at the grain boundary causes minor contrast variations in HAADF. (b) In low-angle annular dark field (LAADF) imaging the strain field at the grain boundary can be detected through its distortion of adjacent atomic sites and subsequent dechanneling of the electron beam from the cation columns. (c) LAADF image of uniformly spaced dislocations at the grain boundary.

(Fig. 5.7(b), (c)) images.

Fig. 5.7(c) shows a low resolution LAADF image of the dislocation array where the strain field at the grain boundary is clearly visible. The average spacing between the individual dislocation cores is determined to be (11.7±0.4) nm. According to Franck’s formula this would suggest a twist angle of $\sim 1.9^\circ$, which is consistent with CBED measurements on both sides of the grain boundary. Due to the symmetry of the SrTiO$_3$ lattice the dislocations are arranged in a two dimensional network. Here, we image the strain field of one set of dislocations
Figure 5.8: (a) HAADF and (b, c) LAADF images of the SrTiO$_3$/Nb: SrTiO$_3$ low-angle twist grain boundary obtained from a thin part of the sample. The corresponding high magnification HAADF image is shown in Fig. 5.2.

running perpendicular to the beam direction. For the second set only the dislocation cores are visible, since their strain fields lead to displacements of the atoms in beam direction that reduce the effect of dechanneling from the atom columns.

The sample thickness, which varies in our case between 10 nm and 30 nm, may also affect the strain contrast in LAADF and HAADF images [125]. Fig. 5.8 shows HAADF and LAADF images of the same grain boundary in a thinner part of the specimen. As discussed above, we find contrast changes between the right and the left side of the bicrystal due to their orientation relative to the zone axis. The additional contrast at the grain boundary, however, is different compared to the results obtained in the thicker part of the sample. The HAADF images (Fig. 5.8(a) and the corresponding high magnification image Fig. 5.2) show increased intensity between the dislocation cores extending into the left side of the bicrystal, which in this case is tilted off axis. In the LAADF images
the difference between the thick and the thin part of the specimen is even more prominent. As shown in Fig. 5.8(b, c), the bright band at the grain boundary disappears in the thin region. This raises the question of whether there is only one set of dislocations in this part of the sample, running parallel to the beam direction. This would be possible if the region is thinner than the average spacing between dislocations, i.e. thinner than ~12 nm. The answer is not clear since the strain contrast in LAADF and HAADF imaging is thickness dependent. Extensive image simulations are required to determine the effect of strain in SrTiO$_3$ on ADF STEM images. Qualitatively, we expect a similar trend as in the case of Si which has been systematically studied by Yu et al. [125].

5.3.4 Composition of the dislocation core from EELS analysis

The chemistry of the dislocation core was measured on the atomic scale using Ti-L$_{2,3}$ (Fig. 5.9(a)) and O-K edge (Fig. 5.9(b)) EELS. An ADF STEM image was recorded to locate the dislocation core and to place the electron probe on its center. Each spectrum was acquired for 20s during which the drift was negligible. The Ti-L$_{2,3}$ edge on the dislocation core reveals a reduction of the Ti oxidation state from 4+ in bulk SrTiO$_3$ and a decrease of the crystal field splitting by $(0.4\pm0.1)$ eV, similar to the results by Zhang et al. [120] using the spatial difference technique. It has been shown that dislocations in SrTiO$_3$ are sensitive to beam damage, resulting in oxygen vacancies and a reduced Ti valence. In order to rule out beam damage in our case, we have acquired a series of 20 spectra (each for 6 s) on the same dislocation core. No changes on the Ti-L$_{2,3}$ and the O-K edge were observed. Additionally, we have studied dislocation cores
at various thicknesses of the sample. Changes of the Ti-L\textsubscript{2,3} and the O-K edges on the dislocation core due to electron beam induced damage were only observed in the thinnest region of the sample (<10 nm) at which oxygen is driven out of the sample and the Ti valence is strongly reduced. The following EELS measurements were performed in thicker parts of the sample which showed no effect of beam damage.

Significant changes on and off the dislocation core were also observed for the O-K near-edge structure (Fig. 5.9(b)) showing a strong reduction of the second peak. This is suggestive of either reduced Sr (as the 2nd peak is attributed to Sr 4d states), or increased oxygen vacancies surrounding the excited oxygen atom. Quantitative simulations would be needed to distinguish the two cases. Zhang et al. [120] reported an increase of the Ti/O ratio in screw dislocation cores. We also find a small increase in the Ti/O ratio in the dislocation core but no further systematic study has been done. To quantify the compositional changes of the dislocation core compared to bulk SrTiO\textsubscript{3} Sr-M\textsubscript{3} and Ti-L\textsubscript{2,3} EELS from four individual cores have been analyzed. We find an increase of the Ti/Sr ratio by (15±5) %, suggesting a Sr deficient core structure, in contrast to the samples studies by Zhang et al. [120] who found no significant change of the Ti/Sr ratio. The difference in the relative Sr concentration in the dislocation core is likely due to different preparation conditions of the two bicrystals. EELS measurements from ordered regions of the grain boundary between the dislocations cores show no significant changes of the Ti-L\textsubscript{2,3} and O-K fine structure, compared to the bulk, suggesting that chemical changes are limited to the dislocation core.
Figure 5.9: (a) Ti-L and (b) O-K EELS measured on and off a screw dislocation core at the SrTiO$_3$/Nb: SrTiO$_3$ low-angle twist boundary.

5.3.5 Asymmetry of the concentration of Ti$^{Core}$ across the dislocation core

Spatially resolved EELS measurements across the dislocation core were performed on the VG HB-501 STEM with a probe size of $\sim$ 2.0 Å. Fig. 5.10(a) shows an HAADF image of a dislocation core at the low-angle grain boundary, where
the left side of the bicrystal is oriented on the (100) zone axis. With the same imaging conditions used to obtain Fig. 5.10(a), we perform atom-by-atom EELS measurements. Specifically, the Ti-L$_{2,3}$ edge has been recorded, with an energy resolution of 0.5 eV. We obtained a scan across the dislocation core (Fig. 5.10(b)), showing near-edge structure changes of the Ti-L$_{2,3}$ edge close to the dislocation core. Using multiple curve resolution analysis, two reference spectra were extracted and used for a non-linear least-squares fit of the experimental data. The fit (solid line) shows good agreement with the experimental data. The two components, Ti$^{4+}$ and Ti$^{3+}_{\text{Core}}$ of reduced Ti valence, are shown at the bottom of Fig. 5.10(b). The Ti$^{3+}_{\text{Core}}$ spectrum shows a shift to a lower energy and a shape change that would suggest an increased fraction of Ti$^{3+}$. This decomposition of the Ti-L$_{2,3}$ spectra into two components relies on the ionic character of the material, it would fail for more covalent compounds [4].

The spatial distribution of Ti$^{3+}_{\text{Core}}$ relative to the position of the dislocation core, determined by the simultaneously recorded ADF signal, is shown in Fig. 5.11(a). The peak in the Ti$^{3+}_{\text{Core}}$ EELS signal is not where one would expect the dislocation core to be, given the ADF data. The experimental results were fitted with a Gaussian extended by a third and a fourth moment. There is an obvious asymmetry (negative third moment) in the profile across the dislocation which does not resemble the observed ADF signal. The amount of beam broadening in a crystal depends on its thickness and the crystal orientation, hence, the beam propagation in the two sides of the bicrystal is expected to differ. However, the asymmetry observed in the EELS signal cannot be explained by beam broadening since it would also affect the ADF signal and cause a similar asymmetry in ADF, which was not found. To determine the influence of the tilt on the EELS signal, we have rotated the bicrystal about the horizontal, so that the right side
Figure 5.10: (a) HAADF image of the screw dislocation at the SrTiO$_3$/Nb: SrTiO$_3$ low-angle twist boundary, where the left side is oriented on the (100) zone axis. The dots in (a) represent the probe positions for the spectra in (b). (b) Ti-L$_{2,3}$ EELS across the dislocation core fitted (solid lines) using the two reference spectra displayed at the bottom.
Figure 5.11: Concentration of Ti$^{\text{Core}}$, the Ti-L$_{2,3}$ fingerprint of the dislocation core, in the vicinity of the dislocation core where in (a) the left side and in (b) the right side of the bicrystal is oriented on the (100) zone axis. The solid lines are Gaussian fits extended by a third and a fourth moment.

is on the (100) zone axis. The resulting fraction of Ti$^{\text{Core}}$, as determined from a scan across a different dislocation core, is shown in Fig. 5.11(b). The profile now exhibits a small positive third moment, indicating the change in asymmetry.

