STOICHIOMETRY CONTROL IN OXIDE THIN FILMS BY PULSED LASER DEPOSITION

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Stoichiometry control in oxide thin films by pulsed laser deposition

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Cover image: Reflection High Energy Electron Diffraction patterns of SrTiO$_3$ thin films on SrTiO$_3$ substrates grown with pulsed laser deposition at various partial oxygen background gas pressure conditions. The colorscale and the level of detail of the image are manipulated.

The research described in this thesis was carried out within the Inorganic Materials Science group, Department of Science and Technology and the MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands. This research is supported by the Dutch Technology Foundation STW, which is part of the Netherlands Organization for Scientific Research (NWO) and partly funded by the Ministry of Economic Affairs (project number 10760).

Stoichiometry control in oxide thin films by pulsed laser deposition
Ph.D. thesis, University of Twente, Enschede, The Netherlands
Copyright © 2017 by Rik Groenen
Printed by Ipskamp Printing, Enschede, The Netherlands
DOI: 10.3990/1.9789036544504
STOICHIOMETRY CONTROL IN OXIDE THIN FILMS BY PULSED LASER DEPOSITION

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof. dr. T.T.M. Palstra,
volgens besluit van het College voor Promoties
in het openbaar te verdedigen
op woensdag 20 december 2017 om 12:45 uur

doorn

Rik Groenen

geboren op 9 maart 1984
te Zevenaar
Dit proefschrift is goedgekeurd door de promotoren

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Chapter 1

Stoichiometry control in oxide thin films

1.1 Introduction

In 1959 Richard Feynman for the first time discussed the synthesis of materials via manipulation of single atoms in his famous talk ‘There’s Plenty of Room at the Bottom’. Since then, the advances and achievements in the field of nanotechnology have lead to functionalised materials, devices and technology with increasingly smaller integrated circuits and denser data storage.

The term nanotechnology itself was first used by Norio Taniguchi, professor of Tokyo University of Science in 1974, to describe processes such as thin film deposition exhibiting control on the order of a nanometer. His definition of nanotechnology,

Nano-technology mainly consists of the processing of separation, consolidation, and deformation of materials by one atom or one molecule,

still stands today and romantically summarises the essence of materials science and engineering at nanoscale dimensions. Advances in fabrication processes and characterisation techniques have made it possible to synthesise, characterise and manipulate material at the atomic scale. At these dimensions, quantum effects dominate the properties of materials such that intrinsic material bulk properties are altered or lost and new phenomena and properties can emerge. This creates new pathways and possibilities for new applications. A good example is the giant magnetoresistance effect, widely applied in magnetic field sensors in hard disk drives and all sorts of sensors.

\(^1\)This famous lecture was given at an American Physical Society meeting at Caltech on December 29, 1959.
A highly interesting class of materials are complex metal oxides, for their rich variety of interesting physical properties such as ferroelectricity, ferromagnetism and superconductivity. A widely investigated sub-group within the complex metal oxides are the perovskite metal oxides. The term ‘perovskite’ originates from the discovery of the calcium titanium oxide (CaTiO$_3$) mineral in 1839, but is nowadays used to describe the family of crystals with an ABO$_3$ stoichiometry. The unit cell of perovskites has rare-earth or metal A and B cations and six oxygen atoms, forming a BO$_6$ oxygen octahedra in the centre of the cubic with the A cation in its corners.

The properties of (perovskite) complex metal oxides are highly sensitive to slight deviation from the ideal crystal stoichiometry. Therefore, a general challenge in the synthesis of complex oxide nanostructures and thin films is the control of the stoichiometry and herewith control of thin film properties. This challenge has driven the development of many thin film deposition techniques. For the growth of complex metal oxides, Molecular Beam Epitaxy (MBE) and Pulsed Laser Deposition (PLD) are most widely mentioned for their capability of growing near stoichiometric highly crystalline complex metal oxide thin films.

### 1.2 Pulsed Laser Deposition

In PLD, target material is ablated using a high intensity pulsed laser which results in a plasma plume that expands towards a substrate on which it condenses. Due to the high supersaturation during the deposition pulse, PLD has shown its potential for the stoichiometric transfer of materials containing volatile species like lead, bismuth, ruthenium and sodium. The breakthrough for PLD came with the synthesis of the high T$_c$ superconducting YBa$_2$Cu$_3$O$_7$ in 1987,[2] which was of superior quality to that of films deposited with other techniques. This emphasised the potential of PLD for (near)stoichiometric transfer of species and the growth of complex oxide films with high crystalline quality.

Several growth parameters can be set to influence the deposition and growth processes such as laser fluence, laser spot-size on the target, target-substrate
distance, background gas conditions and the substrate temperature. Typically by optimising these settings, a high quality epitaxial thin film can be obtained. To obtain insight in the fundamental growth processes, PLD thin film growth has been extensively studied using for instance in situ Reflection High Energy Electron Diffraction (RHEED) by monitoring the surface diffraction pattern of the growing film. This diffraction pattern is the result of the grazing incidence interaction of the electron beam with surface of the substrate or film. From these investigations an improved understanding and description of growth processes has been obtained. It was shown that the oscillating behaviour in the intensity of this two dimensional diffraction pattern relates to oscillating step density with unit cell height differences, where a single oscillation therefore relates to the growth of a single monolayer. From these studies it is generally accepted that many processes involved in PLD growth are understood and described by kinetic models. The highly supersaturated and pulsed nature of the flux of material results in short time scale interactions that dominate the growth process over thermodynamic processes.\[^{3–10}\] Nowadays RHEED is widely used for in situ growth monitoring.

But the often narrow growth parameter window for optimised growth shows that obtaining stoichiometric films using PLD is far from trivial. For example, early research suggested a complex ablation process for SrTiO\(_3\), where it was shown that the composition of the SrTiO\(_3\) films becomes nonstoichiometric when the laser fluence is reduced below a certain threshold.\[^{11}\] This emphasised the importance of having control over the uniformity of the laser intensity at the target as well as the pulse to pulse stability. From this work, an ablation fluence of 1.3 J/cm\(^2\) is

![Figure 1.2: Schematic representation of a typical PLD experiment geometry, including a target carousel holding five targets and heater on which a substrate is mounted. A laser pulse interacts with the target to form an ablation plume which expands towards the substrate. The RHEED electron gun is presented in bottom right corner, where an electron surface diffraction pattern is shown by the yellowish spots opposite of the gun on the (phosphorus) screen.](image-url)
suggested, which is a widely used standard.

Next to laser parameters, the background gas conditions affect the ablation process, plume characteristics and film growth. Strong interaction occurs between the laser ablated plasma with the background gas that affects the physical and chemical characteristics of the plasma constituents. This subsequently affects film growth, composition, structure and therefore film properties.

1.3 Plume and film characteristics

Over the years, many studies have been performed investigating plume characteristics using a wide range of experimental techniques such as Absorption Spectroscopy (AS) and Optical Emission Spectroscopy (OES) combined with langmuir probe measurements and mass spectrometry.\textsuperscript{[10,12–18]} The propagation dynamics and composition of the plume has been studied by imaging and spectrally resolving the self emission of exited species (often neutral species) in the expanding plume with fast photography techniques. From these studies, much insight has been obtained regarding the interaction of plume constituents and background gas. This includes collisions between species affecting the dynamics of the expanding plume, the spatial distribution of species and the ionisation and excitation processes. Generally it has been concluded that a typical PLD plasma plume composition consists of neutral atoms, oxidised species, ions and electrons travelling at different velocities, where the distribution of species strongly depends on the interaction with the background gas. Early research showed that in high vacuum, the plasma propagation dynamics can be characterised by a free ballistic expansion. At higher pressures, the plume thermalises, where it shows a shock-wave type propagation as a result of the expanding plume compressing the surrounding background gas. For a typical target to substrate distance of 50 mm used in PLD, this transition occurs within a narrow pressure range from $10^{-2}$ and $10^{-1}$ mbar,\textsuperscript{[12]} in which the kinetic energy of species is lowered from 10 to 100eV, to less than 1eV.\textsuperscript{[19–21]} It has been shown that the propagation of the plume towards a heater is also affected by the heater temperature. An elevated heater temperature results in a local decrease in gas density, decreasing interaction of the plume with the background gas.\textsuperscript{[22,23]}

Clearly, the kinetic energy of species in the plasma and subsequent adatoms is highly tuneable by experimental parameters. Therefore, much research has focussed on the relation between the kinetics of arriving species, adatom energy and film characteristics, including surface kinetics, kinetic growth modes and film morphology.\textsuperscript{[20,24–27]} For example, an enhanced film smoothness was correlated to increased kinetic energy of arriving species at lower background gas pressure. It is argued that below a coverage of half a monolayer, high energy species impinge into the small two dimensional islands on the substrate, causing them to break up into smaller islands.\textsuperscript{[25]}
1.3 Plume and film characteristics

High kinetic energy of arriving particle may also lead to sputtering effects. Studies on homoepitaxially grown SrTiO$_3$ films suggest that suppression of preferential resputtering of material is essential for obtaining stoichiometric films in homoepitaxial SrTiO$_3$ studies. It is shown that near stoichiometric SrTiO$_3$ films were obtained only when the kinetic energy of arriving species is relatively low, namely when ablating with low laser energy density or in high oxygen pressure.$^{[20,26]}$

In line with these observations, other work outlines growth characteristics of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) thin films related to the kinetic energy of arriving species. It is observed that at low pressure, preferential resputtering of manganese resulted in a reduced manganese content compared to high pressure grown films. By controlling the adatom energy, the surface quality and stoichiometry of LSMO thin films were improved.$^{[27]}$

Other studies suggest a relation between film stoichiometry and mass dependent distribution of cations in the plume. A widely cited extensive study on SrTiO$_3$ homoepitaxially grown films, investigating the relation between fluence and film stoichiometry, concluded that stoichiometric films were obtained only under optimised laser conditions at a fluence of 0.3 J/cm$^2$.\textsuperscript{2} It was shown that films grown at relative lower fluence and relative larger laser irradiation area have a Sr excess where higher fluence and a smaller ablation area would result in a Ti excess in the film.$^{[28-30]}$ These observed deviations are ascribed to preferential ablation, where at higher fluences, it is concluded that a difference in the angular distributions of ejected Sr and Ti in the ablation plume alters the cation ratio in the grown films.$^{[29]}$ In this work, films have been grown in high vacuum where interaction and collisions of species with the background may be neglected. But also in high pressure conditions, variations in film stoichiometry were observed depending on laser fluence. It is suggested that this is the result of an intricate balance between both incongruent ablation resulting in a Sr or Ti rich plume, as well as a preferential mass and pressure dependent scattering of (typically lighter (Ti)) plume species with the background gas.$^{[20,31]}$

These studies mainly relate cation ratio of arriving species to film stoichiometry. But the oxygen background gas environment also affects the plume chemistry and composition by chemical (oxidation) reactions between plume and background (oxygen) gas. Furthermore, the oxygen from the background affects the surface chemistry, where adatoms interact with the oxygen from the background.

\textsuperscript{2}In this work, correlations are observed between the laser fluence and the out-of-plane lattice constant of the crystal structure, which relates to lattice defects and cation nonstoichiometry. Both Sr and Ti defects result in a film lattice expansion in c-axis direction as measured with XRD measurements

\textsuperscript{3}Note that a different laser, namely a ThinFilmStar TUI LASER is used in this work, likely operating at 193 nm. This results in a significantly different optimal fluence compared to typically used fluence of 1-2 J/cm$^2$, as the ablation mechanism including absorption of light strongly depends on the wavelength and energy. Furthermore, compared to other generally used 248 nm excimer lasers (Coherent Compex and LPX series), the TUI LASER has a shorter pulse length different energy distribution over the pulse length.
An investigation on plasma properties in relation to La$_{0.6}$Sr$_{0.4}$MnO$_3$ film growth shows strong chemical interaction of plasma species with oxygen background gas to form metal-oxygen species.$^{[32]}$ It is suggested that the oxygen in the film is administered by both metal-oxygen and the oxygen background, depending on background gas pressure. In more detailed work from the same authors, the origin of oxygen in the film is investigated using a $^{18}$O isotope labelled La$_{0.6}$Sr$_{0.4}$MnO$_3$ target, where the $^{18}$O isotope is used as a tracer.$^{[18]}$ It is shown that for an oxygen pressure $>10^{-2}$ mbar, the oxygen background gas pressure is the most important source to contribute to the oxygen composition of the as-grown thin films, instead of the oxygen from target or substrate. When growing films at $10^{-1}$ mbar on $^{18}$O$_2$ exchanged substrates, it is stated that almost all oxygen originates from the background gas and almost none from the substrate or target. These studies identify the complex role ascribed to oxygen in the PLD process and subsequent characteristics of the grown film, explaining the typical narrow pressure window in which a desired composition and crystalline structure is obtained.

### 1.4 Scope of this thesis

Clearly, the characteristics of PLD grown oxide thin film such as morphology, structure and electrical properties are the result of a complex interplay between growth parameters affecting plume dynamics, chemistry and surface growth kinetics and chemistry. It has been shown that specifically oxygen plays an important role in these processes, where the oxygen in the grown film, depending on background gas conditions, originates from the target, the background gas and/or substrate. Nonetheless, still limited are detailed studies on plume chemistry and composition in relation to surface growth characteristics and chemistry, resulting in specific film characteristics. Here, especially required is a focus on the sources and role of oxygen and species oxidation. Film characteristics include not only film stoichiometry and structure, but also growth kinetics studied with RHEED. Furthermore, several studies have focussed on investigating the composition of the plume with OES. These measurements rely on spontaneous emission and can deliver valuable information. However, the analysis of spontaneous emission yields reliable results only in the early stages of plasma expansion when the plasma is still very hot. Interpretation of results in later stages of propagation is difficult, especially at higher background gas pressure when the plume thermalises and the plume self emission is significantly reduced.

In this thesis, an investigation on the propagation dynamics and composition of laser ablated SrTiO$_3$ and YBiO$_3$ plasmas is outlined. The results are related to an investigation of growth and structural characteristics of thin films of these materials. SrTiO$_3$ is chosen as it is widely used as model material system for fundamental studies on the influence of growth parameters on oxide thin film characteristics such as crystal structure and surface morphology.$^{[29-31]}$
For the characterisation of the plasma plume, optical self emission imaging and OES is used. Furthermore, the spatiotemporal mapping of simultaneously present species in these complex oxide plasmas using Laser Induced Fluorescence (LIF) gives an unique insight in the composition and element specific characteristics of the plume. The research presented in this thesis was carried out in parallel and close collaborations with the Laser Physics and Non-Linear Optics group at the University of Twente. The LIF studies including theory, experimental background and results which are presented in this thesis, have been thoroughly overviewed in the thesis of Kasper Orsel Ph.D.\[33\]

The studies on SrTiO$_3$ plume and film characteristics show a clear dependence between the oxidation of species in the plasma plume and film growth characteristics, including growth kinetics and film cation (non)stoichiometry. Furthermore the initial growth of homoepitaxially grown SrTiO$_3$ is investigated in specific pressure conditions. From these studies, the role of oxygenation through the substrate on the stoichiometry of the grown film is discussed. Subsequently, results and observations are extrapolated to material system containing a volatile element, by investigating the relation between plume and film characteristics of grown YBiO$_3$ thin films, containing volatile bismuth.

## 1.5 Thesis outline

This thesis consists of five chapters. Chapter one gives an overview on current state knowledge and challenges that are identified from studies focussing on understanding and elucidating relevant physical mechanisms in PLD. From this the motivation of the work outlined in this thesis is presented.

Chapter 2 outlines a general overview on laser ablation characteristics and the experimental methods that were used to investigate laser ablated plume dynamics and composition, including OES and LIF. Next, an overview is given on the experimental methods used for sample fabrication and characterisation.