Comparing the two profiles, we find that the maximum Ti$^{\text{Core}}$ concentration does not coincide with the position of the dislocation core. Instead, it is shifted
from the left (Fig. 5.11(a)) to the right (Fig. 5.11(b)) as the bicrystal is tilted from one channeling condition to the other. This can neither be explained by the geometry of the dislocation since we are only rotating about an axis normal to the interface nor by beam damage since in both cases the EELS scan across the dislocation core was performed from the left to the right. The asymmetry of the EELS signal was consistently observed for more than five dislocation cores in either crystal orientation.

This raises the important question about the ultimate resolution of core-level spectroscopy in the STEM. It has been shown that a significant EELS signal can be obtained from regions where the probe has negligible intensity due an effective nonlocal potential representing the inelastic scattering [126]. The change of asymmetry of the EELS signal with crystal orientation found here might suggest that this nonlocality is more prominent for zone-axis crystals. As the crystal is tilted off-axis the effective potential for inelastic scattering changes and might result in a more local EELS signal. This would explain the asymmetry of the Ti$^{\text{Core}}$ signal, which is larger on the side of the bicrystal that is oriented on zone axis.

5.4 Conclusions

Strain at the low-angle SrTiO$_3$/Nb:SiO$_2$ twist grain boundary is partially relieved by the formation of a network of screw dislocations at the boundary. The cores of one set of dislocations running parallel to the beam direction appear dark in the ADF STEM images. EELS on the dislocation core reveals a reduced Sr/Ti ratio compared to the bulk suggesting Sr deficient cores. The second set, orthogonal to the latter, is imaged by its strain field which leads to additional
contrast in LAADF imaging. In a thin part of the sample the additional contrast at the boundary is strongly reduced possibly due to only one set of dislocations being present in this region of the specimen.

Image simulations have been used to study the effect of channeling on the fringe contrast for a 20 nm thick tilted SrTiO$_3$ crystal. Multislice simulations suggest channeling of the electron probe on the atomic columns for small tilts, $\theta < 1^\circ$, in which the Sr columns act as beam guides. Only for larger tilts is the channeling effect strongly reduced and the fringe contrast approaches the value predicted by a purely incoherent imaging model.

Ti-L$_{2,3}$ EELS across the dislocation core shows an asymmetry between the EELS and the ADF signal which changes as the orientation of the bicrystal is varied. The maximum fraction of Ti$^{Core}$, which is the Ti-L$_{2,3}$ fingerprint of the core, is obtained on the zone axis oriented side of the bicrystal, ~ 1 apart from the position of the dislocation core. This asymmetry of the EELS signal can not be explained by the geometry of the dislocation or beam broadening; rather, it might demonstrate the nonlocal character of the effective inelastic scattering potential, which changes as the crystal is tilted off axis. This becomes critical when conclusions are to be drawn from spatially resolved EELS data.
CHAPTER 6
ASYMMETRIC INTERFACE PROFILES IN LaVO$_3$/SrTiO$_3$
HETEROSTRUCTURES GROWN BY PULSED LASER DEPOSITION

Surface segregation effects play an important role in the growth of traditional III-V semiconductor heterointerfaces. Here we show that segregation processes can also set an upper limit to the obtainable interface sharpness in perovskite oxide heterostructures. In particular, the structure of LaVO$_3$/SrTiO$_3$ superlattices was studied on the atomic scale by electron microscopy and spectroscopy. The vanadate layers exhibit a growth asymmetry, with diffuse lower and atomically-abrupt upper interfaces, caused by preferential Sr surface segregation. Switching the SrTiO$_3$ termination layer does not change the interface abruptness, which excludes the interfacial polar discontinuity as the driving force for the observed growth asymmetry.

6.1 Introduction

Perovskite oxides have received considerable attention due to the wide variety of ground states available in closely lattice-matched crystal structures and the potential for combining these properties in heterostructures at the atomic scale [1–3]. Advances in growth techniques, in particular molecular beam epitaxy and pulsed laser deposition (PLD), have allowed high quality materials with complex structures, such as quantum wells and superlattices to be fabricated, sometimes with atomic-layer precision [4, 15].

However, for most systems there are intrinsic limitations to the abruptness of an interface. Polar discontinuities that occur at many oxide heterointerfaces can drive electronic as well as atomic reconstruction at the interface [4, 36, 127]. For
traditional semiconductors, the perfection of heterostructures has been shown to be limited by surface segregation processes, which result in interfacial composition gradients [128]. Well studied examples include In surface segregation during the growth of GaAs on InAs [128, 129], Ga segregation in the AlAs/GaAs [128, 130] system and surface segregation of both substrate atoms for Si/GaAs and Si/GaP [131, 132]. Although oxide heterointerfaces may be less susceptible to these effects, since they are typically grown at much lower temperatures as compared to the thermodynamic (melting) temperatures of the constituents, at the atomic scale surface segregation may still arise.

In this Chapter, we present a study of the microscopic structure of LaVO$_3$/SrTiO$_3$ superlattices and heterostructures by scanning transmission electron microscopy (STEM) in combination with electron energy loss spectroscopy (EELS). Depending on the growth sequence, LaVO$_3$ on SrTiO$_3$ or SrTiO$_3$ on LaVO$_3$, we find that the interface is either diffuse or atomically abrupt. Switching the SrTiO$_3$ termination layer before the growth of the LaVO$_3$ layer does not result in a sharp lower interface. Our measurements suggest that Sr surface segregation effects set the upper limit to the interface abruptness of this system, at least under the growth conditions used in this study.

6.2 Methods

6.2.1 Sample preparation

LaVO$_3$/SrTiO$_3$ heterostructures were grown on TiO$_2$ terminated (001)-oriented SrTiO$_3$ substrates by PLD using single phase LaVO$_4$ polycrystalline and SrTiO$_3$
single crystal targets. The films were grown at a temperature of 550°C and an oxygen partial pressure of $10^{-6}$ Torr, which are optimal growth conditions for LaVO$_3$ in the layer-by-layer mode [133].

6.2.2 Experimental techniques

The interface structures of the LaVO$_3$/SrTiO$_3$ films are studied by annular dark field (ADF) imaging in a 200 kV FEI Tecnai F20-ST STEM with a minimum probe size of 1.6 Å [123] and a convergence semiangle of $(10 \pm 1)$ mrad. The chemical and electronic structures are probed on an atomic scale using spatially resolved EELS performed on the Tecnai F20-ST, which is equipped with a monochromator and a Gatan imaging filter (GIF) 865-ER. The energy resolution was $\sim 0.6$ eV as measured from the FWHM of the zero loss peak.

6.3 Results and discussion

6.3.1 ADF imaging of LaVO$_3$/LaVO$_4$ heterostructures and multilayers

Figure 6.1(a) shows an ADF-STEM image of a LaVO$_3$/SrTiO$_3$ superlattice, where the thickness of the vanadate layers was varied while that of the SrTiO$_3$ layers was kept constant. For all three vanadate layers, we find that the lower TiO$_2$/LaO/VO$_2$ interface is more diffuse compared to the atomically-abrupt VO$_2$/LaO/TiO$_2$ upper interface grown above it. The average r.m.s. interface
Figure 6.1: (a) ADF-STEM image of a LaVO$_3$/SrTiO$_3$ superlattice grown on TiO$_2$ terminated SrTiO$_3$ viewed along a $[001]$ zone axis. (b) Averaged ADF line profile across the LaVO$_3$ and SrTiO$_3$ layers of (a). The three LaVO$_3$ layers exhibit a growth asymmetry, with an atomically sharp upper and a more diffuse lower interface.