Chapter 3 outlines the investigation on the propagation dynamics and composition of laser ablated SrTiO$_3$ plasma studied by OES and LIF. A specifically relevant gas pressure range is defined which is the focus of further growth studies in this thesis. It is shown that within this range, with increasing oxygen background gas pressures, gradual oxidation of species occurs.

In chapter 4, the results on plume composition are related to SrTiO$_3$ film growth studies. A clear relation between the oxidation of titanium and grown film characteristics is observed. From RHEED and X-ray Diffraction (XRD) studies, stoichiometric SrTiO$_3$ growth under nonstoichiometric growth conditions is understood by oxidation of species where the oxygen originates from the substrate.

In chapter 5, the performed studies are extrapolated to a material system, YBiO$_3$, containing volatile bismuth, which typically challenges optimisation of growth parameters. It is shown that yttrium strongly oxidises under all conditions, where limited chemical interaction of plume species with the background gas
is observed. Furthermore, the structure of grown films, investigated with XRD and X-ray Photoelectron Spectroscopy (XPS), strongly depends on background gas conditions, where at low pressure no bismuth is incorporated in the film. These observations are related to the investigated plume composition, where no clear correlation is observed between plume and film composition. Therefore, an additional role of oxygen background gas on target and substrate surface chemistry is discussed.
Chapter 2

Pulsed laser deposition plume and film characterisation

2.1 Introduction

For the investigation of laser ablated plasma in a Pulsed Laser Deposition (PLD) experiment, in relation to grown film characteristics, several experimental methods have been used which are outlined in this chapter. First, a brief overview on relevant mechanisms involved in material laser ablation is given. A theoretical model on plasma plume dynamics is proposed which is applied to obtained results on the optical self emission imaging experiments outlined in chapter 3. The experimental setup for the optical self emission imaging and Optical Emission Spectroscopy (OES) measurements is overviewed. Next, a brief introduction is given on Laser Induced Fluorescence (LIF), overviewing the basic methodology and experimental setup. It is again noted that LIF measurements have been performed and previously overviewed in the thesis of Kasper Orsel Ph.D.,\[33,34\], where a thorough and elaborate overview can be found regarding all relevant theory and details on the used experimental setup and methods. Lastly, the SrTiO$_3$ and YBiO$_3$ thin film growth experiment methods are outlined including experimental techniques used for the characterisation of the grown films, with focus on film growth characteristics, morphology and stoichiometry.

2.2 Pulsed laser ablation characteristics

When a target material such as a metal or complex oxide ceramic is ablated with a high intensity laser, a plasma of material is formed and expands normal to the target surface. This ‘plume’ of particles consists of excited or ground state neutrals, electrons and ions. A schematic impression of the various stages of the ablation process in Fig. 2.1. When using a laser with a pulse length of several nanoseconds
or longer, the ablation and deposition process can be described in five different stages.\(^1\) The stages are not completely separated and overlap in time.\(^{15,35}\)

1. The laser light interacts with the target and is absorbed mainly by the electrons in the material.\(^{10,36}\) The electrons transfer their energy to the atoms in the solid in a period of tens of picoseconds, resulting in a strong heating of the radiated volume. This stage is dominated by laser-solid interactions.

2. Over a range of tens of picoseconds to tens of nanoseconds, a thin layer of vapour is created by material ejected from the heated volume of the target. This vapour continues to absorb energy from the laser, resulting in a strongly ionised plasma at the surface of the target, consisting of singly or multiply ionised target components. Considering a typical complex metal oxide ABO\(_x\) target stoichiometry this results in e.g. A\(^+\), B\(^+\), O\(^+\), A\(^{2+}\), etc. This stage is dominated by laser-gas or laser-plasma interactions.

3. After the laser pulse has ended, in the range between tens of nanoseconds and several microseconds, the plume expands adiabatically. Simultaneously, there are collisions and chemical reactions of the plasma constituents. When ablating in vacuum, this is the final stage where the shape, chemical and velocity distribution of the plasma plume reaches asymptotically constant values expanding ballistically in a highly forward directed plume. In this

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\(^1\) Widely used for PLD applications are KrF excimer laser at 248 nm, with a typical pulse length of 20-30ns. These type of lasers were among the first to meet necessary requirements for material ablation and thin film deposition research, i.e. energy density, pulse stability, general straightforward operation and handling. Occasionally other specification lasers are used for film deposition purposes such as Nd:YAG lasers, that operate at 1064 nm or at 2\(^{nd}\), 3\(^{rd}\) or 4\(^{th}\) harmonic, respectively 532 nm, 355 nm or 266 nm. Next to a different wavelength, also pulse characteristics such as pulse length are different which alters the ablation process and plume film characteristics which must be taken into account when optimising parameters.
stage, most of the ions in the plasma plume recombine with electrons from the plasma to become neutrals.

4. When target ablation takes place in an (oxygen) background gas, expansion starts ballistically. However, after several microseconds, the interaction of the plume constituents with the background gas dominate the plume expansion. At this stage, the plasma consists of ions (A\(^+\), B\(^+\)), atoms (A, B, O) and molecules (AO, BO, O\(_2\), AO\(_2\), BO\(_2\), etc, depending on species oxidation states). All of these constituents are to be considered as highly dynamic, as the concentrations of these species are depending on the location in the plume and are expected to show rapid changes as well.

5. The plasma plume reaches the substrate after several microseconds in vacuum, or tens of microseconds in a background gas. The plasma constituents, including the oxygen from the background gas if present, interact with the substrate, which leads to the growth of a thin film of material.

This schematic shows that even in the case of congruent material ablation, which means that the stoichiometry of the target is maintained in the atomic species present in the plasma in the first two stages, the ratio and chemical state in which they arrive at the substrate is not intrinsically stoichiometric. Material density, distribution, velocity and oxidation state vary during the subsequent stages during plume expansion. As part of this thesis, the background gas dependent propagation dynamics of the expanding plume is investigated, which results are understood in a kinetic model to be discussed in the next section.

### 2.2.1 Propagation dynamics

Several studies have outlined kinetic models to understand and describe the complex expansion of a laser ablated plasma plume based on an adiabatic expansion.\(^{15}\) Furthermore, it is observed that a temperature gradient introduced by a heating geometry affects the local gas density and reduces resistance of the background gas on the plume propagation.\(^{22,37,38}\) Inspired by these models, here a straightforward kinetic model is introduced which is used in chapter 3 to describe the behaviour of an assigned front position of the plume. The model includes the influence of a temperature gradient which is assigned to affect the gas density of the environment by assuming the ideal gas law.

First, to describe the front position of the plume, a simple kinetic model is proposed, describing the drag force on a particle propagating through a medium with a certain relative density. The force exerted on a particle travelling through a medium can be expressed as:

\[
F_d = -C_d n_g(x) v(x)
\]  

(2.1)

with a drag constant \(C_d\), a local density \(n_g(x)\) and particle velocity \(v(x)\) at a spatial position \(x\), which here is the position of the particle when travelling from target
Figure 2.2: Schematic representation of a kinetic model describing the propagation of a particle with initial velocity $V_0$ travelling through a medium, experiencing a drag force due to a medium density $N_g(T(x))$. A substrate with radius $r_1$ and temperature $T_1 > T_0$ induces a density gradient from substrate to target.

to substrate, as indicated in Fig. 2.2. From the equations of motion, the drag force is rewritten as $F_d(x) = m_p a(x) = m_p \frac{dv(x)}{dx} \frac{dx}{dt} = m_p \frac{dv(x)}{dx} v(x)$, with $m_p$ the mass of the particle. Substitution in 2.1 results in:

$$-C_d n_g(x) dx = m_p dv(x)$$

This leads to an expression for the velocity of a particle at position $x$:

$$v(x) = v_0 - \frac{C_d}{m_p} \int_0^x n_g(x) dx$$

(2.3)

To introduce the effect of temperature on local density the ideal gas law is used in which an isobaric process ($\Delta P = 0$) is assumed. From this assumption the ideal gas law easily relates the normalised density and the temperature at constant volume and pressure as follows:

$$n_g = \frac{PV}{RT} \rightarrow \frac{n_g(r)}{n_0} = \frac{T_0}{T(r)}$$

(2.4)

This shows that the normalised density is equal to the inverse of the normalised temperature. Next step is therefore to determine the local temperature $T(r)$, when a temperature gradient occurs due to heating. Instead of a 1D temperature gradient model which is used in other studies [37], here a 2D spherical heating gradient is used, which represents the actual geometry more accurately. Generally, the rate of heat transfer through a spherical shell is as follows:

$$Q_c = -kA \frac{dT}{dr}$$

(2.5)

with $A$ the surface of the shell and $k$ the gas thermal conductivity. Without discussing detailed derivations, assuming an ideal monoatomic gas with atomic

\footnote{A pressure difference in a vacuum chamber would result in a flow of gas, which is assumed to be unlikely.}
mass $M$, for the thermal conductivity it is given that $k \propto \sqrt{\frac{T}{M}}$. For a half shell situation substitution results in:

$$Q_c = -\sqrt{\frac{T}{M}} (2\pi r^2) \frac{dT}{dr} = -2\pi r^2 a T^{\frac{1}{2}} \frac{dT}{dr} \rightarrow -\frac{Q_c}{2\pi r^2 a} dr = T^{\frac{1}{2}} dT$$

(2.6)

where $a = \sqrt{\frac{1}{M}}$ which for the sake of simplicity is a substitution that cancels out in Eq. 2.7, and $A = 2\pi r^2$ is the surface of a half sphere. So this expression relates the change of temperature and the radius of the shell. This gives the general solution for $Q_c$:

$$-\frac{Q_c}{2\pi a} \int_{r_i}^{r} \frac{1}{r^2} dr = \int_{T_i}^{T} T^{\frac{1}{2}} dT \rightarrow Q_c = \frac{4\pi a}{3} \left( \frac{1}{r} - \frac{1}{r_i} \right) \left( T^{\frac{3}{2}} - T_i^{\frac{3}{2}} \right)$$

(2.7)

Subsequently this expression is solved for an upper and lower boundary condition. Considering the physical experimental setup, the typical heating geometry can be approximated with a certain area with radius $r_1$ with a certain setpoint temperature $T_1$ and a substrate at a certain distance $r_2$ with temperature $T_2$. To determine the expression for the temperature $T(r)$ at specific distance from the ‘heated’ radius, the solution for $Q_c$ with lower boundary $r_i = r_1$ and $T_i = T_1$ is equated to $Q_c$ with upper boundary conditions $r = r_2$ and $T = T_2$ into equation 2.7 resulting in an expression for $T(r)$:

$$T(r(x)) = \left[ \left( \frac{1}{r(x)} - \frac{1}{r_1} \right) \left( \frac{r_1 r_2}{r_1 - r_2} \right) \left( T_2^{\frac{3}{2}} - T_1^{\frac{3}{2}} \right) + T_1^{\frac{3}{2}} \right]^{\frac{2}{3}}$$

(2.8)

By substituting $n_g$ in Eq.2.3 with the expression from Eq.2.4, the expression for the velocity of a particle travelling through a medium with a present temperature gradient is given as:

$$v(x) = v_0 - \frac{C_d n_0}{m_p} \int_{0}^{x} \frac{T_0}{T(r(x))} dx$$

(2.9)

The two spatial components $r$ and $x$ as distance from heated substrate to target and vice versa are related as $r(x) = (r_2 - r_1) - x$. Summarising, this kinetic model describes the velocity of a particle starting from a target at position $x = 0$, $r_2$ with initial velocity $v_0$, travelling through a medium with initial density $N_0$ and temperature $T_0$. The velocity of the particle experiences a drag $\frac{C_d n_0}{m_p}$ resulting in decreasing $v(x)$. The density through which the particle travels depends on a temperature gradient from $r_1$ to $r_2$. When $T_1 > T_0$, with $T_0$ as room temperature, the contribution of drag decreases, resulting in an increased velocity at $v(x)$. In section 3.2 this model is used in qualitatively understanding the propagation behaviour of the front of the expanding plume.

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3There is no pressure dependence in the thermal conductivity because increasing the pressure both increases the number density of the gas and decreases the mean free path; these changes exactly cancel for an ideal gas. The thermal conductivity of a ‘real gas’ (i.e., a gas at conditions where it does not obey the ideal gas law) exhibits a dependence on pressure that increases with increased deviation from ideal gas behaviour.
2.3 Optical Emission Spectroscopy

To be able to examine the propagation dynamics model and investigate the plume dynamics and composition, the plume expansion is recorded by imaging the light emitted by the plume using a fast photography setup. Characteristic for a PLD experiment is the clearly visible bright plasma plume as shown in Fig. 2.3, where the colour of the plume depends on the ablated target material. As introduced, this emission of light is the result of the strong increase in temperature of the target material by the absorption of photons of the laser pulse during the ablation process. The plasma generated by the ablation laser is initially very hot (>10,000K) and dense, leading to not only an ablation but also an excitation of internal degrees of freedom of the target constituents that may decay through spontaneous emission.\textsuperscript{[15,36]} This ionised material not only expands due to the high density and temperature gradient with its surrounding, but also emits photons due to the spontaneous decay of these excited energy states from higher to lower levels. Typically a wide spectrum of light is emitted with many spectral lines at wavelengths corresponding to various electron transitions in the excited species. This process is called spontaneous emission, schematically represented in Fig. 2.4.

From the plume self emission, the plume propagating dynamics and composition can be studied by imaging the self emission of the excited plume species with an ICCD fast photography camera and spectrograph setup. The analyses typically involve the investigation of the relative ratios between the intensity of identified neutral or oxide lines. By monitoring these ratios over time, the evolution of the composition of the plasma is studied. Next to composition, other plasma characteristics can be deducted such as excitation and electron temperature. This is discussed more thoroughly in section 3.4. The next section outlines the experimental methods used to perform OES measurements.

![Figure 2.3: A photograph of a PLD experiment with the typical whitish glow of a laser ablated SrTiO\textsubscript{3} plasma plume expanding towards a clamped SrTiO\textsubscript{3} substrate, radiating brightly orange due to the high substrate temperature.](image-url)
2.3 Optical Emission Spectroscopy

Figure 2.4: A simple two energy level diagram representing an atom or molecule with two energy levels, an upper level $E_2$ and lower level $E_1$. On the left a representation of spontaneous emission, where the decay from upper to lower level state results in the emission of a photon. On the right absorption of a photon is represented by blue light, resulting in the excitation from lower to upper level. Subsequently an fluorescence photon is emitted with slightly lower energy and therefore red-shifted.

2.3.1 Experimental setup

The self emission of the laser ablated SrTiO$_3$ and YBiO$_3$ plasmas is detected using an ICCD camera (Andor IStar CCD 334 with GEN 3 18-A3 image intensifier, 380-1090 nm wavelength range, <3 ns optical gate width). In the camera, a photocathode collects light which is converted to electrons. These electrons are accelerated using high voltage gating electronics, where the signal is amplified using a microchannel plate (MCP), depending on the applied potential. The electrons interact with a phosphor screen, which image is subsequently collected on a CCD chip. The MCP functions as a gating mechanism which can be switched extremely fast, determining the gate resolution of as low as <3 ns. For OES, an Andor Shamrock163 Czerny-Turner spectrograph is used, with several 500 nm blaze gratings available varying from 300 lines/mm ($\sim$1.5 nm spectral resolution) to 1200 lines/mm ($\sim$0.34 nm spectral resolution). The camera (and spectrograph) is connected to a two-lens system, which is mounted on a viewport perpendicular to the propagation direction of the plume. When using the spectrograph, the entrance slit is aligned with the propagation direction of the plume. In this way, spectral images consist of one spectrally resolved axis and one spatially resolved axis.

For optimised data acquisition, the gating electronics are triggered externally by the laser, allowing for imaging the plume at specifically well determined delay times from the moment of ablation. Several experimental settings can be altered, with a main focus on obtaining optimal signal-to-noise ratio for reliable data processing. Gate width and MCP gain were adjusted for each image in order to compensate for the reduction of the plume intensity during expansion. The ratio between gate (TTL) width and time delay, or typical time scale of expansion, is kept as low as possible to prevent ‘blurry’ images and obtain a high as possible time resolution. Furthermore, the camera has an integrate-on-chip (IOC) feature which allows multiple measurements to be integrated on the CCD before data collection.
In combination with fast gating this allows for measurements on multiple plumes to reduce noise.

### 2.4 Laser Induced Fluorescence

Next to OES, the element specific composition of laser ablated SrTiO$_3$ and YBiO$_3$ plasmas is studied with LIF, which has specific advantages over OES. The expanding plume undergoes a wide transition in temperature, from elevated temperatures above 10,000K in a partially ionised state to lower temperatures of \(\sim 1,000\)K. The plume only significantly radiates via spontaneous emission in the initial stages of propagation when the plasma temperature is significantly high. But in this initial state the excitation process is to a large extent unspecific due to the thermal nature of the excitation, which excludes quantitative measurements. In later stages of plasma plume expansion the temperature is too low to significantly excite species to allow spectroscopic detection. In order to still obtain spectral information in this stage of the thermalised plume, LIF enables detection of plasma constituents even when the plasma has thermalised and no longer spontaneously emits light. With LIF, in combination with Absorption Spectroscopy (AS), it is possible to identify and map relative density distributions of specific species during PLD plume expansion.

#### 2.4.1 Theoretical and experimental aspects

The fluorescence of species is induced by the absorption of laser photons, exciting atoms and molecules which subsequently relax through spontaneous emission of photons. An excited state typically decays to several different lower levels, including the level from which it was excited. In the latter case, the fluorescence wavelength is similar to the excitation laser. For all other decay channels, the emitted fluorescence has a longer wavelength, i.e., it is red-shifted with regard to the excitation laser, as shown in Fig. 2.4. It is generally desirable to detect fluorescence that is shifted in wavelength. Namely, this allows the use of spectral filters to discriminate the LIF fluorescence from stray light originating from the excitation laser, such as reflected and scattered light at the entrance and exit windows of the experimental setup.

To perform LIF on typical PLD plumes, the necessary specifications of the experimental setups depend on the characteristics of species which are investigated. Most atoms and small molecules have electronic transitions in the UV and visible wavelength region. A most suitable source for light in this range is a tunable dye laser, which can generate light in the range of 400 nm to 900 nm. Frequency doubling the output of the dye laser allows to generate wavelengths in the UV up to 200 nm. Also, the used pulsed lasers should generate sufficiently short pulses of a few nanoseconds duration. In this case, the temporal resolution with which the evolution of the plasma plume can be monitored is limited by the lifetime of the
2.4 Laser Induced Fluorescence

Figure 2.5: A top view schematic of the PLD chamber (a) with two pairs of two aligned ports allowing for a laser light sheet to pass through and excite the species in the plasma plume to generate LIF. No substrate heater is present order to obtain an unobstructed propagation of the excitation laser during plasma analysis. (b) shows a side view of the chamber with two ports on top. One port is used for the access of the ablation excimer laser beam. The second port allows a perpendicular positioning of the ICCD camera with respect to the plume propagation direction to monitor the fluorescence from the plasma plume. Image is adapted from Orsel. [33]

excited state, which for most of the strong atomic lines is in the order of several to tens of nanoseconds.

2.4.2 Experimental setup

For the LIF setup a Twente Solid State Technology B.V. custom built PLD chamber is designed including necessary windows for optical accessibility of the plasma. Ablation of the target material is performed using a Lambda Physik CompexPro 205 excimer laser at a wavelength of 248 nm and a repetition rate of up to 10 Hz. The laser provides up to 600 mJ of energy in a pulse of about 30 ns duration (FWHM). The laser beam is clipped with a 15x4mm$^2$ mask to ensure a (close to) tophat shaped laser beam profile. The beam is imaged onto a target through a simple one-lens optical system resulting in a spot-size of 2.42x0.91mm$^2$. Through control of the laser output energy, the laser fluence at the target is kept constant at $1.3\pm10\% \text{ J/cm}^2$.

Most atoms and small molecules have electronic transitions in the UV and visible region. Therefore, for the generation and detection of LIF an optically pumped (by frequency doubled Nd:YAG laser (Spectra-Physics Quanta-Ray DCR3, 532 nm, 7ns FWHM) dye laser (Spectra-Physics Quanta-Ray PDL-2) is used that generates narrowband light pulses of several ns in time with a tunable wavelength
over a very broad spectral region (540 nm to 900 nm). To extend the range of available excitation wavelengths, a second harmonic generation setup is added, capable of converting the output of the dye laser into the UV region of 270 nm to 450 nm. Using cylindrical telescope optics the LIF excitation beam is transformed into a thin sheet. It illuminates a cross section of the plasma plume in the plane of the forward propagation from the ablation spot on the target to the center of the deposition substrate. The sheet has an in-plane focus of approximately 0.4 mm thickness and a width of 50 mm. For the studies on YBiO₃ plasmas a sintered target consisting of 99.99%-purity Y₂O₃ and Bi₂O₃ in a one-to-one molar ratio was used during all measurements. For the studies on SrTiO₃ plasmas single crystal 10x10x0.5mm² targets were used.

2.5 Thin film growth studies

This section outlines the experimental methods used for the PLD thin film growth studies on homoepitaxial grown SrTiO₃ and YBiO₃ grown on LSAT substrates. During growth the film structure is monitored using in situ Reflection High Energy Electron Diffraction (RHEED). With RHEED the growth rate is monitored and information is obtained on the films surface morphology and structure.

2.5.1 Substrates and targets

Single crystal substrates, SrTiO₃(001) and (LaAlO₃)₀.₃(Sr₂TaAlO₆)₀.₇(LSAT)(001) were supplied by Crystec GmbH, Germany with a typical size of 5x5x0.5mm³ and a miscut angle with respect to the desired crystal plane <0.2°. SrTiO₃ substrates were chemically treated to ensure TiO₂ termination. The substrates were annealed in a tube furnace to achieve ordered terrace steps. Before annealing, the substrates were visually inspected for surface contaminations using an optical microscope. When required, substrates were cleaned using acetone and ethanol under ultrasonic agitation. Subsequently substrate morphology is investigated with AFM to confirm single termination for SrTiO₃ and the presence of terrace steps for all substrates. Samples were glued with Leitsilber silver glue on a flag-style sample plate. Upon loading the substrates into vacuum they were heated to ~150°C in order to cure the glue and clean the sample surface. For SrTiO₃ thin film growth studies, a single crystal 1" round SrTiO₃ target was used. For YBiO₃ thin film growth studies a sintered target consisting of 99.99%-purity Y₂O₃ and Bi₂O₃ in

The UV excitation wavelengths for LIF on both YBiO₃ and SrTiO₃ plasmas as presented in this work in the range from 250 to 350 nm are generated by frequency doubling the output of a dye laser pumped with the second harmonic (532 nm) output of a Q-switched Nd:YAG laser (7 ns FWHM). The UV output has a pulse duration of 4 ns FWHM. Depending on the used dye (to be able to access the wavelength range of interest) for SrTiO₃ studies the UV output had a spectral bandwidth of 8.1 pm and an energy of 75 µJ per pulse, for YBiO₃ a spectral bandwidth of 1.6 pm and an energy of 80 µJ/pulse. For the detection of LIF an intensified CCD camera (Standford Computer Optics 4Picos), equipped with a custom zoom lens system.
a one-to-one molar ratio was in-house fabricated. The excimer laser beam was scanned over the target surface during ablation to prevent drilling.

### 2.5.2 Pulsed laser deposition setup

All films were grown with a PLD system from Twente Solid State Technology B.V. as part of a cluster setup, located at the nanolab, MESA+ university of Twente, Enschede. This cluster setup allows for sample fabrication and analysis in ultra high vacuum (UHV) where the PLD chamber is connected via a central storage chamber to an Omicron Nanotechnolgy GmbH (Oxford instruments) scanning probe microscope (SPM) and an Omicron surface analysis chamber. A 248 nm Coherent LPX excimer laser with a pulse duration of 25 ns was used for ablation of target materials. A rectangular 15x4 mm\(^2\) mask is used to clip the laser beam and herewith creates a well defined and top hat shaped homogeneous laser spot with uniform energy density on the target. The laser energy is controlled and altered using a variable beam attenuator positioned in the optical path. The background gas pressure in the PLD chamber was typically \(\sim 10^{-8}\) mbar.

During deposition film growth was investigated by monitoring the surface structure using RHEED. A STAIB instruments RHEED setup was used for in situ growth monitoring studies operated at 30 keV. In the used setup, RHEED operation is possible for pressures up to 0.3 mbar due to a differential pumping stage.\(^7\) Sample heating was done using a resistive heater or an infrared laser heating system. The resistive heater allows for accurate temperature control up to \(\sim 850^\circ\)C. For higher maximum substrate temperature and fast temperature modulation, a 120W Coherent Quattro FAP laser heating setup is used, directly heating sample plates on which substrates are glued. The maximum achievable sample temperature is 1100\(^\circ\)C. The spot-size of the infrared laser is about 1cm\(^2\) and aligned on the backside of the sample plate before every deposition. The sample plate temperature is measured using an infrared thermometer, for good laser absorption and close to black-body radiation the back of the sample plate is roughened and oxidised.

### SrTiO\(_3\) growth parameters

Growth of homoepitaxial SrTiO\(_3\) was performed at a varying fluence of 1.0, 1.3 and 2.1 J/cm\(^2\). The laser repetition rate was set to 1 Hz. The spot-size on the target was 2.3 mm\(^2\). The target-to-substrate distance was set to 50mm. The background gas pressure was set to varying absolute and partial oxygen pressures as is outlined in more detail in the following chapters, being main focus of this work. The substrate temperature was set to 710\(^\circ\)C and heated using laser heating.\(^5\) After

\(^5\)This somewhat odd number results from preliminary growth studies using the resistive heating setup in which a relatively large temperature gradient is present between setpoint temperature of 850\(^\circ\)C measured with a thermocouple inside the resistive heating element and the actual sample temperature of 710\(^\circ\)C.
growth samples cooled down at a rate of 30°C/min in 100 mbar of oxygen.

**YBiO$_3$ growth parameters**

Growth of YBiO$_3$ on LSAT substrates was done at a fluence of 1.8 J/cm$^2$. The laser repetition rate was set to 1 Hz. The spot-size on the target was 2.3 mm$^2$. The target to substrate distance was set to 50mm. The background gas pressure was set to varying absolute and partial oxygen pressures. The substrate temperature was set to various temperatures at 10$^{-1}$ mbar of oxygen pressure and at 670°C at varying background gas pressure. Samples were heated using laser heating. Samples were cooled down at a rate of 30°C/min in 100 mbar of oxygen.

### 2.5.3 In situ Reflection High Energy Electron Diffraction

During growth, the substrate surface structure is investigated with in situ RHEED. A schematic overview of a typical RHEED-PLD setup and main working principle is shown in Fig. 2.6a. The electron beam is focused on a substrate, under a grazing angle. A photo-luminescent (typically phosphorous) screen in combination with a CCD camera is used to measure the intensity of reflected electrons.

The electrons are reflected of the sample surface, where the crystal structure of the surface gives rise to diffraction peaks on the RHEED screen. Due to the grazing incidence, the electrons only interact with the very top layer of the crystal. Therefore, for an atomically flat surface, the reflected pattern is understood as a diffraction pattern of a two dimensional crystal surface. This pattern is calculated based on the reciprocal lattice structure. In three dimensions, a reciprocal lattice consists of points. However, the reciprocal lattice of a two dimensional crystal is not represented by points, but by lattice rods, due to the reduction of dimension as schematically is represented in Fig. 2.6(b). These rods intersect the reciprocal lattice points of a similar bulk crystal. Diffraction conditions are satisfied where these rods of reciprocal lattice intersect the so-called Ewald sphere. The Ewald sphere construction relates the wavevector of the incident electron beam with the diffraction conditions of a crystal lattice.

The relationship $\vec{k} = \vec{k}_0 - \vec{k}_i$ defines the scattering wavevector $\vec{k}$ as a function of the wavevector of the incident beam $\vec{k}_0$ and the wavevector $\vec{k}_i$ at any intersection between the Ewald sphere and the reciprocal lattice. Here $\vec{k}_0 = 2\pi/\lambda$ is the radius of the Ewald sphere with $\lambda$ being the electron wavelength. $\vec{k}$ therefore relates to the crystal plane spacing. The peak which is found at an angle of reflection equal to the incidence angle is called the specular reflection. Many of the reciprocal rods meet the diffraction conditions. Only a selected few rods give rise to peaks on the RHEED screen, due to the grazing incidence angle of electron beam used in the setup. Intersections of the reciprocal lattice rods with the Ewald sphere lie on concentric circles, called the Laue circles. Therefore, the spots on the RHEED screen, in case of an atomically flat surface and resulting 2D diffraction pattern, lie on these concentric Laue circles as is shown in Fig. 2.7(a). The azimuthal angle of
the sample with respect to the Laue circle is aligned in such a way that a circular pattern is observed perpendicular to the sample surface, i.e., perpendicular to a certain crystal plane orientation. These crystal orientations are labeled with their corresponding in-plane \([hk]\) values.

When the crystal surface is roughened with (small) surface asperities, transmission of electrons yield additional diffraction peaks as can be seen in Fig. 2.7(b). In this case the reciprocal space consists of a three-dimensional lattice instead of two-dimensional lattice rods. The shape of the diffraction spots depends on the size and characteristics of the surface asperities. The collected pattern in this case is formed from the Ewald sphere intersecting this three-dimensional lattice. Such three-dimensional patterns do not show a clear dependence of azimuthal and polar rotations of the sample with respect to the incident electron beam. If only two-dimensional spots are observed, again the sample can be considered atomically smooth and the diffraction pattern is related to the in-plane surface crystal structure of the sample.

The time-evolution of the intensity of the specular spot can be recorded during PLD growth. The intensity scales with the inverted step density on the sample surface; the highest intensity is found for complete coverage at which step density is lowest. During hetero-epitaxial growth, the intensity of the RHEED pattern is also influenced by the type of scattering atoms and their scattering cross-sections. Alternatively, instead of monitoring the intensity of the specular spot to study the formation of layered thin films, the full-width-half-maximum (FWHM) of the peak shape may also be investigated. The FWHM roughly scales inversely with the
2.6 Thin film characterisation

Before and after growth, the sample surface morphology, structure and stoichiometry were studied using various techniques. The sample morphology is investigated with Atomic Force Microscopy (AFM). Sample structure, stoichiometry and thickness is investigated with X-ray diffraction (XRD) diffraction and X-ray Reflectivity (XRR). A theoretical tool used for fitting and quantifying XRD measurements is overviewed. Sample composition and stoichiometry is investigated using X-ray Photoelectron Spectroscopy (XPS).

2.6.1 Scanning Probe Microscopy

Sample surface morphology was measured using AFM (Bruker ICON Dimension AFM). Height information is obtained by monitoring the position of laser spot which is reflected at the top of the tip-cantilever. AFM is performed in tapping mode (TM), where the tip is oscillated close to its resonance frequency. The amplitude of the oscillation is reduced when the tip approaches the sample surface. Moreover, the phase signal is a measure of the samples elasticity, adhesion and friction interactions with the tip.
2.6 Thin film characterisation

2.6.2 X-ray Photoelectron Spectroscopy

Thin film stoichiometry and electronic structure were studied using X-ray spectroscopy (XPS). Measurements were performed in situ on an Omicron nanotechnology GmbH (Oxford Instruments) Surface Analysis system, with a background pressure of 5x10^{-11} mbar. Measurements were done using a monochromatic Al Kα X-ray source (XM1000) with a kinetic energy of 1486.7 eV, and analysed using a 7 channel EA 125 electron analyser operated in CAE mode.