One possible explanation for the observed growth asymmetry is the presence of Sr surface segregation. In this scenario, it is assumed that, as the LaVO$_3$ is grown on atomically flat SrTiO$_3$, the total free energy of the system is reduced by a fraction of the Sr atoms of the last SrTiO$_3$ layer segregating to the surface. Subsequently, as the following LaVO$_3$ layers are grown, a fraction of the Sr atoms of the previous layer moves to the surface, thus causing the degradation of the interface abruptness. Since, in this model, it is energetically preferred for Sr to be on the surface, the growth of SrTiO$_3$ on LaVO$_3$ should result in an atom-
ically abrupt SrTiO$_3$/LaVO$_3$ interface.

A second point, that has to be taken into account, is the polar nature of perovskite oxides. While, in the [001] direction, SrTiO$_3$ is composed of charge neutral sheets of SrO and TiO$_2$, the alternating LaO and VO$_2$ layers in LaVO$_3$ are charged +1 and −1, respectively. Joining these two materials results in a polar interface which changes characteristics from n- to p-type as the SrTiO$_3$ termination layer is switched from TiO$_2$ to SrO. Polar interfaces have been shown to cause structural as well as electronic reconstruction [4, 36]. To exclude the effect of the polar discontinuity as a possible driving force for the here observed growth asymmetry, we have grown 3uc-thick LaVO$_3$ films on both TiO$_2$- and SrO-terminated SrTiO$_3$. In the latter case, the termination was switched by adding a single layer of SrVO$_3$ between the LaVO$_3$ and the SrTiO$_3$ substrate using a polycrystalline Sr$_2$V$_2$O$_7$ target. Finally, both films were capped with 15uc of SrTiO$_3$. Due to the deposition of a full unit cell of SrVO$_3$ to obtain the change in the termination layer, the top interface remains p-type VO$_2$/SrO/TiO$_2$ for both samples, while the bottom interface is switched from n- to p-type.

ADF-STEM images of the two structures are shown in Fig. 6.2. We find that in both cases, the upper interface is a factor of ~3 more abrupt than the lower interface, a trend that persists as the LaVO$_3$ layer thickness is increased to more than 20nm. This suggests that atomic reconstruction due to the polar interface is not the driving mechanism causing the observed growth asymmetry, since in that case the abruptness of the upper and the lower p-type interface of the sample grown on SrO-terminated SrTiO$_3$ should have been the same. The trend of a more diffuse lower interface remains as the thickness of the vanadate layer is increased. The change in the integrated intensity across the LaVO$_3$ layer is displayed in Fig. 6.2(c). Long tails at the bottom interfaces indicate that not only
Figure 6.2: ADF-STEM images of a 3uc thick LaVO$_3$ layer grown on (a) TiO$_2$- and (b) SrO-terminated SrTiO$_3$. In (b) the termination layer was switched by adding a single layer of SrVO$_3$ before the growth of the LaVO$_3$ layer. (c) Averaged ADF line profiles across the LaVO$_3$ layers of (a) and (b). In both cases, the lower interface is more diffuse than the upper interface suggesting that the interface polarity is not the driving force for the growth asymmetry.

surface segregation but also sub-surface diffusion is present. Note that due to differences in the sample thickness and probe shape, a quantitative comparison of the two profiles is not possible.

### 6.3.2 Spatially resolved electron energy loss spectroscopy across LVO$_3$/LaVO$_4$ interfaces

The chemical composition and the bonding were probed at the atomic scale using spatially resolved EELS. Ti-L$_{2,3}$, V-L$_{2,3}$ and La-M$_{4,5}$ edges were recorded simultaneously and the relative concentrations were determined by integrating the Ti (V, La) edges from edge onset to ~15eV (~16eV, ~12eV) above the edge onset. The respective fractions are shown in Fig. 6.3 for the VO$_2$/LaO/TiO$_2$
Figure 6.3: Fraction of Ti, V and La across the LaVO$_3$/SrTiO$_3$ interfaces. (a) LaVO$_3$ grown on TiO$_2$-terminated SrTiO$_3$, forming the VO$_2$/LaO/TiO$_2$ interface. (b) The SrTiO$_3$ termination layer was switched by adding a single layer of SrVO$_3$ before the growth of the LaVO$_3$ film, resulting in the VO$_2$/SrO/TiO$_2$ interface.

and the VO$_2$/SrO/TiO$_2$ interface of $\sim$20nm thick LaVO$_3$ films grown on TiO$_2$- and SrO-terminated SrTiO$_3$. Intriguingly, in the first case the La and the V concentration profiles are offset by $\sim$0.6 nm, which corresponds to $\sim$1.5 uc. In the ideal case of atomically sharp interfaces (Fig. 6.4(a)) the offset should only be 0.5 uc. However, if Sr surface segregation is included, as sketched in Fig. 6.4(c), La atoms move down by 1 uc, causing an increase in the offset between the La and V concentration to 1.5 uc. For the second interface, VO$_2$/SrO/TiO$_2$, La atoms also move down by 1 uc in the presence of Sr surface segregation (Fig. 6.4(d)), however, this places the onset of the La concentration only 0.5 uc below that of V. Hence, the large offset of the La and the V concentration at the VO$_2$/LaO/TiO$_2$ interface is consistent with, and expected from, the model of Sr surface segregation.

Figure 6.5 shows concentration profiles across the first LaVO$_3$ layer of the LaVO$_3$/SrTiO$_3$ superlattice from Fig. 6.1. Here, the concentrations were normal-
Figure 6.4: Illustration of the effect of Sr surface segregation on the LaVO$_3$/SrTiO$_3$ heterostructure. (a), (b) The ideal interface structures for LaVO$_3$ grown on TiO$_2$- and SrO-terminated SrTiO$_3$, respectively. If Sr surface segregation is included, a fraction of the La atoms in the first vanadate layer moves down by 1uc, resulting in an onset of the La concentration (c) 1.5 uc and (d) 0.5 uc below that of V in the two respective cases. The arrows in (c) and (d) indicate the La (red) and V (blue) concentration in each layer.

The physical origin for the segregation process is not clear at this point. While the difference in ionic radii of La$^{3+}$ and Sr$^{2+}$ could drive Sr$^{2+}$ (as the bigger ion) to the surface, bonding effects are also believed to contribute since a similar segregation effect was not observed in LaTiO$_3$/SrTiO$_3$ superlattices [4]. The cation interdiffusion at the lower LaVO$_3$/SrTiO$_3$ interface may also be assisted by the formation of transient oxygen vacancies during the SrTiO$_3$ growth. Our choice of the oxygen partial pressure was limited, by the stability of the LaVO$_3$, to $10^{-6}$ Torr, which is lower than the optimum condition of SrTiO$_3$. 

Figure 6.4: Illustration of the effect of Sr surface segregation on the LaVO$_3$/SrTiO$_3$ heterostructure. (a), (b) The ideal interface structures for LaVO$_3$ grown on TiO$_2$- and SrO-terminated SrTiO$_3$, respectively. If Sr surface segregation is included, a fraction of the La atoms in the first vanadate layer moves down by 1uc, resulting in an onset of the La concentration (c) 1.5 uc and (d) 0.5 uc below that of V in the two respective cases. The arrows in (c) and (d) indicate the La (red) and V (blue) concentration in each layer.
Figure 6.5: (a) ADF-STEM image of the first vanadate layer in the LaVO$_3$/SrTiO$_3$ superlattice show in Fig. 6.1. The growth direction is from left to right. The dotted line in (a) represents the path of the probe for the concentration profiles in (b). (b) La and V concentration across the vanadate layer normalized to the total concentration of the layer. (c) The V and the inverse Ti concentration profiles almost track each other, indicating that the observed growth asymmetry is dominated by A-site cation intermixing.

at which the LaTiO$_3$/SrTiO$_3$ heterostructure from Ref. [4] was prepared. For LaTiO$_3$/SrTiO$_3$ superlattices grown at a reduced oxygen partial pressure of 10$^{-6}$ Torr the higher vacancy concentration causes cation intermixing at both the upper and the lower interfaces.