2.6.3 X-ray Diffraction

To determine film structure and thickness of the homoepitaxially grown SrTiO$_3$ films and YBiO$_3$ on LSAT films, XRD and XRR experiments were performed using a PANalytical X’Pert MRD. For the homoepitaxially SrTiO$_3$ grown films, a high resolution setup was used including a triple axis analyser on the diffracted beam side and a two-crystal and four-crystal Ge (220) monochromator on the incident beam side.

For the studies on SrTiO$_3$, the out-of-plane lattice parameter is a general indication of cation (non)stoichiometry.$^{[28,42]}$ This is the result of the ionic bonding characteristic of SrTiO$_3$ where its crystalline structure strongly depends on Coulomb interaction of the charged species. Nonstoichiometry and its accommodation in SrTiO$_3$ requires the arrangement of charged species in the SrTiO$_3$ system accordingly. Theoretical computations$^{[43,44]}$ and experimental observations$^{[45]}$ present the effect of the Coulomb interaction on the crystalline structure of STO.$^6$ The overall reaction to a deviation of stoichiometry, causing a certain vacancy type of defect, is an outward response of the first nearest neighbour atoms due to Coulomb repulsion, resulting in a chemical induced strain.$^{[44]}$ Therefore, films exhibiting c-axis values comparable to bulk SrTiO$_3$ of 3.905Å can be regarded as stoichiometric, where a lattice vacancy induces chemical strain resulting in an increase in volume of the unit cell and an increased c-axis for in-plane strained films. Although this chemical strain depends on the nature of the vacancy in this work only the general lattice expansion is investigated as indication of (non)stoichiometry.$^7$

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$^6$A detailed overview on SrTiO$_3$ defect chemistry is given in the Ph.D thesis work “Defect Engineering of SrTiO$_3$ thin films for resistive switching applications” by Wicklein.$^{[46]}$

$^7$Regarding the specific nature of defect vacancies, it is stated that the ratio of chemical strain $e_c$ to stoichiometry defect deviation $\delta$ for $V_{Sr}$ (0.030) is significantly lower than for $V_{Ti}$ (0.402). Although an oxygen vacancy $V_0$ tends to cause a relatively large lattice expansion, the resulting strain is low since the elongation is predominantly along the $Ti - V_0 - Ti$ direction and attraction along the $O - V_0 - O$ direction, where both reaction almost zero each other out with $e_c/\delta = 0.001$. Also, if an oxygen vacancy is introduced near a cation vacancy to form a di-vacancy the strain tensor is reduced since the oxygen vacancy locally compensates and shields the electrostatic potential and reduces the chemical strain, respectively $e_c/\delta(V_{SrO}) = -0.008$ and $e_c/\delta(V_{TiO}) = 0.26$. Nonetheless it is concluded that generally Ti vacancies have a much stronger effect on chemical strain than strontium vacancies, concluding that in the case of a significant lattice expansion, even in the case of a sample with Sr/Ti composition ratio < 1 as determined from for instance quantitative XPS, likely still Ti vacancies are present, suggesting a more complex structure instead of just Sr or SrO vacancies.$^{[44]}$
The SrTiO$_3$ film lattice parameter with respect to the substrate is measured by performing symmetrical $\theta$-2$\theta$ scans with which the out-of-plane lattice constant of the film and substrate is determined. For a more thorough quantification of these results, a model is used and fitted, from which relevant parameters can be obtained, such as accurate film thickness, lattice expansion and crystallinity. This model and simulation is created by Dr. S. Stepanov and is a recognised web service for remote X-ray calculation which can be accessed and addressed through a remote server.\[47\] The model requires various parameters characteristic for the thin film layer stack and substrate for the simulation of the corresponding X-ray diffraction characteristics, not outlined in detail here.\[48,49\] An overview of a typical measurement and simulation is given in Fig. 2.8. Most important parameters for this work as input in the simulation model are the out-of-plane lattice constant of the film with respect to the substrate ($\delta a/a$) with ($a$) the substrate lattice constant and $\Delta a$ the deviation of the film lattice constant with respect to the substrate. This determines the position of the film Bragg reflection. Next, the film thickness ($d(\text{Å})$) which determines the shape of the film peak and the Laue fringe periodicity. Then the interface roughness ($\sigma$) which affects the matter of decay of the diffracted signal (and fringe amplitude) at angles away from the film or substrate peak. Lastly the Debye-Waller coefficient $W_h$, which is a
correction factor for thermodynamic effects such as the measure of the movement of atoms with a value between zero and unity where this also can be used to describe amorphousness or a lacking crystallinity. In the simulation this affects the amplitude of Laue thickness fringes, as they are a result of the coherence between individual layers in the film.\textsuperscript{8} In chapter 4 these simulations are used to quantify XRD measurements on homoepitaxially grown SrTiO\textsubscript{3} films, giving insight in the detailed characteristics of these films.

\textsuperscript{8}Jasper Smit MSc. is acknowledged for his internship work at Stanford University, during which a Matlab Gui is designed for conveniently simulating XRD measurements based on the Stepanov simulation program.\textsuperscript{[50]}
Chapter 3

Controlling oxidation in SrTiO$_3$ plasmas

Abstract
The propagation dynamics and spatiotemporal element specific composition of laser ablated SrTiO$_3$ plasmas is investigated with Optical Emission Spectroscopy (OES) and Laser Induced Fluorescence (LIF). The propagation dynamics undergo a transition from ballistic to diffuse and thermalised propagation which occurs in a relative small pressure regime between $10^{-2}$ and $10^{-1}$ mbar. In this regime, a strong dependence of oxidation of plume constituents on background gas pressure conditions is observed. With LIF, spatiotemporal element specific distribution of Ti, TiO and SrO with LIF is mapped. Oxidation of species occurs especially in the front edge of the plume. For Ti a gradual oxidation occurs with increasing partial oxygen pressure, which is absent for Sr which appears to oxidise strongly. The oxidation from the background gas, not so much the target, is responsible for species oxidation.

Part of the work discussed in this chapter is published in: Kasper Orsel, Rik Groenen, Bert Bastiaens, Gertjan Koster, Guus Rijnders and Klaus Boller, Influence of the oxidation state of SrTiO$_3$ plasmas for stoichiometric growth of pulsed laser deposition films identified by laser induced fluorescence, APL Materials 3, 106103, 2015. [51]
3.1 Introduction

PLD film growth is characterised by a complex interplay between adjustable growth parameters affecting plume dynamics, chemistry and subsequent surface kinetics and chemistry of arriving adatoms, as has been introduced in chapter 1 and 2. Typically it is understood that film stoichiometry is determined by the kinetics and stoichiometry of arriving particles, but is also affected by oxygen originating from several sources. This includes the target, the substrate and background gas, which oxidises plume species or arrived adatoms at the surface. The contribution of each source strongly depends on the background gas conditions. To identify the relation between plume and film stoichiometry and the role of these sources of oxygen, a detailed understanding of the chemical nature of arriving species is required.

This chapter outlines a detailed study on the characteristics of the laser ablated \( \text{SrTiO}_3 \) plasma plume. The spatial and temporal distributions of individual constituents in the plasma plume are investigated, focussing on the relation between background gas conditions and plume dynamics and chemistry. As outlined in chapter 2, for the investigation of plume characteristics, OES and LIF studies have been performed. First the plume propagation dynamics at varying background gas pressures is investigated by recording the plume self emission during propagation. It is shown that transition from ballistic to diffuse propagation occurs in a relative small pressure regime between \( 10^{-2} \) and \( 10^{-1} \) mbar of oxygen or argon pressure. In similar (partial) oxygen background gas conditions OES measurements are performed to investigate the plume composition. The OES studies show a gradual oxidation of species with increasing partial oxygen pressure. Based on a detailed identification of spectral lines and corresponding electron energy levels, the excitation temperature of the expanding plume at varying background gas conditions is discussed.

Subsequently, LIF measurements are overviewed from which the spatiotemporal element specific plume composition is determined in varying background gas conditions. These measurements verify the gradual oxidation of Ti as observed with OES. Also, for partial oxygen pressure \( >8 \cdot 10^{-2} \) mbar no significant amount of Ti neutrals arrives at the substrate. These results are used and discussed in chapter 4 in relation to \( \text{SrTiO}_3 \) thin film growth studies in similar growth conditions.

3.2 Plume propagation dynamics

The propagation dynamics of the \( \text{SrTiO}_3 \) plume were investigated by imaging the plume self emission with a gated intensified charge-coupled device (ICCD) camera, allowing a short time resolution of \( \sim 5 \) ns. The propagation dynamics were recorded by time-lapse imaging, by changing the time delay between the laser and the gating pulse to the ICCD. Plume expansion was recorded from the moment of ablation to \( \pm 200 \) \( \mu \)s after ablation in a range of background gas conditions. The
3.2 Plume propagation dynamics

Oxygen background gas pressure was set to values between $10^{-6}$ mbar to $10^{-2}$ mbar with logarithmic increments and subsequently to $10^{-1}$ mbar with linear increments of $2 \times 10^{-2}$ mbar. Furthermore, partial oxygen pressure settings have been investigated, where oxygen is mixed with argon keeping a constant total pressure of $8 \times 10^{-2}$ mbar. Laser fluence for all measurements was set to 1.3 J/cm$^2$ with a spot size on the target of 2.3 mm$^2$.

Figure 3.1 shows false colour normalised intensity maps of the expanding plasma plume at three pressure conditions of $10^{-1}$ mbar, $10^{-2}$ mbar and $10^{-3}$ mbar at three different delay times after ablation. The measurements performed at pressure conditions below $10^{-3}$ mbar show nearly identical self emission intensity maps. For pressures $\leq 10^{-3}$ mbar the plume expands rapidly, where the (visible) front of the plume arrives at the substrate at 50 mm at $\sim 5 \mu$s. For $10^{-2}$ mbar, the plume also rapidly expands, but slight plume confined is observed due to increasing interaction with the background gas. At $10^{-1}$ mbar, strong plume confinement is observed already in initial stages of propagation, at 1 $\mu$s. Also, the general propagation velocity significantly decreases. This is clearly observed when comparing the middle images, both at 4 $\mu$s after ablation. The front of the plume arrives at the substrate after $\sim 20 \mu$s.

For the remainder of this work, the transition in propagation dynamics in the narrow pressure regime of $10^{-2}$ mbar and $10^{-1}$ mbar is a key observation. All plume investigation and film growth studies are performed in this specific pressure regime.

For pressure conditions between $10^{-2}$ and $10^{-1}$ mbar, intensity maps were recorded at smaller pressure increments of $2 \times 10^{-2}$ mbar. For a qualitative comparison of propagation dynamics, a plume front position at each delay time was determined. This front was determined by discretising the normalised self emission maps with an intensity threshold, above which the intensity is interpreted as representing (excited) species in the plasma plume. Although the value of this threshold has no physical substantiation, it is a valid approach to process the intensity maps to qualitatively investigate the propagation dynamics of the plume. Changing the threshold leads to an overall minimal shift of the front position curves, but qualitative conclusions in general kinetic behaviour can still be drawn.

Figure 3.2(a) shows the front position against the delay time (black asterisks) in a pressure range of $10^{-2}$ to $10^{-1}$ mbar of oxygen background gas pressure. At $10^{-2}$ mbar (and below, not shown), a linear relation between front position and time is observed, indicating a ballistic expansion. For increasing pressure, the front of the plume slows down significantly. To quantify these curves, the propagation model introduced in chapter 2, Eq. 2.9, is used and fitted to the measurements.

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1 Camera settings as introduced in section 2.3 were optimised for every specific pressure and delay time setting to obtain a significant signal-to-noise ratio. The intensity maps therefore have a very qualitative nature. Settings for TTL gate width, pulse integration and MCP gain for the measurements were set to respectively 5 ns for all delay times except for the measurement at $10^{-1}$ mbar and 20 $\mu$s (25ns), integration of 5 pulses for the measurements at 1 $\mu$s and 10 pulses for the other delay times and an increasing MCP gain with increasing delay time of 1500, 1500 and 4095 (arb. units) for $10^{-1}$ mbar and 1500, 2200 and 3000 (arb. units) for $10^{-2}$ mbar.
Controlling oxidation in SrTiO$_3$ plasmas

![Figure 3.1](image)

**Figure 3.1:** Normalised self emission intensity maps of the expanding SrTiO$_3$ plume over time at $10^{-1}$, $10^{-2}$ and $10^{-3}$ mbar. Delay time after ablation is indicated in the bottom left corner of each intensity map. Intensity maps recorded for pressures $\leq 10^{-3}$ mbar are (nearly) identical.

shown by the solid coloured green, red and blue lines. It is noted that in the model no spatial temperature gradient $T(x)$ is included, as the presented measurements have been performed at room temperature.\(^2\) The model shows that for lower pressure conditions, the front position expands linearly with an initial constant velocity $v_0$ (in green). The subsequent slowing down is quite well fitted by the model (red curve). For expansion in $10^{-2}$ to $4 \cdot 10^{-2}$ mbar background pressure, the drag model describes the full behaviour of the plume front position from target to

\(^2\)Although a temperature gradient induced by a heater does affect the propagation of the plume, in the model understood by a local density decrease towards the heater, the grown films described in chapter 4 are heated locally with laser heating. It is verified with the model and empirically that this geometry of heating does not significantly affect the plume dynamics. In the case of resistive heating, including a significantly larger heated area, the affect of this temperature gradient is much more profound and must be taken into account when performing a pressure dependent study.
3.2 Plume propagation dynamics

Figure 3.2: Propagation dynamics of the expanding SrTiO$_3$ plasma plume within an oxygen background gas pressure range from $10^{-2}$ to $10^{-1}$ mbar, fitted with a propagation model. (a) shows the position of the front of the plasma as function of the propagation time at various background gas pressure settings. For pressure $>6\cdot10^{-2}$ mbar, a transition from a drag to a diffuse propagation occurs (blue line). (c) and (d) show the values for fit parameters in the model, the prefactor $C_{dn_0}$ (c) and the velocity of the front of the plume at 50 mm (d).

For the measurements at $\geq 6\cdot10^{-2}$ mbar, the drag model does not fully describe the expansion behaviour of the plume anymore. Instead of a continuous decrease in front velocity suggested by the drag model, the plume expansion in later stages of propagation shows a linear dependence on time. This indicates a constant

\[ C_{dn_0} = 2.3 \pm 10^5 \]

A relative constant value for the prefactor $C_{dn_0}$ is found, which includes the species mass and the normalised gas density. Here no further attention is given to a deepened physical understanding, as this model is mainly used for a qualitative description.
Controlling oxidation in SrTiO\textsubscript{3} plasmas

velocity of the front position. This is understood as a transition from drag to diffuse propagation, indicated with the blue line. The velocity of the front at the position of the substrate (50 mm) is shown in Fig. 3.2(d). the velocity strongly decreases from $\sim$14.5 km/s to $\sim$1 km/s.\textsuperscript{4}

Summarising, the pressure dependent propagation dynamics of (the front of) the plume can be described in three ‘regimes’:

- Near ballistic regime, ballistic plume expansion in $<10^{-2}$ mbar pressure, the front velocity is constant <13 km/s
- Drag regime, significant slowing down of the plume for pressure $>10^{-2}$ mbar. A simply drag model describes the front position of the plume at pressure in between $10^{-2} \leq 4 \cdot 10^{-2}$ mbar
- Diffuse regime, the front position of the plume moves with constant velocity <2 km/s for pressures $\geq 6 \cdot 10^{-2}$ mbar, after initial drag behaviour.

Although these measurements have been performed in absolute oxygen pressure, similar self emission imaging measurements have been performed in argon pressure (not shown here). Similar plume propagation behaviour and expansion dynamics were observed at equal pressure conditions, which has also been observed in other studies.\textsuperscript{[52]} Also, when using mixtures of argon and oxygen, the propagation dynamics of the plume only depends on the absolute total pressure. This observation enables to tune and separate plume kinetics from species oxidation by using partial oxygen pressure settings, as is discussed in the next section.