6.4 Summary and conclusions

In conclusion, we have shown that surface segregation effects can limit the interface abruptness in perovskite oxide heterostructures. For LaVO$_3$ grown in the layer-by-layer mode on SrTiO$_3$, Sr segregates to the surface causing cation
interdiffusion at that interface. By contrast, when SrTiO$_3$ is grown on LaVO$_3$, the interface becomes atomically sharp. The growth asymmetry remains as the polar LaVO$_3$/SrTiO$_3$ interface is switched from n- to p-type.
Electrons at interfaces, driven to minimize their free energy, are distributed differently than in bulk. This can be dramatic at interfaces involving heterovalent compounds. Here we profile an abrupt interface between V $3d^2$ LaVO$_3$ and V $3d^0$ LaVO$_4$ using electron energy loss spectroscopy. Although no bulk phase of LaVO$_3$ with V $3d^1$ configuration exists, we find a nanometer-wide region of V $3d^1$ at the LaVO$_3$/LaVO$_4$ interface, rather than a mixture of V $3d^0$ and V $3d^2$. The two-dimensional sheet of $3d^1$ electrons is a prototypical electronic reconstruction at an interface between competing ground states.

### 7.1 Introduction

Recent advances in oxide thin film growth and probe techniques have revealed a host of important considerations for the electronic structure at interfaces. For example, carrier depletion has been found to limit the superconducting critical current at cuprate grain boundaries [32]. Reduced surface magnetism limits the magnetoresistance of manganite tunnel junctions [31]. In these examples, atomic scale doping of the interface was found to significantly improve device performance. The role of this doping is to compensate for deviations of the surface electronic structure from the bulk, which can often occur in response to the electrostatic boundary conditions at the interface [36]. These deviations can be large in multivalent transition metal oxides, for which significant charge shifts are energetically accessible.

In addition to being a mechanism for degrading bulk-like properties in de-
vice geometries, electronic interface reconstructions also present a unique synthetic opportunity to create new artificial states between two materials. Recent examples include interface ferromagnetism induced between two paramagnets [10], and conducting interfaces induced between two insulators [4, 5]. These phenomena have stimulated theoretical efforts to examine interface phases created by charge transfer in artificial structures [127, 134]. The examples of interface phases given above utilize valence states that are accessible in bulk form. Here we demonstrate experimentally that interface reconstructions can also be used to induce and stabilize non-bulk-like valence states via a similar mechanism.

The multivalent LaVO$_x$ shows a variety of electronic and magnetic properties as the vanadium valence changes from 3+ to 5+ [135–138]. LaV$^{3+}$O$_3$, with a 3d$^2$ shell configuration, is a Mott insulator, whereas LaV$^{5+}$O$_4$ is a band insulator with a 3d$^0$ configuration. Intriguingly, bulk LaVO$_x$ lacks a structural phase corresponding to V$^{4+}$ [139]. However, at the interface between LaV$^{3+}$O$_3$ and LaV$^{5+}$O$_5$, continuity of the charge distribution implies that the vanadium valence should transition through 4+, at least in an average sense. Microscopically, the question is whether this is achieved through a mixture of the ground state 3d$^0$ and 3d$^2$ configurations, likely to be favored by a Maxwell construction from the bulk phases, or whether a local region of 3d$^1$ configured vanadium ions can be stabilized by the interface.

In this Chapter, we present a study of the microscopic electronic structure of LaVO$_x$ films by spatially resolved electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM). Vanadium L edge fingerprints for V$^{3+}$, V$^{4+}$ and V$^{5+}$ were established from bulk reference samples and used for the characterization of the vanadate films and the interface be-
tween $\text{LaV}^{3+}\text{O}_3$ and $\text{LaV}^{5+}\text{O}_4$. We find that $\text{LaVO}_3$ grows epitaxially on the SrTiO$_3$ substrate, resulting in atomically flat surface regions, whereas $\text{LaVO}_4$ nucleates on a thin $\text{LaVO}_3$ layer and forms polycrystalline 3D islands. At the $\text{LaV}^{3+}\text{O}_3/\text{LaV}^{5+}\text{O}_4$ interface our EELS measurements reveal a two-dimensional layer of $3d^1$-configured $V^{4+}$ has been stabilized, thus achieving an interface charge configuration that was not accessible in bulk $\text{LaVO}_x$.

7.2 Methods

7.2.1 Sample Preparation

$\text{LaVO}_x$ films were grown on TiO$_2$ terminated (001)-oriented SrTiO$_3$ substrates by pulsed laser deposition (PLD) using single-phase LaVO$_4$ polycrystalline targets. The $\text{LaVO}_x$ films studied here were grown at $T_g=800^\circ\text{C}$ and $P_{\text{O}_2}$ of $10^{-5}-10^{-4}$ Torr, conditions for which $\text{LaVO}_3$ and $\text{LaVO}_4$ are stabilized simultaneously, resulting in mixed phase growth [133].

7.2.2 Experimental Techniques

The microstructures of the $\text{LaVO}_x$ films are studied by annular dark field (ADF) imaging in a 200kV FEI Tecnai F20-ST STEM with a minimum probe size of 1.6 Å [123] and a convergence semi-angle of (91)mrad. The chemical and electronic structures are probed on an atomic scale using spatially resolved EELS, performed on both a vacuum generator (VG) HB-501 100kV dedicated STEM (10mrad), which is equipped with a parallel electron energy loss spectrometer,
and on the Tecnai F20-ST fitted with a monochromator and a Gatan imaging filter (GIF) 865-ER. The energy resolution, as measured from the FWHM of the zero loss peak, was 0.5eV and 0.6eV in these two respective cases.

7.3 Results and Discussion

7.3.1 V-L and O-K electron energy loss spectroscopy of vanadates

Figure 7.1 shows V-L$_{2,3}$ and O-K EELS spectra of bulk LaVO$_3$, SrVO$_3$ and LaVO$_4$. The first two main peaks of the spectra are the V-L$_3$ and L$_2$ edges. At higher energies the peaks are dominated by the O-K edge fine structure, however, extraction of the O-K edge is hampered by the proximity of the V-L$_{2,3}$ edge. Large changes of the O-K and the V-L$_{2,3}$ edge fine structure are observed, in which the changes of the V-L$_{2,3}$ edge peak position are dominated by the change of the vanadium valence from 3+ to 4+ to 5+ [140, 141]. With increasing vanadium valence, the V-L$_{2,3}$ peak position shifts by 0.9eV ($V^{4+}$) and 1.7eV ($V^{5+}$) towards higher energies. This spectral signature can be used to determine the vanadium valence in materials with predominantly ionic character, as the V-L$_{2,3}$ edge can be reasonably described by a superposition of the spectra corresponding to the different valence states [4, 142].
Figure 7.1: V-L\textsubscript{2,3} and O-K electron energy loss spectra taken from bulk LaVO\textsubscript{3}, SrVO\textsubscript{3} and LaVO\textsubscript{4}. The dashed lines indicate the L\textsubscript{3} peak position, which shifts to higher energies as the vanadium valence increases. The shaded region of the spectra is due to V-L\textsubscript{2,3} excitations only, whereas at higher energies the EELS signal is composed of V and O-K edge contributions. The measurements were performed on the FEI Tecnai F20-ST equipped with a GIF 865-ER.

7.3.2 Mixed phase growth of LVO\textsubscript{3} and LVO\textsubscript{4}

Figure 7.2(a) shows a cross-sectional ADF-STEM image of a LaVO\textsubscript{x} film grown on SrTiO\textsubscript{3} viewed along a substrate [001] zone axis. As expected for these growth conditions we find two regions in the film: the brighter regions show a uniform, well-crystallized, smooth film, whereas the darker regions appear to be 3D islands that nucleated during the growth. The composition was probed using spatially resolved EELS. Figure 7.2(b) shows V-L\textsubscript{2,3}/O-K spectra for the smooth regions of the film and the 3D islands, respectively. For better compar-
Figure 7.2: (a) Cross-sectional ADF image of a LaVO$_3$ film grown at $T_g=800^\circ$C and $P_{O_2}=10^{-4}$ Torr showing mixed phase growth of 3D LaVO$_4$ islands and flat LaVO$_3$ on a SrTiO$_3$ substrate. (b) V-L$_{2,3}$/O-K electron energy loss spectra taken from an island and from the smooth film, respectively. (c) AFM image of the same film showing both flat regions of LaVO$_3$ and 3D islands of LaVO$_4$.

A comparison of the fine structure, the spectra were normalized to the integrated intensity under the V-L$_{2,3}$ edge. On the 3D islands the V-L$_3$ peak shifts by $E \sim 1.7$eV towards higher energies. This energy shift and the direct comparison of the spectra with the V fingerprints (Fig. 7.1) are consistent with a vanadium valence change from $V^{3+}$ in the smooth film to $V^{5+}$ in the 3D islands. Hence, under these growth conditions there is two phase growth of uniform, smooth LaVO$_3$ and 3D LaVO$_4$ islands. Figure 7.2(c) shows an atomic force microscopy (AFM) image representative of the film, confirming the formation of 3D islands and regions of atomically flat surface, which correspond to LaVO$_4$ and LaVO$_3$, respectively.
Figure 7.3: (a) Low magnification ADF image of a LaVO$_3$ film grown at $T_g=800^\circ$C and PO$_2=10^{-4}$ Torr, where LaVO$_3$ 3D islands are marked with arrows. (b) Higher magnification ADF image of a LaVO$_3$ film grown at $T_g=800^\circ$C and P$_{O_2}=10^{-5}$ Torr showing a bright band at the interface between the LaVO$_4$ and the SrTiO$_3$ substrate. (c) The crystal structure of the monoclinic LaVO$_4$ recorded along the [010] crystallographic direction for the area marked by the box in (b). (d) The sharp interface between the LaVO$_4$ and the bright band.

The reduced contrast of the LaVO$_4$ islands compared to the LaVO$_3$ layer is due to the relative orientation of the crystals compared to the electron propagation direction. ADF STEM images of crystals are sensitive to crystal orientation [81], because channeling of the probe on the atom column for crystals oriented on zone axis leads to contrast enhancement in the ADF STEM image. As the crystal is tilted off axis, the channeling effect is reduced and the contrast diminishes. In Figure 7.2, the LaVO$_3$ and the SrTiO$_3$ substrate are aligned on zone axis whereas the LaVO$_4$ polycrystalline islands are mostly oriented off axis. Figure 7.3(c) shows a high resolution ADF-STEM image of a region in a LaVO$_4$ island that is oriented on the zone axis. The difference between the LaVO$_4$ (Fig. 7.3(c)) and the SrTiO$_3$ crystal structure (Fig. 7.3(d)) is apparent. SrTiO$_3$ shows the typical cubic perovskite structure, whereas LaVO$_4$ is monoclinic with
monazite type structure (P21/c, a=7.047 Å, b=7.286 Å, c=6.725 Å, \( \gamma =104.85^\circ \)) [143], viewed in Fig. 7.3(c) along the LaVO\(_4\) [010] direction.

### 7.3.3 Probing the electronic structure at the LVO\(_3\)/LVO\(_4\) interface using spatially resolved EELS

Figure 7.3(b) and (d) show a bright band between the LaVO\(_4\) and the SrTiO\(_3\) substrate, which suggests a chemical change for zone-oriented crystals. EELS on the bright layer confirms the presence of LaVO\(_3\), i.e. the 3D LaVO\(_4\) islands do not nucleate directly on the SrTiO\(_3\) substrate, but on a thin (2nm) LaVO\(_3\) layer. This raises an interesting question of how the microscopic transition from V\(^{3+}\) to V\(^{5+}\) is made at this abrupt interface. To explore this, we have measured V-L\(_{2,3}\) edge spectra across the interface between the thin LaVO\(_3\) layer and the LaVO\(_4\) island. Figure 7.4 shows the result of a scan across the interface. The probing path is indicated by the dotted line in the ADF image (Fig. 7.4(c)).

By decomposing the V L\(_{2,3}\) near edge structure into a linear combination of V\(^{3+}\), V\(^{4+}\) and V\(^{5+}\) components (Fig. 7.4(b)), we can monitor the change of V valence at the interface. The results of this three component fit are shown in Figure 7.5(a) and (c). As expected, we find the transition from V\(^{3+}\) in the thin bright layer to V\(^{5+}\) in the LaVO\(_4\) islands. However, at the crossover between these valence states we find a significant contribution of V\(^{4+}\) (i.e. V in a 3d\(^1\) configuration), with an area accounting for close to one electron at the LaVO\(_3\)/LaVO\(_4\) interface. The residuals, i.e. the standard deviation of the experimental data from the fit, are constantly low across the interface in the three component case.
Figure 7.4: (a) V-L$_{2,3}$ electron energy loss spectra recorded across the LaVO$_4$/LaVO$_3$ interface (dotted lines). The solid lines show the fits to the experimental spectra using reference spectra shown in (b). (c) ADF image of the interface where the electron beam position is denoted by the white dotted line. The measurements (a,c) were performed on the VG HB-501 100kV dedicated STEM equipped with a parallel electron energy loss spectrometer.

A fit of this series of spectra with only two components ($V^{3+}$ and $V^{5+}$) as shown in Figure 7.5(b) results in large residuals at the interface, indicating the presence of a third component. Hence, at the LaVO$_3$/LaVO$_4$ interface the vanadium valence varies smoothly from $V^{3+}$ to $V^{5+}$, passing through a region of $V^{4+}$ at the interface.

Microscopically, the local electronic distribution is not phase separated into
Figure 7.5: (a) The fractions of $V^{3+}$, $V^{4+}$ and $V^{5+}$ across the interface obtained by a 3-component fit to the experimental data shown in Fig. 7.4(a) and the residuals of the fit. These fractions were used to color code the fits to the experimental data in Fig. 7.4(a). (b) A 2-component fit of the data using $V^{3+}$ and $V^{5+}$ reference spectra results in large residuals at the interface. (c) Total vanadium valence across the LaVO$_4$/LaVO$_3$ interface as determined from (a).
only the bulk-accessible 3d$^0$ and 3d$^2$-configured V d-states, but also includes a thin layer of 3d$^1$ V atoms at the interface. The 3d$^1$ state would not be expected from the bulk available phases, nor is it required from continuity of the wavefunction in an average sense, highlighting the very different electronic response at the interface.

### 7.4 Conclusions

In summary, we have shown that the non-bulk-like charge state, 3d$^1$ V, can be stabilized at the LaVO$_3$/LaVO$_4$ interface. Here an interface between two competing ground states (the 3d$^2$ Mott insulator and 3d$^0$ band insulator) has led to a two-dimensional sheet of intermediate valence 3d$^1$ electrons. As there is a large family of closely lattice-matched transition metal oxides with different and exotic ground states, other electronic reconstructions and intermediate valence states may also be stabilized by this approach.
La$_{0.7}$Sr$_{0.3}$MnO$_3$ is a conducting ferromagnet at room temperature. Combined with thin SrTiO$_3$ they have the potential to perform as highly-spin-polarized magnetic tunnel devices with tunneling magneto-resistance of up to 1800% [144]. However, when shrunk to dimensions below an apparent critical thickness, the structures becomes insulating and the ferromagnetic ordering strongly suppressed [145–151]. Interface spin and charge modulations are thought to create an interfacial dead layer, thus fundamentally limiting the use of this material in small dimensions [31, 147, 152, 153]. The thickness of this intrinsic dead layer, however, is still controversial [31, 145–153]. Using spectroscopic imaging at the atomic scale, we have now correlated the degradation of the magnetic and transport properties of manganite/titanate multilayers with a higher degree of intermixing at the interfaces and the presence of extended cation defects in the La$_{0.7}$Sr$_{0.3}$MnO$_3$ layers. When these extrinsic defects are eliminated by optimizing the interface structure and the stoichiometry of the La$_{0.7}$Sr$_{0.3}$MnO$_3$, metallic ferromagnetism at room temperature can be stabilized in 5-unit-cell-thick manganite layers, reducing the limit for the intrinsic interfacial dead layer to two unit cells or less (i.e. less than 0.8 nm/interface).