**3.3 Plume composition with Optical Emission Spectroscopy**

The plume composition at varying background gas conditions was investigated by performing OES measurements on the plume expansion. The self emission of the expanding SrTiO\textsubscript{3} plume was projected onto the entrance slit of an imaging spectrograph with a 300 lines/mm 500 nm blaze grating, coupled to an ICCD camera. The entrance slit of the spectrograph was oriented in line with the plume expansion direction. This results in images with spectral wavelength (nm) on the x-axis and propagation distance z(mm) on the y-axis. System settings were set to obtain optimised signal to noise ratio, at minimised TTL width settings.\textsuperscript{5}

Assuming atomic Ti(47.9u) and Sr(87.6u) species are present in the front of the plume, their kinetic energies at these velocities translates to $\sim$10-100 eV at $\leq 10^{-2}$ mbar and $\sim$0.1-0.5 eV at $10^{-1}$ mbar, comparable to values observed in other work.\textsuperscript{[17]}

\textsuperscript{5}Settings for TTL gate width for $10^{-1}$ mbar and $10^{-2}$ mbar with increasing delay time are respectively 20 ns, 40 ns, 120 ns and 50 ns, 50 ns, 100 ns. Images result from the integration of 10 pulses for the measurement at 2 \textmu s at $10^{-2}$ mbar, for all other measurements images are the integration over 20 pulses. The MCP gain was for all measurements set at a maximum value of 4095(arb. units).
Figure 3.3: Time-resolved OES on the expanding plume. (a) shows normalised spectra at three different delay times at $10^{-1}$ mbar oxygen pressure, where (b) shows spectra at $10^{-2}$ mbar oxygen pressure. Lines have been identified corresponding to neutral and single oxidised Sr and Ti species.

Figure 3.3 shows OES measurements of the expanding SrTiO$_3$ plume in a wavelength range of $\sim$ 430-670 nm at an oxygen background gas pressure of $10^{-1}$ mbar (a) and $10^{-2}$ mbar (b). These values are the outer limits of the investigated pressure range. Measurements are shown for three different delay times. The spectra show spectral lines corresponding to mostly exited neutral Ti, Sr and oxidised species. Emission lines corresponding to mostly neutral Sr and Ti are present at shorter wavelengths in between 450 nm and 500 nm, where lines corresponding to oxidised species are present at longer wavelengths in between 600 nm and 670 nm. For the measurements at $10^{-1}$ mbar, shown in Fig. 3.3(a), a decrease in the intensity of spectral lines corresponding to neutral species is observed over time. Simultaneously, spectral lines corresponding to oxidised species increase in intensity. At $10^{-2}$ mbar, presented in Fig. 3.3(b), the intensity of the lines corresponding to neutral species with respect to oxidised lines remains significantly higher over time. It is noted that the delay times of the selected spectra.

To identify and assign the various lines various databases were consulted. Furthermore, spectra from an SrO and TiO$_2$ target were investigated. Lines were identified based on comparison of the various spectra. A detailed identification of individual transitions in terms of electron energy levels is not possible, because due to the limited resolution of the used grating in these measurements, the observed lines are actually groups of many lines and therefore many transitions.
do not correspond. These spectra have been chosen to show the compositional evolution of the plume from the time of ablation to the time of interaction with the substrate. The plume expands much more rapidly at lower pressure, therefore shorter delay times have been chosen.

To exclude the difference in propagation dynamics for these two presented pressure conditions, similar measurements were performed in partial oxygen pressure at a total pressure of $8 \cdot 10^{-2}$ mbar. Figure 3.4 shows emission spectra at three different delay times, at $10^{-2}$ mbar partial oxygen pressure, at a total pressure of $8 \cdot 10^{-2}$ mbar. Unlike respectively near full oxidation or lacking oxidation for $10^{-1}$ mbar and $10^{-2}$ mbar total oxygen pressure, here a gradual increase in spectral line intensity corresponding to oxidised species is observed over time. In later stages of propagation, spectral lines corresponding to both neutral and oxidised

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Footnote: A specific value of $8 \cdot 10^{-2}$ mbar is based on film growth experiments as outlined in chapter 4. At $8 \cdot 10^{-2}$ mbar oxygen pressure films of homoepitaxial grown SrTiO$_3$ films near perfect stoichiometric growth is observed. The plume propagation dynamics studies outlined earlier show plume thermalisation occurring at total pressure above $6 \cdot 10^{-2}$ mbar. Therefore, to investigate the role of plume propagation dynamics and oxidation in relation to this near perfect growth, a total pressure of $8 \cdot 10^{-2}$ mbar is used, varying partial oxygen pressure, excluding plume species kinetics. The investigation of film growth using partial oxygen pressure, at high total pressure at which strong plume confinement and species thermalisation occurs, is of main focus in the remainder of this work.
3.3 Plume composition with Optical Emission Spectroscopy

Figure 3.5: Ratio between maximum relative intensities of (groups of) spectral lines corresponding to TiO at a wavelength of $\sim 625$ nm and Ti at a wavelength of $\sim 500$ nm. A clear increase in TiO/Ti with increasing partial oxygen pressure is observed.

species are significantly present.$^8$

To study the oxidation behaviour of Ti over time, in Fig 3.5 the time dependent ratios between the intensities of (a group of) TiO lines at $\sim 625$ nm and a (group of) Ti lines at $\sim 500$ nm are shown.$^9$ In the first stage of propagation up to 8 $\mu$s, a trend in ratio is observed where, with increasing partial pressure, the TiO/Ti ratio increases. After 8 $\mu$s, although the ratio at $10^{-2}$ and $2 \cdot 10^{-2}$ mbar still increases, the ratio for $4 \cdot 10^{-2}$, $6 \cdot 10^{-2}$ and $8 \cdot 10^{-2}$ mbar decreases. This decrease is unlikely explained by an actual decrease in oxidation. More likely, as the spectral line corresponds to monoxidised species, for the higher background gas pressures monoxide species oxidise to higher oxidised states, or TiO to TiO$_2$.\(^{10}\) Also, at higher delay times, the OES signal becomes significantly weak due to the thermalisation of the plume, where the measurements likely do not accurately represent a relative density ratio of species. Besides the weak line intensity due to thermalisation, the general line intensities in relation to species densities is also affected by the plasma excitation temperature. This is investigated and discussed more thoroughly in the following section.

\(^8\)Settings for TTL gate width with increasing delay time are respectively 50 ns, 50 ns, 200 ns. Images resulted from the integration of 10 pulses for the measurement at 2 $\mu$s, for all other measurements images were integrated over 20 pulses. For the MCP gain all measurements were recorded at a maximum value of 4095 (arb. units).

\(^9\)The intensities values are determined from a plot in which the OES intensity images are integrated over distance, normalised by background noise subtraction. Intensity values are determined from the plot as the maximum value in wavelength ranges corresponding to Ti lines or TiO lines. Error margins are based on relative noise-to-signal ratio determined for every measured intensity value.

\(^{10}\)This is supported in following sections discussing fluorescence studies on plume species.
3.4 Plasma excitation temperature

In an emission spectrum, the intensity or the population of spectral lines depends on the excitation temperature of the plasma described by the Boltzmann relation. From this relation, the excitation temperature of the expanding plasma plume can be determined based on the relative intensity of spectral lines as measured with OES, as is performed in this section.

3.4.1 Local Thermodynamic Equilibrium

An emission spectrum emerges from photons that are emitted from species dependent electronic states which are populated through thermal excitations. To be able to relate the species density to intensity of the emission lines, it is required that all constituents of the plasma are described locally by a certain temperature. When energy and temperature are distributed equally over all degrees of freedom, kinetically, electronic excitation, ionisation, the plasma is in so-called local thermodynamic equilibrium (LTE). In this case, the ratio between populations of two different energy levels is described by:

\[
\frac{N_i}{N_k} = \exp \left( \frac{-(E_i - E_k)}{k_B T_{exc}} \right)
\]

(3.1)

and rewritten to:

\[
\Delta \ln \left( \frac{I_k \lambda_k}{g_k A_k} \right) = \frac{-1}{k_B T_{exc}} \Delta E_k
\]

(3.2)

which relates the plasma excitation temperature to the relative intensity of spectral lines. This relation states that the intensity ratio of two spectral lines \( I_1 / I_2 \) of an element is related to the plasma excitation temperature \( k_B T_{exc} \), with \( E_k \) the energy of the upper level, \( g_k \) the multiplicity of the upper level, \( A_k \) the transition probability and \( \lambda_k \) the wavelength of the transition. This relation uses the relative ratio between spectral lines, where it is not necessary to correct measurements for experimental settings differing per measurement. In this case simply normalised OES spectra can be used. If a plasma is in LTE, the excited state population can be related to the temperature of the plasma and the energy of the state through the Boltzmann equation, eq. 3.1\(^{[54]} \). These plasmas are typically characterised with high temperatures, pressures and number densities of species.

Whether PLD plasmas are in LTE is subject of debate. A way to investigate this is to examine the electron density of the plasma through Stark broadening measurements, measuring the broadening of lines caused by collisions of electronics and emitting atoms.\(^{[55]} \) As this electron density needs to be significantly high, LTE likely only applies in the early stages of ablation in the centre part of the plume. Another approach to determine LTE is to separately determine the excitation, ionisation, and kinetic temperature of the plasma plume. If these have large differences, the system cannot be described accurately with a temperature and the LTE condition is not met.\(^{[56,57]} \) Generally for PLD plasmas, LTE likely
3.4 Plasma excitation temperature

Figure 3.6: Normalised OES measurements at three different delay times, 1 µs, 4 µs and 1 µs at 8·10^{-2} mbar total oxygen pressure and 2.1 J/cm² fluence. On the left the measured spectra are shown, on the right spectra are shown which are the results of integrating the OES measurements over distance z(mm). The dashed lines indicated the two selected spectral lines at wavelength $\lambda_1$ and $\lambda_2$ with corresponding electron upper levels $E_1$ and $E_2$, used in the boltzmann plot construction.

does not apply due to the transient nature, low temperatures and species densities, especially in later stages of plume propagation.\textsuperscript{[58]}

But even when not in LTE, investigating the local plasma temperature based on OES measurements is useful in the interpretation and discussion of OES plume composition studies presented in this work. Namely, depending on the species of interest and their specific electron energy levels and transitions, the plasma temperature may affect the relation between line intensities of various elements and the relative densities of species.

3.4.2 Measurements and results

The Boltzmann relation applies to the intensities of single energy level transitions corresponding to a specific element. For sufficient resolution, a high resolution (1800 lines/mm, 500 nm blaze, instead of a 300 lines/mm) grating is used in the spectroscopic setup. Figure 3.6 shows the normalised spectra at three different delay times in a wavelength range between $\sim$490 nm and $\sim$530 nm.\textsuperscript{11} Measurements have been taken at a pressure of 8·10^{-2} mbar total oxygen pressure and a fluence of 2.1 J/cm².

\textsuperscript{11}Measurement parameters have been set such to obtain optimal signal-to-noise ratio. The TTL gate width is respectively 120 ns at 1 µs and 4 µs delay time and 500 ns at 7 µs delay time. For the delay times of 1 µs and 4 µs images are the integration over 50 pulses, at 7 µs delay time integration over 75 pulses. The MCP gain value is set to 3500 (arb. units).
Figure 3.7: Boltzmann plot construction for the measured spectra shown in Fig. 3.6. From the slope of the plots, equal to $-\frac{1}{k_B T_{\text{exc}}}$, the plasma excitation temperature $T_{\text{exc}}$ is derived.

The spectra show well defined sharp spectral lines, mostly corresponding to Ti neutral species. To construct a Boltzmann plot using eq. 3.2, preferably several spectral lines with significant varying upper levels and line intensities are used. The Boltzmann relation states a linear relation between between upper level energies of spectral lines and the natural logarithm of their corresponding line intensities. From the slope of this linear relationship the temperature is derived. But for the measured spectra, basically only two groups of lines have significant intensity, corresponding to an upper level $E_k$ of around 3.3 eV corresponding to the Ti I 3d$^3$($^4$F)$^4$s transition (lines vary in angular momentum) and 2.5 eV corresponding to the Ti I 3d$^2$4s$^2$ transition. Within these two groups the strongest lines are selected at $\lambda_k=498.3$ nm ($E_k=3.34$ eV, $g_k A_{ki}=8.58 \cdot 10^8$) and $\lambda_k=521.2$ nm ($E_k=2.43$ eV, $g_k A_{ki}=3.50 \cdot 10^7$). Peak intensities $I_k$ are determined from the normalised plots as shown in Fig. 3.6. Because only two lines are used, the linearity stated by the Boltzmann relation is not so much tested as it is only assumed and applied. This linear relation between line intensity and energy levels is simple assumed, as using just these two data points trivially result in a linear relation in the Boltzmann plot. This also implies that the temperature of the plasma is relatively low, where only lines are visible with relatively low upper level energy values.

Figure 3.7 shows the Boltzmann plot based on the three shown spectra in Fig. 3.6. The slopes of the plots are translated to a excitation temperature $T_{\text{exc}}$(eV) which values are indicated in the plot. The values show that with increasing delay time the excitation temperature decreases. The indicated error margins are calculated based on noise-to-signal ratio values determined from the OES images.

Next, the time dependent plasma excitation temperature is investigated for the expanding SrTiO$_3$ plasma plume at various oxygen background gas pressures.

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12 The bright line on the outer left side of the spectrum at $\sim$496 nm could correspond to double ionised oxygen (OIII). This could originate during ablation of the oxide target, or possibly the results of laser induced breakdown (LIB). [59]
and laser fluences. Figure 3.8 shows the calculated excitation temperature for the expanding plume at three different partial oxygen pressures of $10^{-2}$, $4\cdot10^{-2}$ and $8\cdot10^{-2}$ mbar of partial oxygen pressure, at a total pressure of $8\cdot10^{-2}$ mbar by addition of argon. Overall, the plasma excitation temperature already shortly after ablation around 0.5 μs decreases below 0.3 eV. The temperature of the plume is generally higher at higher oxygen pressures. A transition is observed at around 8 μs, where for higher partial oxygen pressure an increase in temperature is observed. The increasing error margins with increasing pressure follow from a decreased signal to noise ratio of the spectral lines. This is the result of both a decrease in signal and an increase in background noise signal on the measurements by the arise of broad spectral lines corresponding to oxidised species.

Last, the effect of varying fluence on the plasma excitation temperature is investigated. Fig. 3.9 shows the calculated plasma excitation temperature for the expanding plume at four different fluence conditions of 1.0, 1.3, 1.7 and 2.1 J/cm$^2$ at a total pressure of $8\cdot10^{-2}$ mbar of oxygen pressure. The measurement at 1.3 J/cm$^2$ is similar to the previously presented measurement at $8\cdot10^{-2}$ mbar oxygen. A transition at around 8 μs is observed for all fluence conditions, where the excitation temperature increases again. In the early stages of propagation the temperature shows a fluence dependence, where the temperature is higher for higher fluences. But after an overall decay, no clear fluence dependence seems to be present at later stages in propagation. Overall, the temperature slightly increases, but without a clear fluence dependence.
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Excitation temperature (eV)
Delay time (μs)

0.3
0.25
0.2
0 2 4 6 8 10 12 14 16 18 20

2.1 J/cm$^2$
1.7 J/cm$^2$
1.3 J/cm$^2$
1.0 J/cm$^2$

Figure 3.9: Average excitation temperature of the expanding SrTiO$_3$ plume determined from Boltzmann plots for Ti I lines at varying fluences of 1.0, 1.3, 1.7 and 2.1 J/cm$^2$ at a total pressure of $8 \times 10^{-2}$ mbar oxygen pressure.

3.4.3 Discussion

In the previous section a pressure and fluence dependent excitation temperature is calculated. It is shown that quickly after ablation, the excitation temperature is already as low as 0.3 eV and decreases in the first stages of propagation. At 8 μs an increase in plume excitation temperature for higher oxygen pressure is observed. It is speculated that the overall higher temperature and increase over time at higher pressures could be the results of exothermic oxidation reactions adding energy to the system which results in a temperature increase. The delay time at which this transition occurs quite well overlaps with the delay time at which the transition from drag to diffuse-like propagation of the plume occurs, as shown in Fig. 3.2. This suggests that these oxidation reactions occur during the diffuse propagation of the plume, therefore likely the results of mixing and oxidation of the plume with the background gas.$^{13}$

The excitation temperature also depends on fluence, where higher fluence results in higher plasma temperature. This suggests that initially, part of the laser intensity is translated into “heating” of the plume in terms of an increased excitation temperature and corresponding increased excitation of plume species. When the plume expands in high pressure, species eventually relax and thermalise. Therefore, the extra energy added to the plasma with increasing fluence is nullified. This is a relevant observation in the understanding of the role of fluence, as is

$^{13}$Speculative, the transition observed in plume temperature and propagation dynamics could also be a transition in whether or not LTE conditions apply to the plume characteristics. LTE might apply up until this transition, whereafter the density of the plume is decreased below ‘LTE threshold’ and the system cannot be described anymore by a specific temperature.
discussed more thoroughly with respect to film growth in chapter 4.

Generally, the observation of this significant temperature change of the plasma needs to be taken into account in the interpretation of spectral line intensities related to relative species densities. It must be noted that, as the plume is likely not in LTE, especially in later stages of propagation, the calculated plasma temperature for Ti species could be different from the excitation of other species. Nonetheless, the qualitative thermal behaviour of titanium species might very well apply to all species. Therefore, the temperature change cannot be neglected when translating line intensity ratios to relative species density ratios. In other words, a changing ratio between the intensity of spectral lines of two species could be caused by changing species densities, but also intrinsically due to changing plume temperature.

Therefore it is discussed whether the increase in TiO/Ti intensity ratios presented in Fig. 3.5 represents an actual increase in TiO species density, or is (partially) affected by temperature.\textsuperscript{14} Assuming a temperature change from 0.3eV to 0.22eV for 8 \cdot 10^{-2} mbar pressure, an upper level energy of ~2eV for TiO (lines at ~630 nm) and the upper level energy of the Ti line of ~3.4eV (~500 nm), a change in TiO/Ti intensity ratio of ~5 is calculated from the Boltzmann relation. However, the measurement in Fig. 3.5 shows a ratio change of ~10. From this it can be concluded that decrease in temperature does contribute, but only partially, to the increase in TiO/Ti ratio, implying an actual increase in TiO density.\textsuperscript{15} Also, if the change in intensity ratio between TiO and Ti would be purely caused by changing temperature, the shape of the ratio plot in Fig. 3.5 should be comparable to the temperature plots in Figs. 3.8 and 3.9. For the measurement at 10\textsuperscript{-2} mbar partial oxygen pressure, Fig. 3.5 shows a continues increase in ratio, where the calculated temperature after 8 \mu s is more or less constant, indicating an actual increase in TiO density.

Nonetheless, it is concluded that when comparing spectral lines of single elements (such as Sr and Ti, present immediately after ablation unlike oxidised species) to investigate the elemental stoichiometry of the plume, the specific transitions of these lines and a changing plasma temperature must be taken into account. The changing temperature of the expanding plume affects the population of a transition. When the upper level energies of the lines that are compared are different, the population/line intensity ratio changes with changing temperature. Only when spectral lines of different elements are selected which have comparable upper level energies, the effect of temperature on the population or intensity of the line can be neglected. In this case, the ratio change between spectral line intensities at various stages of propagation represents relative density ratio change of species.

\textsuperscript{14}Of course, as TiO can only be formed during the expansion of the plume, the fact that spectral lines emerge corresponding to TiO in the first place, must relate to a certain increase in TiO density.

\textsuperscript{15}It is noted that the Boltzmann relation applies to spectral lines from atomic species. It is questionable whether the influence of temperature on population of energy levels and corresponding relative line intensity ratio also directly applies to oxidised lines, as these diatomic species have more complex spectra consisting of vibrational and rotational contributions.
3.5 Spatiotemporal plume mapping with Laser Induced Fluorescence

Next to OES, LIF is used to investigate the spatial and temporal distribution of plume constituents in laser ablated SrTiO$_3$ plasma.\footnote{The overview of the results in this section is based on the results sections outlined in the thesis of Orsel\cite{33}, in which also a detailed overview on the theoretical and experimental background of the measurements can be found.} OES is limited to the detection of excited particles that spontaneously fluoresce, only when the plume is significantly hot. Therefore, especially at higher background gas pressures when plume thermalisation occurs, typically the excited state populations are orders of magnitude lower than the ground state populations.\cite{60} In contrast, LIF enables to spatially and temporally selective excite and detect ground state species which is especially useful at longer delay times from the moment of ablation, when the plume has thermalised during expansion towards the substrate.

LIF measurements were performed in similar PLD parameter conditions as the previously discussed OES measurements, at varying partial oxygen pressure, at a total background pressure of $10^{-1}$ mbar.\footnote{Note that the LIF measurements are done at slightly different total pressures, $10^{-1}$ instead of $8 \cdot 10^{-2}$ mbar respectively. The use of $8 \cdot 10^{-2}$ mbar is based on optimal growth of SrTiO$_3$ films discussed in chapter 4 and the pressure at which the plume thermalises, where the latter naturally also applies to a slightly higher pressure of $10^{-1}$ mbar. It is verified and shown in the next chapter that this change has marginal effect on subsequent film characteristics and general conclusions on key mechanisms remain valid, as this work focusses on the composition and oxidation of the plume in the thermalising pressure regime.} A laser fluence of 1.3 J/cm$^2$ was used with a spot size of 2.3 mm$^2$ and a target-substrate distance of 50 mm.

The composition of the plasma plume was investigated at varying background gas conditions, focussing on the elemental composition and oxidation of the plasma constituents. It was attempted to map the position, density and arrival time of all relevant and most likely present plasma constituents, which for SrTiO$_3$ are respectively Ti, TiO, TiO$_2$, Sr and SrO. Limited by the possibilities of the experimental setup, LIF mapping was achieved for Ti neutrals, TiO and SrO. LIF measurements on Sr and TiO$_2$ were not possible as Sr does not have transitions in the wavelength range which could be addressed with the LIF setup. TiO$_2$ has excitation lines in the optical range which are difficult to be measured due to strong background noise form scattering of the LIF laser.

To be able to relate the LIF signal to densities of species, all excitation transitions used were driven into saturation, where the LIF signal becomes proportional to the density of the excited species. However, it is noted that the measurements are not calibrated on an absolute scale, therefore the density of various species as presented in the results in this section can not be absolutely compared.

Figure 3.10 shows LIF normalised spatial distribution measurements of Ti, TiO and SrO for a cross-section of the plasma plume in the propagation plane from the target ($z=x=0$ mm) to the position of the substrate ($x=0$ mm, $z \sim 50$ mm). Images are recorded in $10^{-1}$ mbar oxygen pressure at 20 $\mu$s delay time.
3.5 Spatiotemporal plume mapping with Laser Induced Fluorescence

Figure 3.10: Normalised density distributions of Ti, TiO and SrO species of an ablated and expanding SrTiO$_3$ plasma plume cross-section. The target is positioned at z = x = 0 mm, substrate position is at z = 50 mm. On the left of (a) Ti ground state density is shown, with TiO on the right. (b) shows respectively SrO and TiO. Measurements are performed at 20 µs delay after ablation in a 10$^{-1}$ mbar oxygen pressure background. Lacking signal close to the target is caused by the target loading pin blocking one edge of the LIF excitation beam.

After ablation, at this delay time, first interaction (of the front) of the plume with the substrate occurs, as shown in Fig. 3.2. For easy comparison, for every plume constituent half of the measurement is shown. Figure 3.10(a) shows the distributions of Ti and TiO, where figure 3.10(b) shows the distribution of SrO and TiO under similar conditions. These measurements show a significant spatial separation of the different plasma constituents. It can be seen that SrO is located mainly in the edge of the plume, whereas TiO is largely absent in this edge. Also, TiO is more concentrated in the centre of the plume in a more confined matter, with the highest concentration at around 35 mm from the target. Neutral titanium is even more confined with the highest concentration close to the target around 10 mm.

Figure 3.11 shows the normalised ground state population densities of Ti, TiO and SrO along the propagation axis (at x = 0 mm in Fig. 3.10) as function of the distance from the target at varying partial pressures of oxygen at a total pressure of 10$^{-1}$ mbar. The results show the population densities at a delay time of 35 µs in these measurements, the heater with substrate is removed as it causes significant unwanted optical reflections affecting measurement accuracy.

In this work, of particular interest are specifically the densities and oxidation state of plasma species moving along the propagation axis, especially close to the substrate location, as these species condensate on the substrate. Species away from the propagation axis and subsequently not arriving on the substrate are obviously irrelevant. Essentially growth parameter optimisation is actually a matter of tuning the characteristics of just a small volume of the plume, concerning the species that arrive on the substrate surface.
Figure 3.11: The ground state population densities of Ti, TiO and SrO measured along the propagation axis, \(z (x = 0)\), at different partial pressures of O2. All measurements are done at a delay of 35 \(\mu s\) from target ablation and in \(10^{-1}\) mbar total background pressure. The first 12 mm is not shown as it is obstructed by the target holder.

\(\mu s\) after ablation. At this delay time, already a significant interaction between the plume and the substrate occurs. To emphasise the strong differences in spatial changes of densities, all densities are normalised to the maximum of the Ti, which itself is normalised to unity. Again, the measurements and results show the relative spatiotemporal distribution for the various species, where the ratio in absolute data between different species reflects their ratio in fluorescence yield.

The SrO density is close to the detection limit of \(10^{-3}\) (arb. units.). In 0.00 mbar partial oxygen pressure (\(10^{-1}\) mbar argon) the SrO LIF signal is only about an order above the background noise. This is caused by residual spontaneous emission of the plasma not removed by the background subtraction. For the Ti distribution a decrease of near two orders of magnitude is observed at any distance from the target when the oxygen fraction is increased up to \(8 \times 10^{-2}\) mbar partial oxygen pressure. The density at \(8 \times 10^{-2}\) mbar is similar to the distribution at \(10^{-1}\) mbar of oxygen pressure. For all pressures a decay in Ti is observed towards the substrate (at increasing \(z (mm)\)). For pressures higher then \(6 \times 10^{-2}\) mbar partial oxygen pressure, the measured density of Ti is close to the detection limit. The TiO density distribution is lowest for 0.00 mbar partial oxygen pressure, but increases with about an order at the first pressure increment to \(2 \times 10^{-2}\) mbar partial oxygen pressure. For this pressure, the TiO densities is highest at any distance compared to other pressure conditions. With subsequently increasing pressure, the density decreases again, where the shape of the TiO distribution over distance is similar
Figure 3.12: Total amount of Ti, TiO and SrO in the plasma plume, acquired by spatially integrating the LIF signal over the entire plume as function of the delay with respect to the moment of target ablation, for different partial pressures of oxygen. All measurements are at $10^{-1}$ mbar total background pressure. For the first 20 $\mu$s, a significant part of the plasma plume is blocked by the target holder, therefore not accessible for LIF measurements and not shown in these plots.

For all pressures. Also, the density distribution in $10^{-1}$ mbar oxygen and argon are quite similar. The SrO distribution shows an increase by almost an order of magnitude in density close to the substrate ($z=50$ mm) with increasing partial oxygen pressure, while the density closer to the target slightly decreases. Similar to Ti, the distributions at $8\cdot10^{-2}$ and $10^{-1}$ mbar oxygen are nearly identical.

Figure 3.12 shows the total amount of Ti, TiO and SrO species present in the entire plume as function of delay time after ablation at different oxygen partial pressures. The total number of particles is acquired by spatially integrating the LIF signal for Ti, TiO and SrO over the entire plasma plume, assuming the cylindrical symmetry around the z-axis ($x = y = 0$). Similar to the density distribution in Fig. 3.11, all plots are normalised to the maximum number of particles of Ti, which itself is normalised to unity. The first 20 $\mu$s is not shown, as part of the plasma plume close to the target is blocked by the target holder, therefore not accessible for LIF measurements. Similar to the density distributions, a clear dependence of Ti species on partial oxygen pressure is shown. In $10^{-1}$ mbar argon (no oxygen), the total amount of Ti atoms is nearly constant in time, whereas the Ti amount decreases strongly, with increasing partial oxygen, to almost two orders at $10^{-1}$ mbar of oxygen. The slope of the decrease of Ti over time steepens with increasing partial oxygen pressure. For the amount of TiO an increase of about an order is
observed for the first increment in oxygen to $2 \times 10^{-2}$ mbar partial oxygen pressure. With increasing partial pressure the amount of TiO decreases again, with similar values for the amount of TiO at $10^{-1}$ mbar of oxygen and argon. The amount of TiO particles over time in argon is almost constant, where it slightly decreases over time in all partial oxygen pressure conditions. The total number of SrO species slightly increases with increasing partial oxygen pressure. Also, over time, the number of SrO particles remains almost constant for all pressure conditions. The strong fluctuations in the measurements over time are caused by the large amount of noise in the measurements close to the detection limit.

### 3.5.1 Discussion

Based on the spatiotemporal data presented in Figs. 3.11 and 3.12, it can be concluded that with the introduction of partial oxygen gas, the oxidation of Ti to TiO and of TiO to TiO$_2$ is promoted, suggesting a mixing of the background gas into the plasma plume. Both the species density and amount of constituents of titanium steadily decreases with an increasing partial oxygen pressure. This mixing of the background gas and plasma plume has been previously concluded in other studies.\cite{61} For high partial oxygen pressures, $8 \times 10^{-2}$ mbar and $10^{-1}$ mbar it is observed that no significant amount of neutral Ti reaches the position of the substrate at 50 mm from the target. Over time, both the front of the Ti neutrals distribution and the ‘centre’, where the density of Ti neutrals is highest, move away from the substrate. This indicates overall strong oxidation with distance towards the substrate. Also, the total amount of Ti neutrals when ablated in 0.00 mbar of oxygen, or $10^{-1}$ mbar argon, remains almost constant over time, indicating that little to no oxidation occurs in the plasma plume with the oxygen from the target. This shows that the oxygen from the background gas is responsible for the oxidation of titanium. For $8 \times 10^{-2}$ mbar and $10^{-1}$ mbar oxygen pressure the spatial and temporal density distribution of Ti is very similar, indicating a saturation of mixing of the plume with oxygen resulting in the oxidation of Ti.

This interpretation of the pressure dependent behaviour of Ti is supported when investigating the spatial temporal density distribution of TiO. The measurements show a strong increase of TiO from 0.00 to $2 \times 10^{-2}$ mbar partial oxygen pressure, which subsequently decreases again with increasing partial oxygen pressure increments. Very likely this is explained by oxidation of TiO to TiO$_2$. Unfortunately the TiO$_2$ molecular fluorescence signal to verify this could not be detected with the setup.

For SrO, different behaviour is observed, compared to the gradual oxidation of Ti. In pure argon only little SrO is observed with a fluorescence signal close to the detection noise limit. In oxygen, SrO is formed with only little increase in density with increasing partial oxygen pressure. A clear pressure dependence in the amount of SrO between $2 \times 10^{-2}$ mbar and $10^{-1}$ mbar is absent. This could indicate that Sr oxidises strongly with the oxygen from the introduced background gas. This is supported by the observation that for the first partial oxygen pres-
3.6 Conclusion

The propagation dynamics and spatiotemporal element specific composition of laser ablated SrTiO$_3$ plasmas was investigated with OES and LIF. A transition from ballistic to diffuse propagation was observed which occurs in a relative small pressure regime between $10^{-2}$ and $10^{-1}$ mbar, both for oxygen and argon background gas pressure. In this regime, a strong pressure dependent oxidation of the plume constituents is observed. To separate propagation dynamics from plume chemistry, the plume composition was subsequently investigated in partial oxygen pressure. Here a gradual oxidation of species with increasing partial oxygen pressure was observed. Next, a Boltzmann plot analysis was performed on measured Ti spectra, from which an average plume excitation temperature is determined. It is discussed that the observed decrease in plume temperature must be taken into account when investigating plume composition based on spectral line intensity comparison. Furthermore, an increase in plume temperature with increasing oxygen pressure and fluence is observed, possibly the results of subsequently exothermic oxidation reactions and increased interaction of the laser pulse during initial ablation.