### 8.1 Introduction

Colossal magnetoresistance, metal-insulator transitions, charge/orbital ordering and half-metal ferromagnetism are only some of the intriguing phenomena that occur in manganites and have driven interest in the family of perovskite
manganese oxides (ABO$_3$ perovskite structure, B-site occupied by Mn). With a Curie temperature ($T_c$) of $\sim$370 K, the half-metal La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) has been considered a promising candidate for spintronics applications. However, while complete spin polarization in LSMO was inferred from photoemission measurements [154] and a record tunneling magnetoresistance (TMR) ratio of 1800 % was obtained at low temperature in tunnel junctions with half-metallic manganite electrodes separated by a thin insulating layer of SrTiO$_3$ (STO) [144], the TMR decreases rapidly as a function of temperature and diminishes far below $T_c$. One possible origin for the reduced TMR is the degradation of the ferromagnetic ordering at the interface between the manganite and the STO. These interfacial effects have been suggested to be dominant as the LSMO layer thickness decreases, causing the magnetization and $T_c$ to degrade and the resistivity to increase, ultimately resulting in films that are insulating at all temperatures as the layer thickness decreases below a critical value of 8-13 unit cells [145–150]. This critical thickness for sustaining conductivity below $T_c$ is attributed to an inherent "dead layer" at the interface between LSMO and STO [31, 153, 155]. The reduced $T_c$ and saturation magnetization of thin LSMO films compared to the bulk is believed to be due to spin canting at the LSMO/STO interface [147, 152]. Alternatively, magnetic phase separation into ferromagnetic metallic and less-ordered insulating clusters was proposed as the origin of the degraded properties of the LSMO as the film thickness decreases below a critical thickness [145, 156].

In this Chapter, we use atomic-resolution electron microscopy to show that as the manganite layers in pulsed layer deposition (PLD) grown LSMO/STO multilayers become less stoichiometric (due to changes in the laser spot size), extended defects segregate near the interfaces to compensate for the A-site cation
excess. The presence of such defects in the LSMO layers and of atomic-scale intermixing at the interfaces correlates with the degradation of the magnetic and transport properties of the multilayers. As the microscopic perfection of the structure is improved, the LSMO/STO multilayers can remain ferromagnetic and conducting below $T_c$ at layer thicknesses below 2 nm, i.e. 5 unit cells, with the implication that the upper limit for the interfacial dead layer is now reduced to two unit cells or less. For these ultra-thin manganite layers, we have now obtained a ferromagnetic transition temperature above room temperature in films that are also conducting.

8.2 Methods

8.2.1 Sample Preparation

(LSMO)$_5$/ (STO)$_5$ multilayers were grown at 850-900 °C on TiO$_2$ terminated (001)-oriented SrTiO$_3$ substrates by PLD using a KrF excimer laser at a repetition rate of 4 Hz and a total laser energy of $\sim$35 mJ. La$_{0.7}$Sr$_{0.3}$MnO$_3$ polycrystalline and SrTiO$_3$ single crystal targets were used, and the growth was monitored by reflection high-energy electron diffraction. Two sets of samples were grown at oxygen partial pressures (PO$_2$) of $10^{-3}$ and $10^{-6}$ Torr, varying the laser spot area but keeping the same pulse power. Since the total fluence is kept constant for the growth of all samples, the fluence at the target surface decreases with increasing laser spot size.
8.2.2 Experimental Techniques

The microstructure of the LSMO/STO multilayers was studied by high angle annular dark field (HAADF) imaging in a 200 kV FEI Tecnai F20-ST STEM with a minimum probe size of 1.6 Å [123] and a convergence semiangle of (9±1) mrad. The chemical composition and bonding was probed on an atomic scale using spatially resolved electron energy loss spectroscopy (EELS) performed on the fifth-order aberration corrected NION UltraSTEM 100 [157], which is equipped with a Gatan Enfina spectrometer and enables two-dimensional element and valence-sensitive imaging at atomic resolution [75].

8.3 Results

8.3.1 Structural changes in La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayers with the PLD laser spot size

Figures 8.1(a-d) shows cross-sectional HAADF-STEM images of the LSMO/STO multilayers grown at 10$^{-3}$ Torr and laser spot sizes of 10.2, 7.5, 5 and 1.6x$^{-2}$ cm$^2$, viewed along a substrate [001] zone axis. In HAADF imaging the scattering intensity scales, to first approximation, with the atomic number Z as $Z^{1.7}$, so the brighter stripes in Fig. 8.1(a) correspond to the nominal 5 unit cell thick LSMO layer and the darker ones to the STO layers [78, 79, 158]. The strong dependence of the structural quality of these multilayers on the laser spot size is clearly visible. Starting with abrupt interfaces between the LSMO and the STO for the multilayers grown at larger spot sizes, the interfaces become more gradual and
Figure 8.1: Cross-sectional ADF images of (La$_{0.7}$Sr$_{0.3}$MnO$_3$)$_5$/(SrTiO$_3$)$_5$ superlattices grown at PO$_2$=1 mTorr and at a laser spot size of (a) 10.2, (b) 7.5, (c) 5 and (d) $1.6 \times 10^{-2}$ cm$^2$. As the laser spot size decreases extended defects are introduced in the LSMO layer and the interfaces become more diffuse.

extended defects, some of which appear as dark lines in the HAADF images (Fig. 8.1(c, d)), are introduced as the spot size decreases.

The change in the interface abruptness becomes clear when looking at the HAADF images taken at higher magnification ( insets in Fig. 8.1(a, d)). For the multilayer grown at $10.2 \times 10^{-2}$ cm$^2$ ( inset Fig. 8.1(a)) the interfaces are atomically abrupt, while they are more diffuse as the spot size is reduced to $1.6 \times 10^{-2}$ cm$^2$ ( inset Fig. 8.1(d)). Contrast variations in the LSMO layer suggest that the stoichiometry in the layer deviates from the nominal La$_{0.7}$Sr$_{0.3}$MnO$_3$, possibly due to cation intermixing or the presence of point defects.
8.3.2 Atomic-scale chemical imaging of La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayers and its defects

While HAADF lattice imaging, in which the contrast is dominated by the heavy A-site cations, can be very revealing, complementary information can be obtained through spectroscopic imaging. With recent advances in electron microscopy, in particular the successful implementation of fifth-order aberration correction, a single core-loss EELS spectrum can now be recorded in milliseconds and a full two dimensional spectroscopic image at atomic resolution in under a minute [75]. Here, individual elemental maps were obtained by recording the Ti-L$_{2,3}$, Mn-L$_{2,3}$ and the La-M$_{4,5}$ edges simultaneously, and then fitting the pre-edge with a linear function, subtracting the background and integrating over a part of the near-edge fine structure at each point in the image. The La elemental maps and red-green-blue (RGB) false color B-site maps, obtained by combining the Ti (red channel) and Mn (green and blue channels) maps, of two multilayers grown at 7.5 and 1.6×10$^{-2}$ cm$^2$ are shown for comparison in Fig. 8.2. For both samples the elemental maps and the corresponding concentration profiles (Fig. 8.3 and Fig. 8.4) show clear differences between the upper and the lower manganite interfaces, confirming that the STO layers are predominantly TiO$_2$-terminated and the LSMO layer MnO$_2$-terminated. Additionally we find that the multilayer grown with a smaller laser spot size shows less abrupt interfaces and an extended defect, marked by a white arrow in Fig. 8.2(d). The inferior quality of the second sample can also be seen from the Ti distribution in the B-site map, where patches of weak Ti sublattice are found throughout the LSMO layer (Fig. 8.2(c) and Fig. 8.4(a)), which suggests a higher degree of Mn/Ti intermixing. In electron microscopy it is often difficult to distinguish between
Figure 8.2: Spectroscopic-imaging of La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayers grown at PO$_2$=1 mTorr and at a laser spot size of (a), (b) 7.5 and (c), (d) $1.6 \times 10^{-2}$ cm$^2$. (a, c) La elemental maps and (b, d) red-green-blue false color B-site maps, obtained by combining the Ti (red) and Mn (green and blue) maps extracted from the spectrum images. The multilayer grown with a smaller laser spot size shows less abrupt interfaces and an extended defect, marked by a white arrow in (d). The growth direction is from bottom to top.

true intermixing and broadening of an interface due to the shape of the electron probe (probe tails). However, from the two dimensional B-site map shown here and the Ti map (Fig. 8.4(a)) enhanced intermixing can be directly inferred due to the observed variation of the Ti concentration in the LSMO layer showing a weak Ti sublattice in some areas of the LSMO layers (probe tails would cause broadening of the interfaces, but a correlation of the Ti concentration maxima in the LSMO layers with the B-site sublattice is not expected). Note that sample drift ($\sim 1.0$ Å/min) during the acquisition of a spectroscopic image causes the lattice to appear distorted.
Figure 8.3: Spectroscopic-imaging of a La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayers grown at PO$_2=1$ mTorr and at a laser spot size of $7.5 \times 10^{-2}$ cm$^2$. (a) Ti, (b) Mn and (c) La elemental maps extracted from a 128×157 pixel spectrum image and (d) the simultaneously recorded ADF image. For (a-d) the growth direction is from bottom to top. (e) Concentration profiles across the multilayer obtained by averaging the Ti, Mn and La signal parallel to the interface. The growth direction for (e) is indicated by the black arrow.

Extended defects found in the multilayer grown at a laser spot size of $1.6 \times 10^{-2}$ cm$^2$ (Fig. 8.1(d)) were further studied using spectroscopic imaging. In the elemental maps shown in Fig. 8.5(a) defect is visible in the upper part of the LSMO layer. The combined Mn and Ti concentration is strongly reduced in the region outlined by the white box, suggesting B-site deficiency. However, the simultaneously recorded HAADF image does not show missing columns of atoms at the B-sites, but rather a higher intensity compared to the B-site atom columns in STO or LSMO. This suggests that the B-sites are locally filled by...
La or Sr atoms, resulting in a rock-salt type layer to compensate for A-site excess. High magnification HAADF images also reveal regions in the film where single rock-salt layers are introduced (Fig. 8.6). Recently, the influence of the laser fluence on the stoichiometry of single LSMO films grown by PLD has been demonstrated, showing an increase in the A-site/B-site cation ratio as the fluence increases [159]. These results are consistent with our findings here. The reduction of the laser spot size causes an A-site cation excess in the nominal
Figure 8.5: Spectroscopic-imaging of an extended defect in a \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{SrTiO}_3 \) superlattice grown at \( \text{PO}_2 = 1 \text{ mTorr} \) and at a laser spot size of \( 1.6\times 10^{-2} \text{ cm}^2 \). (a) Ti, (b) Mn, (c) La elemental maps extracted from a 90\times 45 pixel spectrum image and (d) the simultaneously recorded ADF image. The white box indicates a B-site deficient region at the top of a LSMO layer.

\( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) of the multilayer which is accommodated by the introduction of extended defects as observed in Fig. 8.5. The dependence of the STO stoichiometry on the laser fluence is much weaker, and the LSMO/STO multilayers studied here, extended defects are only found in the LSMO layers, mostly in the upper part of the manganite layer.

A second type of defect, which has formed along the growth direction in the upper part of the LSMO layer, is shown in Fig. 8.7. Because of the character of the Sr EELS edges, it is more difficult to obtain a strontium elemental map at the same acquisition time as the Ti, Mn and La maps; however, information about the position of the Sr atoms is contained in the simultaneously recorded ADF image. Here, the La map (Fig. 8.7(c)) shows missing La columns at the center of the defect, but from the ADF image these sites are clearly occupied by some other atomic species. Combined with the information from the Mn and the Ti elemental maps we can conclude that Sr atoms fill the positions of the La sites, which again suggests local off-stoichiometry.
8.3.3 Interplay of structural variation and physical properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayers

The physical properties of an LSMO layer are highly sensitive to variations of the stoichiometry of the film, i.e. A-site/B-site ratio [159, 160]. In order to understand the interplay of the observed structural differences and the properties of the multilayers, transport and magnetic measurements were performed. The temperature-dependent magnetization shown in Fig. 8.8(a) indicates that the magnetic properties of the multilayer vary strongly with the laser spot size. $T_c$ as well as the saturation magnetization increases as the spot size increases from 1.6 to $10.2 \times 10^{-2}$ cm$^2$. Hence, as the superlattice structure and stoichiometry is
Figure 8.7: Spectroscopic-imaging of an extended defect in a La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayer grown at PO$_2$=1 mTorr and at a laser spot size of 1.6×10$^{-2}$ cm$^2$. (a) Ti, (b) Mn, (c) La elemental maps extracted from an 109×80 pixel spectrum image and (d) the simultaneously recorded ADF image. The white open circles indicate the position of the La columns around the defect. The ADF image, which also tracks the position of the Sr atoms, shows clear atomic columns in the center of the defect, while the La concentration is low, suggesting that the defect was formed to accommodate for access Sr in the LSMO layer.

optimized, reducing interdiffusion and the number of defects, the magnetization increases. At the same time, large changes in the temperature-dependent resistivity are observed (Fig. 8.8(c)). Multilayers grown at smaller spot sizes are insulating at all temperatures, however, as the spot size is increased to 10.2×10$^{-2}$ cm$^2$ the sample becomes conducting below T$_c$.

As the oxygen partial pressure is decreased to 10$^{-6}$ Torr similar trends with respect to the laser spot size persist. Figures 8.8(b) and 8.8(d) show the temperature-dependent magnetization and resistivity for the set of samples grown at 10$^{-6}$ Torr. The saturation magnetization as well as T$_c$ increase as the spot size increases and accordingly, the resistivity decreases. The multilayer
Figure 8.8: Temperature dependence of the (a, b) magnetization (zero field cooled, and measured warming under 1000 Oe) and (c, d) resistivity of $(\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3)_{5}/(\text{SrTiO}_3)_{5}$ superlattices grown at various laser spot sizes as indicated in the figure. The multilayers were grown at an oxygen partial pressure of (a, c) $10^{-3}$ Torr and (b, d) $10^{-6}$ Torr. As the laser spot size increases metallic ferromagnetism is stabilized.

The multilayer grown with the largest spot size shows the expected behavior for LSMO, being insulating at temperatures above $T_c$ and metallic below $T_c$. The $T_c$ of this multilayer is determined to be ~298 K. The samples grown with smaller spot sizes, however, remain insulating at all temperatures. This is a remarkable result, since it shows that metallic ferromagnetic LSMO can be stabilized, even for layer thicknesses of ~2 nm, which is far below the previously reported critical thickness. Note that post annealing in oxygen for 10 hours at up to 850 °C had no effect on the properties of the multilayers (Fig. 8.9), which suggests that oxygen vacancies do not dominate the observed behavior. Ti-L$_{2,3}$ and Mn-L$_{2,3}$ EELS
Figure 8.9: Temperature dependent magnetization of (La$_{0.7}$Sr$_{0.3}$MnO$_3$)$_5$(SrTiO$_3$)$_5$ multilayers grown at (a) PO$_2$=1 mTorr and post annealed in oxygen in steps, 3 hours at 400 °C, 3 hours at 600 °C and 10 hours at 850 °C and (b) PO$_2$=10$^{-6}$ Torr and post annealed in oxygen at 600 °C for 10 hours.