Furthermore, the spatiotemporal element specific mapping of Ti, TiO and SrO with LIF shows a change in plume composition depending on the partial oxygen pressure. Overall spatially and temporally, Ti species gradually oxidise, where with increasing partial pressure a gradual decay of Ti neutral species is observed. This coincides with an increase and subsequent decrease of TiO likely to form TiO$_2$. When focussing on the front edge of the plume, when species arrive at the substrate, it is observed that for partial oxygen pressure $>8 \cdot 10^{-2}$ mbar no significant amount of Ti neutrals arrive at the substrate anymore. This is an important observation with respect to the stoichiometry of grown SrTiO$_3$ thin film, as is discussed in chapter 4. Generally, the oxidation from the background gas, not so much the target, is responsible for species oxidation in the SrTiO$_3$ plume. This also applies to the oxidation of Sr, where little SrO is present when ablating in pure argon. But unlike Ti, no clear pressure dependence in the amount of SrO seems present for the investigated partial oxygen pressure range, suggesting...
that Sr oxidises much stronger than Ti. As is discussed in the next chapter, these results provide a direct link and predictability for controlling the chemical plasma composition and subsequent growth characteristics of SrTiO$_3$ thin films growth studies.
Chapter 4

Controlling stoichiometry in SrTiO$_3$ thin film growth

Abstract

From structural and kinetic growth studies with XRD and RHEED analysis of homoepitaxial SrTiO$_3$ films grown under different oxidising conditions, it is shown that both stoichiometry as well as surface diffusivity is determined by the oxidation of arriving species, instead of the commonly assumed mass distribution in the plasma plume and the kinetic energy of the arriving species. It is observed that the SrTiO$_3$ stoichiometry depends on the composition of the background gas during deposition, where in a relative small pressure range between $10^{-2}$ mbar and $10^{-1}$ mbar partial oxygen pressure, the resulting film becomes fully stoichiometric. In relation to the results from chapter 3, at a partial pressure condition at which full oxidation of titanium occurs, stoichiometric growth is observed coinciding with a transition in kinetic growth characteristics from three-dimensional (3D) to two-dimensional (2D) atomically smooth growth. This strong relation between sticking and mobility of species at the growth surface and their oxidation state is the result of an intricate balance between oxygen from the target material, oxidation of species during the propagation towards the substrate by interactions with the oxygen background gas and oxygen scavenging from the oxide substrate.

Part of the work discussed in this chapter is published in: Rik Groenen, Jasper Smit, Kasper Orsel, Arturas Vaillonis, Bert Bastiaens, Mark Huijben, Guus Rijnders, Gertjan Koster, Research Update: Stoichiometry controlled oxide thin film growth by pulsed laser deposition, APL Materials 3, 070701, 2015.[63]
4.1 Introduction

The perovskite SrTiO$_3$ exhibits a wide range of interesting properties such as ferroelectricity, superconductivity, resistive switching and thermoelectricity. For this material, these properties are often related to impurity doping,[64] strain[65] and/or an imperfect or defective crystal. The properties of the latter is mainly determined by (high) concentrations of oxygen vacancies allowed by the stability of SrTiO$_3$ under reducing conditions due to the multivalency of Ti.[66] Because of the relatively weak binding of the oxygen and the high oxygen-ion mobility, vacancies can be introduced by annealing at low pressures ($<10^{-5}$ mbar). SrTiO$_3$ crystals and thin films can be fabricated with varying oxygen vacancy concentrations, which transform its electronic properties from wide band gap insulator into a good conductor. However, besides oxygen vacancies, this property can also strongly be related to the cation stoichiometry of SrTiO$_3$ where even marginal compositional variations lead to changes in electrical, dielectric and thermal properties.[30,67,68]

Besides its interesting properties, SrTiO$_3$ is widely used as model material system for fundamental studies on the influence of growth parameters on oxide thin film characteristics such as crystal structure and surface morphology.[29–31] This is because of its simple ABO$_3$ cubic (A, B being metal cations) perovskite structure as well as the possibility of homoepitaxial growth. Here, thermodynamic factors of different surface energies related to for instance lattice misfit and corresponding thermodynamic growth modes can in principle be excluded and the growth can be described entirely kinetically, which is the basis of the current models describing PLD growth processes.[4,5,9] In these studies, investigating the effect of oxygen (partial) pressures on these kinetic growth processes, the unavoidable variations in oxygen stoichiometry could be ‘repaired’ by a simple post-annealing procedure. On the other hand, any resulting variations in cation stoichiometry cannot be corrected afterwards and therefore a full control of the properties demands tuning of the cation stoichiometry during the thin film growth processing.

4.1.1 Stoichiometric growth of SrTiO$_3$ thin films

To understand the relation between the chemistry and oxidation of species in relation to film growth characteristics, structure and stoichiometry, this chapter outlines growth studies based on the results in the previous chapter, which has given new insight in the chemistry of laser ablated SrTiO$_3$. In chapter 3, it has been shown that the plume shows a significant change in not just its propagation dynamics, but also in species dependent oxidation. In a small pressure regime between $10^{-2}$ and $10^{-1}$ mbar, the titanium species in the plume undergo a transition from neutral to a fully oxidised state, as summarised in Fig. 3.12. It has been shown that, by using a partial oxygen pressure, maintaining a constant total pressure, a high controllability of the ratio between neutral and oxidised species can be obtained. This opens the possibility of separating the propagation dynamics from the plume chemistry.
This chapter outlines the results on homoepitaxial film growth studies with focus on the relation between synthesis, morphological and structural properties of homoepitaxially grown SrTiO$_3$ films in the pressure regime between $10^{-2}$ and $10^{-1}$ mbar. This is subsequently related to the investigated plasma plume characteristics. As these films are grown with a variation in background pressure of only one order of magnitude, it is expected that the observed changes in thin film characteristics are dominated by variations in the composition of the plasma plume. Subsequently, the influence of laser fluence on film stoichiometry at specific background gas conditions is investigated, supporting the role of plume oxidation in relation to film stoichiometry. Lastly, based on the results of these growth studies, a more thorough investigation is outlined on the initial growth of homoepitaxial SrTiO$_3$ at specific underoxidised conditions, discussing the role of oxygenation through the surface and subsequent film stoichiometry. Based on the obtained results, a schematic model is presented which summarises the suggested relations between growth parameters, plume characteristics and the structural properties of grown SrTiO$_3$ films.

4.2 SrTiO$_3$ thin film growth studies

In this section the experimental results on growth and characterisation of homoepitaxially grown SrTiO$_3$ at varying background gas pressures is outlined, in line with the results given in the previous chapter regarding the characterisation of the expanding SrTiO$_3$ plasma plume.

Two sets of thin SrTiO$_3$ film samples have been grown by PLD: the first series were grown at an absolute pressure of $10^{-2}$, $2\cdot10^{-2}$, $4\cdot10^{-2}$, $6\cdot10^{-2}$, $8\cdot10^{-2}$ and $10^{-1}$ mbar oxygen; for the second series a mixture of oxygen and argon was used, where the total pressure was kept at $8\cdot10^{-2}$ mbar and partial pressures of $10^{-2}$, $2\cdot10^{-2}$, $4\cdot10^{-2}$, $6\cdot10^{-2}$, $8\cdot10^{-2}$ mbar of oxygen. These conditions are similar to the conditions used in the previous chapter investigating the effect of background gas on the plasma plume characteristics. In both sets, the growth temperature was kept constant at 710°C. As described in chapter 2, a combined chemical and thermal treatment was applied to achieve a single TiO$_2$ termination of the STO substrates$^{[39]}$. The laser fluence was set to 1.3 J/cm$^2$ with a laser repetition rate at 1 Hz, spot size of 2.3 mm$^2$ and a target-substrate distance of 50 mm. All films were monitored during growth using reflection high energy electron diffraction (RHEED) to study the surface morphology and the in-plane crystal structure. Furthermore, by monitoring the time-dependent evolution of the specular spot intensity, information is obtained about the kinetic growth characteristics. Based on RHEED oscillations, the growth rate is determined. The growth rate is translated to a total deposition time for growing 100 monolayers (ML). For a bulk lattice constant of 3.905 Å, this results in ~39 nm thick films. It is important to note that a nonstoichiometry, associated with an increase in unit cell volume$^{[42]}$, therefore results in a thicker film. After growth, all films have been
cooled down to room temperature with 50 °C/min at 100 mbar of oxygen pressure to remove oxygen vacancies. To investigate the surface morphologies of the grown films, atomic force microscopy (AFM) images have been made. X-ray Diffraction (XRD) was used for structural characterisation of the thin films, focusing on the changes in the out-of-plane lattice constant, corresponding to defects due to nonstoichiometry by performing 2θ/ω symmetrical scans around the (002) Bragg reflection of SrTiO$_3$ as this is the strongest out-of-plane reflection.

### 4.2.1 Thin film growth and RHEED analysis

#### Absolute oxygen pressure

Figure 4.1 shows the RHEED specular spot intensities for the grown films for the initial first ~1200 laser pulses. In all pressure conditions, the initial growth shows typical oscillatory behaviour, where the oscillating specular spot intensity is generally assigned to an oscillating step density, with the intensity inversely depending on the number of steps on the surface. The presence of oscillations represents a layer-by-layer growth mode, in which a single oscillation represents a single unit cell thick layer of grown material.[7,69] For the samples grown at an absolute oxygen pressure of $10^{-2}$, the oscillations gradually damp out. With increasing pressure, the amount of oscillations increases, where for $8 \times 10^{-2}$ and $10^{-1}$ mbar, the oscillations remain for the full length of the deposition, and layer-by-layer growth is maintained for the full stack of 100 monolayers. For $10^{-1}$ mbar an aliasing effect can be observed with minima at 350 and 700 seconds. This effect arises from the pulsed nature of material flux, where a full coverage deviates from an exact integer number of pulses. The growth speed, determined from the oscillation periodicity, decreases with increasing pressure, from ~13 pulses/ML at $10^{-2}$ mbar to ~22 pulses/ML at $10^{-1}$ mbar.

The corresponding RHEED diffraction patterns in the [01] direction after growth of 100 monolayers are shown in Fig. 4.2. Patterns were taken after high pressure cool down to room temperature with the PLD chamber subsequently pumped down to a base pressure of ~10$^{-7}$ mbar. A typical diffraction pattern of a TiO$_2$ single terminated SrTiO$_3$ substrate surface is shown, as well as diffraction patterns of SrTiO$_3$ films deposited at increasing pressures are shown. The most striking qualitative difference is the presence of a 3D transmission pattern for growth pressures up to $6 \times 10^{-2}$ mbar. Such 3D pattern is formed by dominantly transmission electron diffraction through small surface asperities on a roughened surface, which was confirmed by rocking the incident beam to ensure the fixed position of diffraction spots on the phosphorus screen. Differences in overall intensity between images are caused by a varying filament current or a small change in angle between sample and the grazing electron beam, resulting in a slightly changed diffraction condition affecting the individual spot intensity. The patterns at $8 \times 10^{-2}$ and $10^{-1}$ mbar show clear 2D 0$^\text{th}$-order spots, while for $10^{-1}$ mbar, also Kikuchi lines are visible, indicating a high degree of crystallinity. These 2D pat-
4.2 SrTiO$_3$ thin film growth studies

Figure 4.1: RHEED specular spot intensity as function of time, for various oxygen gas pressure conditions. Inset shows an enlargement of the first two oscillations, which illustrate the decreasing growth speed with increasing pressure.

Pattens are very similar to those of a typical (1x1) pattern of a single TiO$_2$-terminated SrTiO$_3$ substrate, indicating that the top surface is atomically flat.

An investigation on the in-plane position of the diffraction spots, as emphasised with the horizontal lines outlined to the substrate peak position, shows that for the films grown at highest pressure conditions, the surface structure is identical to that of the substrate. Even the relative intensity difference between the main and side spots qualitatively resembles the substrate diffraction pattern. This weaker intensity of the side spots compared to the main specular spot has been reported to be the signature of a TiO$_2$ single terminated SrTiO$_3$ substrate.[70] Presumably, a mixed terminated substrate shows stronger side spots as a result of a difference in structure factor between strontium and titanium atoms.
Figure 4.2: RHEED diffraction patterns after each deposition of 100 monolayers of SrTiO$_3$ at indicated absolute oxygen pressures. The arrows indicate a transition between a 3D diffraction pattern at lower pressures and a 2D diffraction pattern above 6·10$^{-2}$ mbar.

Figure 4.3: RHEED diffraction patterns after each deposition of 100 monolayers of SrTiO$_3$ at indicated oxygen partial pressures, where the total pressure was kept at 8·10$^{-2}$ mbar by adding Ar; The two right-most panels represent samples grown at a total pressure of 10$^{-1}$ mbar. The arrows indicate a transition in the type of pattern corresponding to a 3D pattern at lower pressures and a 2D pattern above 6·10$^{-2}$ mbar.

**Partial oxygen/argon pressure at constant total pressure**

Figure 4.3 shows the RHEED surface diffraction patterns in [01] direction after growth varying the oxygen partial pressure, similar to Fig. 4.2. Indicated with the arrows is the transition from a 3D to 2D surface diffraction pattern for the films grown at respectively 6·10$^{-2}$ mbar and 8·10$^{-2}$ mbar partial oxygen pressure, a similar transition to the films grown at absolute oxygen pressure.

RHEED specular spot intensities of films grown at various partial oxygen pressures are shown in Fig. 4.4. Insets show the growth speed for every sample based on the oscillations periodicity, which again are used to determine the total
deposition time for growing 100 monolayers. As introduced, while varying the partial oxygen pressure, the total pressure is kept at $8 \cdot 10^{-2}$ mbar. For the film grown at zero partial oxygen pressure, a pure argon background gas pressure is used. For the film grown at $8 \cdot 10^{-2}$ mbar a pure oxygen background gas pressure is used. Two more samples are presented for which the total gas pressure was set to $10^{-1}$ mbar. A partial pressure of $8 \cdot 10^{-2}$ mbar was used and a total pressure is $10^{-1}$ mbar of oxygen, as presented in Fig. 4.4.

For the samples grown at $10^{-2}$-$4 \cdot 10^{-2}$ mbar partial oxygen pressure, a signif-
Controlling stoichiometry in SrTiO$_3$ thin film growth

Figure 4.5: AFM imaging for morphological characterisation. (a) Film grown at $2 \times 10^{-2}$ mbar partial oxygen pressure, 8$\times$10$^{-2}$ mbar total pressure. Surface morphology is representative for all films grown at partial pressure $< 6 \times 10^{-2}$ mbar oxygen. (b) Film grown at 8$\times$10$^{-2}$ mbar oxygen pressure. Surface morphology is representative for all films grown at a partial oxygen pressure $\geq 6 \times 10^{-2}$ mbar.

A significant drop in specular spot intensity is observed after a number of oscillations, where this number increases with increasing pressure. For the samples grown at $>6 \times 10^{-2}$ mbar partial oxygen pressure, the overall intensity decreasingly damps with increasing pressure, where oscillations maintain for the full recording of the specular spot intensity. In contrast to the films grown at absolute oxygen pressures, the growth speed is more or less constant at $~22$ pulses per monolayer for partial oxygen pressures above $2 \times 10^{-2}$ mbar.