8.4 Conclusions

In conclusion, LSMO/STO multilayers with manganite layer thicknesses of ~2 nm can exhibit ferromagnetism with $T_c$ above room temperature and remain metallic below $T_c$, if the structure is optimized by tuning not only the oxygen partial pressure and growth temperature but also the laser fluence at the target. For smaller spot sizes, hence larger fluences, the quality of the multilayer deteriorates. This results in less abrupt interfaces, and an LSMO A-site/B-site cation ratio in excess of one, which is accommodated by the introduction of ex-
Figure 8.10: Background-subtracted (a) Ti L-edge and (c) Mn L-edge spectra across a \((\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3)/(\text{SrTiO}_3)\) multilayer grown at \(\text{PO}_2=1\ \text{mTorr}\) and a laser spot size of \(7.5\times10^{-2}\ \text{cm}^2\). Each spectrum is an average of all spectra in a spectrum image along a line parallel to the interfaces. The ADF image recorded simultaneously with the spectroscopic image is shown in (b). The fine-structure of the Ti L- and Mn L-edges is highly sensitive to changes in the Ti and Mn valence. In (a) and (c) no significant fine-structure changes are observed, suggesting that the Ti and the Mn valences across the layers remain constant (within the experimental uncertainty).

tended defects and leads to a reduction of the magnetization and an increase of the resistivity such that the multilayers remain insulating at all temperatures. The laser fluence corresponding to the smaller spot size is typical for previous PLD grown LSMO/STO multilayers [150, 161], which might explain their inferior properties. This work suggests that the intrinsic critical thickness has yet to be reached, even for 5 unit cell LSMO layers which are virtually all interface.
CHAPTER 9
CONCLUSIONS

ADF-STEM imaging in combination with spatially-resolved EELS has been used to study the structure and bonding at interfaces involving perovskite oxides. A good understanding of the near-edge fine structure of core-loss spectra is essential in this work and was therefore reviewed in Chapter 2, with particular emphasis on transition-metal L_{2,3} edges and O-K edges for perovskite oxides.

The core-loss EELS signal is closely related to the local density of states partitioned by site, element and angular momentum, however, the effect of the core-hole created during the excitation process needs to be taken into account. Transition metal L_{2,3} edges are, for example, dominated by multiplet effects due to the correlations between the 2p core hole and the 3d electrons. Atomic multiplet calculations have successfully been used to predict the L_{2,3} fine structure. In these calculations solid-state effects are introduced as a perturbation. The symmetry of the crystal field surrounding the transition metal is, for example, included by projecting the atomic multiplet results onto the appropriate symmetry group which results in splittings within the L_2 (and L_3) edges. The transition metal L_{2,3} edge fine structure is therefore a powerful probe of the valency and the coordination of the transition metal atom. In Chapter 7 this was used to demonstrate electronic reconstruction at the LaVO_3/LaVO_4 interface. For the O-K edge the 1s core hole has only small effects on the spectral shape and it can therefore be interpreted on the basis of partial DOS calculations. The O-K ELNES for transition metal oxides can be divided into three regions. The features within the first ~5 eV above edge onset are dominated by transition metal 3d states and are therefore sensitive to the valency of the transition metal ion. The peaks 5-10 eV above edge onset are attributed to states derived from oxygen
p and the A-site cation d orbitals. At higher energies the ELNES is dominated by bands of higher-energy metal states. A large collection of O-K edges “fingerprints” for perovskite oxides was established and can be used as reference for future work.

With this understanding of the ELNES, interfaces between perovskite oxides have been studied using spatially resolved EELS. For cross-sectional samples where the interface plane is aligned parallel to the beam direction, the bonding at the interface can be studied by stepping the electron probe across and recording the EELS spectrum at each point. However, we need to keep in mind that for typically TEM cross-sections one averages over 30-50 atoms in projection. This technique therefore relies on uniform interfaces which was the case for most oxide-oxide heterointerfaces examined in this work. When SrTiO$_3$ is grown on Si, however, the layer is not uniform, but it islands due to a phase-separation instability. This was shown in Chapter 4 by imaging these atomically thin, buried SrTiO$_3$ layers through the substrate in plan-view geometry. The success of this technique is based on the self-focusing of the electron probe by channeling in the crystalline substrate. In Chapter 3 the evolution of the channeling signal in Si was directly measured and the results showed good agreement with multi-slice simulations. As the electron probe propagates down a silicon atom column it is progressively focused onto the column, reaching its maximum at 12 nm. If the region on the plan-view sample is carefully selected so that the thickness of the Si substrate corresponds to 12 nm, the visibility of the SrTiO$_3$ islands can be enhanced by a factor of four, which made it possible to image these thin layers in plan-view. Note, however, that while electron channeling enhances the visibility of on-column atoms, it suppresses the contribution from off-column atoms. It can therefore be used as a filter to selectively image the atoms that are
the most aligned with the atomic columns of the substrate.

In Chapter 5 a low-angle twist grain boundary in SrTiO$_3$ was studied. For this work the sample was oriented so that one side of the boundary was aligned on a zone axis, while the other side was tilted ~2° off the channeling condition and therefore appeared much darker. The effect of small tilts on the fringe contrast in SrTiO$_3$ was analyzed using multislice simulations. For 20 nm thick crystals and small tilts, $\theta < 1°$, the electron probe still channels on the atomic columns and the Sr columns act as beam guides. Only for larger tilts is the channeling effect strongly reduced. From the materials point of view, the relative tilt of the two crystals with respect to each other causes strain at the twist grain boundary which is partially relieved by the formation of a network of screw dislocations. The cores of one set of dislocations running parallel to the beam direction appeared dark in the ADF STEM images. EELS on the dislocation core revealed a reduced Sr/Ti ratio compared to the bulk suggesting Sr deficient cores, which was supported by changes in the O-K edge fine structure. The second set, orthogonal to the latter, was imaged by its strain field which leads to additional contrast in LAADF imaging.

In Chapters 6-8 three oxide heterointerfaces were analyzed. In LaVO$_3$/SrTiO$_3$ multilayers a growth asymmetry was observed resulting in diffuse lower and atomically-abrupt upper vanadate interfaces. Polar discontinuities that occur at many oxide heterointerfaces can drive electronic as well as atomic reconstruction at the interface. For this system it was shown, however, that switching the SrTiO$_3$ termination layer does not change the interface abruptness, which excludes the interfacial polar discontinuity as the driving force for the observed growth asymmetry. Instead, the results suggest that the asymmetry is caused by preferential Sr surface segregation during growth. Sim-
ilar segregation processes play an important role in the growth of traditional III-V semiconductor heterointerfaces. Although oxide heterointerfaces were believed to be less susceptible to these effects, since they are typically grown at much lower temperatures as compared to the thermodynamic (melting) temperatures of the constituents, this work shows that surface segregation has to be taken into account and can set an upper limit to the obtainable interface sharpness in perovskite oxide heterostructures.

In an approach to stabilize an intermediate valence state by electronic interface reconstruction, the interface between the 3d$^2$ Mott insulator LaVO$_3$ and the 3d$^0$ band insulator LaVO$_4$ was studied. Although no bulk phase of LaVO$_x$ with V 3d$^1$ configuration exists, a nanometer-wide region of V 3d$^1$ is stabilized at the LaVO$_3$/LaVO$_4$ interface. This is one example of electronic interface reconstruction, which in this case leads to the stabilization of a non-bulk like charge state at the interface. Given the large family of closely lattice-matched transition metal oxides with different and exotic ground states, electronic reconstruction presents a unique synthetic opportunity to create new artificial states between two materials.

Up to this point spectroscopic information about the various heterointerfaces was obtained by stepping along a line across the interface (EELS line profiles). With recent advances in electron microscopy, in particular the successful implementation of fifth-order aberration correction, smaller probe sizes and higher beam currents are achievable which allows two-dimensional chemical maps to be recorded at the atomic-scale. This was demonstrated in Chapter 8, were the microstructure of La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayers was studied and related to changes in the physical properties of the system. Using spectroscopic imaging, the degradation of the magnetic and transport properties of
these manganite/titanate multilayers was correlated with a higher degree of intermixing at the interfaces and the presence of extended cation defects in the La$_{0.7}$Sr$_{0.3}$MnO$_3$ layers. The microscopic quality of the multilayers was shown to be strongly dependent on the PLD laser spot size. For smaller spot sizes the quality of the multilayer deteriorates. This results in less abrupt interfaces, and an La$_{0.7}$Sr$_{0.3}$MnO$_3$ A-site/B-site cation ratio in excess of one, which is accommodated by the introduction of extended defects and leads to a reduction of the magnetization and an increase of the resistivity such that the multilayers remain insulating at all temperatures. Using larger spot sizes the interface structure and the stoichiometry of the La$_{0.7}$Sr$_{0.3}$MnO$_3$ was optimized. Under these conditions La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrTiO$_3$ multilayers with manganite layer thicknesses of ~2 nm exhibit ferromagnetism with $T_c$ above room temperature and remain metallic below $T_c$. 


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