Summarising, with increasing (partial) oxygen pressure, layer-by-layer growth is more strongly maintained, indicating improved film smoothness, supported by the surface diffraction patterns which show a similar 3D to 2D transition. Improved film smoothness implies an improved surface diffusion, or mobility of particles on the substrate. Current growth models suggest a pressure dependent diffusion activation energy, which increases with increasing pressure as the results of the thermalisation of arriving species. But these results point to an additional important parameter, namely, the oxidation of species in the plasma. When growing in partial oxygen pressure, excluding species kinetics, a transition towards surface smoothening is observed with increasing partial oxygen pressure. This suggests that diffusion depends on not just kinetics, but also on the oxidation of arriving species.

4.2.2 AFM Surface morphology

To investigate the surface morphologies of the grown films, AFM images have been made. Standard tapping mode in air settings have been used. Figure 4.5(a) shows the measurement on a film grown in $2 \times 10^{-2}$ mbar partial oxygen pressure and represents the morphology measured for all films grown at partial oxygen...
pressures \( \leq 6 \times 10^{-2} \) mbar. Figure 4.5(b) shows the measurement on a film grown at \( 8 \times 10^{-2} \) mbar partial oxygen pressure and represents the morphology for all films grown at partial oxygen pressures \( \geq 8 \times 10^{-2} \) mbar. The morphology shows a transition between these pressure regimes. For \( \leq 6 \times 10^{-2} \) mbar, although the initial substrate vicinal steps are still visible, films are roughened with small surface asperities present with height differences of several monolayers. The lateral size of these particles is around 10-20 nm, in good agreement with the 3D pattern observed with RHEED as a result of transmission of electrons through small surface asperities. On the other hand, the films grown at \( \geq 8 \times 10^{-2} \) mbar show a morphology quite similar to the substrate, with clear vicinal steps with single monolayer height difference. This is in agreement with the observed 2D RHEED diffraction pattern resulting from sub-monolayer roughening.

### 4.2.3 XRD structural characterisation

As introduced in section 2.6.3, deviations of the film out-of-plane lattice parameter with respect to the substrate (3.905 Å) is an indication of cation nonstoichiometry. To investigate film stoichiometry, the structural properties of the grown films are studied with XRD. Figure 4.6 shows 2\( \theta \)/\( \omega \) symmetrical scans around the (002) Bragg reflection of SrTiO\(_3\) for samples grown at absolute (a), and partial (b) oxygen background gas pressure from \( 10^{-2} \) to \( 10^{-1} \) mbar.

Figure 4.6(a) shows measurements on films grown at varying absolute oxygen pressures. For the films grown at \( 10^{-2} \), \( 2 \times 10^{-2} \) and \( 4 \times 10^{-2} \) mbar, film peaks are visible indicated with a red arrow. The corresponding lattice parameters are respectively 3.927±0.001 Å, 3.935±0.001 Å, and 3.933±0.001 Å. At \( 6 \times 10^{-2} \) mbar, a transition is observed in the position of the film peak shifting towards the substrate peak, visible as a shoulder peak next to the substrate peak. For the film grown at \( 8 \times 10^{-2} \) mbar, no distinguishable film peak is present. For the film grown at \( 10^{-1} \) mbar, a shoulder peak is again visible. The shift in peak position left from the substrate peak corresponds to an increase of the film c-axis with respect to the substrate and therefore to an increased unit cell volume which is understood being caused by cation nonstoichiometry, or point defects in the lattice. As for the film grown at \( 8 \times 10^{-2} \) mbar the film is nearly indistinguishable from the substrate, this film is most stoichiometric. For all films, Laue oscillations around the film peaks are observed resulting from the coherence between individual layers in the film and indicate high crystalline quality.

Figure 4.6(b) shows measurements where films have been grown at partial oxygen pressures. As indicated total pressure is kept at \( 8 \times 10^{-2} \) mbar by addition of argon. The measurement indicated with 0.00 mbar represents the results of a sample grown at pure \( 8 \times 10^{-2} \) mbar argon pressure. Deviating from the total pressure of \( 8 \times 10^{-2} \) mbar, the top measurement is the result of a film grown at a total pressure of \( 10^{-1} \) mbar, with partial pressure of \( 8 \times 10^{-2} \) mbar oxygen.

Unlike the films grown at absolute oxygen pressure, showing a more abrupt transition in film peak position with increasing pressure, a more gradual transition
Figure 4.6: XRD $2\theta/\omega$ scans for SrTiO$_3$ film grown at absolute (a) and partial (b) oxygen pressure around the (002) Bragg reflection of the SrTiO$_3$ substrate. In (b), the total pressure is kept at $8 \cdot 10^{-2}$ mbar by addition of argon, except for the upper film, grown at $8 \cdot 10^{-2}$ partial pressure, $10^{-1}$ mbar total pressure. Film peaks are indicated with the red arrows, where the peak positions for the films grown in partial oxygen pressure show a gradual trend in position, shifting towards the position of the substrate peak with increasing pressure.

is observed for increasing partial pressure. The peak position increases towards the value of the substrate peak. For the films grown at $6 \cdot 10^{-2}$ mbar and $8 \cdot 10^{-2}$ mbar partial pressure, the film is nearly indistinguishable from the substrate. The film grown at a partial pressure of $8 \cdot 10^{-2}$ mbar at total pressure of $10^{-1}$ mbar shows again a marginal contribution of a shoulder peak next to the substrate peak. In all measurements Laue oscillations indicate a high degree of crystallinity and coherence of individual monolayers in the film. Again, as the increase in unit cell volume is the result of point defects in the film lattice, the increase in partial oxygen pressure results in a decrease in defects related to an improved
stoichiometry up until a nearly stoichiometric film grown above $6 \cdot 10^{-2}$ mbar partial oxygen pressure.

To verify in-plane strain, reciprocal space map scans have been performed for the non-stoichiometric films. Figure 4.7 shows the result of a map scan around the (103) reflection for the film grown at $10^{-2}$ mbar of partial oxygen pressure. In agreement with the results presented in Fig. 4.6, a film peak is observed with decreased out-of-plane value compared to the substrate. Laue oscillations are also observed and indicated. The in-plane value of the film is equal to that of the substrate which indicates an in-plane strained lattice. The 'smearing', or broadening of the substrate peak in the $\omega$ scan direction is related to the limited crystalline quality of the SrTiO$_3$ substrate.

### 4.2.4 Discussion

In chapter 3 it is shown that the composition of the background gas has a strong influence on the plasma plume composition and propagation dynamics. To be able to correlate the plasma composition directly to the thin film growth, growth studies have been performed in similar background gas pressure conditions, outlined in this chapter. When relating the results from the spectroscopic studies with the results from the kinetic growth and structural characterisation of the grown SrTiO$_3$
Controlling stoichiometry in SrTiO₃ thin film growth

In thin films, important correlations are observed. First, with increasing partial oxygen pressure, a decrease of Ti and increase of oxidised species is observed in the plume composition. Also with increasing partial oxygen pressure a trend (Fig 4.6(b)) in film stoichiometry is observed. Furthermore, at around $6 \cdot 10^{-2}$ mbar partial oxygen pressure, a transition occurs from non-stoichiometric to stoichiometric growth as determined by XRD measurements. Also at this pressure condition of $6 \cdot 10^{-2}$ mbar partial oxygen pressure, neutral atomic titanium ceases to reach the substrate, as shown in Fig. 3.10. Lastly, both Ti and Sr reach the substrate in an oxidised state, which are respectively TiO, TiO₂ and SrO. All these correlations strongly suggest that (full) oxidation of plasma constituents is a necessary requirement for stoichiometric growth of SrTiO₃. Furthermore, Laue oscillations around the Bragg reflection in the XRD measurements, related to a high coherence between individual monolayers, imply homogeneously distributed defects, or nonstoichiometry. This means that these defects are continuously building up during the process of nucleation and monolayer growth and therefore mainly depend on the composition and oxidation state of arriving species.

4.3 Fluence dependent film stoichiometry

Next to the studies investigating the role of the background gas, the relation between laser fluence and film structure and stoichiometry is studied. This section outlines the results on structural characterisation of SrTiO₃ film grown at varying fluence. Films are grown in two different pressure conditions of $10^{-2}$ mbar absolute oxygen pressure (ballistic regime) and $10^{-2}$ mbar partial oxygen pressure, at $8 \cdot 10^{-2}$ mbar total pressure (thermalised regime).

4.3.1 Results and discussion

In Fig.4.8, XRD scans are shown of samples deposited using different laser fluences (maintaining the same spot size). Figure 4.8(a) shows samples grown at an absolute oxygen pressure of $10^{-2}$ mbar. Figure 4.8(b) shows films grown at an oxygen partial pressure of $10^{-2}$ mbar with a total pressure of $8 \cdot 10^{-2}$ mbar. The growth speed in pulses per monolayer is indicated for all grown films. For the films grown at an absolute pressure of $10^{-2}$ mbar (ballistic expansion), the laser fluence affects the stoichiometry of the films, as can be concluded from the position of the

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1 Note that the LIF measurements are done at slightly different total pressures, $10^{-1}$ mbar instead of $8 \cdot 10^{-2}$ mbar respectively. However, it was verified that this small difference does not have a significant effect on the results. This is based on XRD measurements as presented in Fig. 4.6(b), from comparing results of the films grown at $8 \cdot 10^{-2}$ mbar O₂ and $8 \cdot 10^{-2}$ mbar PO₂, $10^{-1}$ mbar $P_{tot}$ and LIF measurements from comparing results in similar pressure conditions (not presented).

2 It is noted that, as shown in section 2.6.3, titanium or titanium oxide lattice defects have a more significant effect on the increase in unit cell volume compared to strontium or strontium oxide defects. Therefore, the measured lattice expansion for nonstoichiometric SrTiO₃ films possibly relate to specifically titanium (non)stoichiometry.
4.3 Fluence dependent film stoichiometry

![Graph showing growth speed versus fluence for absolute and partial oxygen pressures](image)

**Figure 4.8:** XRD $\theta - 2\theta$ scans of films grown at three different laser fluences at $10^{-2}$ mbar absolute (a) and partial (b) pressure, with a total pressure of $8 \cdot 10^{-2}$ mbar.

Film peak which changes with fluence. For the film grown at a total pressure of $8 \cdot 10^{-2}$ mbar (diffusive expansion), the peak position does not change, indicating a similar stoichiometry for all films. In both pressure conditions, the growth speed as determined from RHEED oscillations periodicity (not shown here) increases with increasing fluence.

This observation supports the earlier outlined interpretation regarding the role of pressure and oxidation of the plume in relation to film growth. The fluence most likely affects the elemental specific spatial distribution in the ballistic regime because of mass differences between plume species, resulting in a fluence dependent film stoichiometry. The fact that stoichiometry improves with increased fluence is possibly the result of an ‘improved’ spatial distribution of species, where a more stoichiometric composition of species arrives at the substrate. In high pressure conditions in which the plume thermalises and propagates diffusively, the fluence does not affect the film stoichiometry, it does influence the growth speed, or flux of material towards the substrate. This supports oxidation model where film stoichiometry is determined by the oxidation state of arriving species. Namely, the plume confinement in the diffuse regime suppresses the effect of fluence affecting the elemental specific distribution in the ballistic regime.
4.4 Initial growth; role of substrate oxygenation

This section outlines a more thorough quantification of the XRD measurements by means of a fit model, from which more detailed information regarding the c-axis lattice parameter, thickness and crystallinity of the grown SrTiO$_3$ films is obtained. It is shown that the thickness of the highly single crystalline layer does not correspond to the expected film thickness as determined from RHEED during growth. From the investigation of initial growth related to the film structural characterisation it is shown that, as oxidation of species is necessary for stoichiometric growth, the substrate also acts as an oxygen source for under oxidised species.

4.4.1 XRD simulations results

For a further quantification of the out-of-plane XRD scans, measurements are simulated and fitted using the model given by Stepanov (Stepanov X-ray Server). Typical fitting parameters that define a heterostructure include among others the number of layers, defined by the individual normal strain with respect to the substrate $(d a/a)$, the thickness $(d)$, interface roughness $(\sigma)$ and the Debye-Waller coefficient. The latter is a correction factor for thermodynamic effects such as the measure of the movement of atoms with a value between zero and unity. In the simulation this can also be used to describe a matter of amorphousness or a lacking crystallinity. A more detailed outline of the model transcends the focus of this work and can be found elsewhere.

The main focus of this investigation is the accurate determination of the position of the film peak and the lattice parameter of the film. Furthermore, the model includes layer thickness which translates to a specific periodicity of Laue oscillations, as these Laue oscillations are the results of a finite size effect by coherence between well defined individual monolayers within a finite size film. By correctly fitting the measured periodicity of Laue oscillations the film thickness was determined accurately within monolayer thickness accuracy.

In Fig. 4.9 the XRD $2\theta/\omega$ scans including the Stepanov model simulations for SrTiO$_3$ film grown at partial oxygen pressure around the (002) Bragg reflection of the SrTiO$_3$ substrate are shown. For most films, a simple one-layer system, in which the film is defined as highly crystalline (Debye-Waller factor of 1) with a specific d-spacing translated to a out-of-plane strain relative to the substrate $(d a/a)$ and total film thickness $d$ (Å), results in accurate simulations. Only for the film grown in pure argon (PO$_2$=0.00 mbar), a value of 0.4 as Debye-Waller factor results in the most accurate fit, indicating a much lower film crystallinity. Values for the above mentioned parameters are given in table 4.1. The earlier outlined decreasing d-spacing with increasing partial pressure is now quantified, where for the film grown at 6·$10^{-2}$ mbar partial oxygen pressure the d-spacing is

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$^3$In other words, relative shift of the position of the film peak with respect to the substrate peak position, which equals the change in c-axis of the film relative to the c-axis of the substrate. The c-axis lattice constant for SrTiO$_3$ is 3.905
4.4 Initial growth; role of substrate oxygenation

Figure 4.9: XRD $2\theta/\omega$ scans at different partial oxygen pressures and their fits to the Stepanov model.

nearly equal to the substrate, while further increasing the pressure the d-spacing increases again.\textsuperscript{4}

The thicknesses determined from these simulations, based on the Laue oscillation periodicity, remarkably deviate from the original aim of a 100 monolayers or $\sim 39$ nm thick films, based on (initial) RHEED oscillations. For the films grown at lower partial oxygen pressure, a smaller value for film thickness is determined, where only for the film grown at highest pressure, thickness of the films is (close to) the expected 390 Å.

\textsuperscript{4}Small deviations in the simulations with respect to the measurements were corrected by the introduction of an extra thin (<1ML) layer with low crystallinity, large roughness and deviating lattice constant (also see table 4.1). Although the values for the chosen physical parameters are likely to be unreliable having interchangeable effects on the simulations, the qualitative presence of such a second layer could be very well explained in the form of a layer representing slight surface roughening, which is the case for all films. Nonetheless, due to their limited relevance, no further attention is given to this extra top layer.
Table 4.1: C-axis strain of the film with respect to the substrate $da/a$ (%) (SrTiO$_3$ lattice constant is 3.905Å) and corresponding film thickness $d$(Å). Note: (*) A Debye-Waller coefficient of 0.4 was used, likely corresponding to a strong decrease in crystallinity. (†) A monolayer thick interface layer was introduced between film and substrate with deviating d-spacing. (‡) A 10Å thin layer with deviating d-spacing on top of the film was used to correct deviations between simulation and measurements.

### 4.4.2 Multi-level film growth model

Here this deviation between the estimated film thickness based on RHEED oscillations and the calculated film thickness based on the periodicity of the Laue oscillations is discussed. Laue oscillations originate from the coherence between individual monolayers within a finite size film, which in its turn has a clear interface with the substrate. This interface results naturally from a density difference between film and substrate, caused by a change in stoichiometry in the film, as is the case for the films with increased d-spacing. Also, even in case the film is identical to the substrate, a single monolayer with deviating d-spacing at the interface causes a finite size effect. In this case the film "distinguishes" itself from the substrate by this deviating interstitial layer, which subsequently gives rise to Laue oscillations. This is likely the case for the 6·10$^{-2}$ mbar grown film.

Coherence between the individual monolayers in the film results subsequently in the occurrence of Laue oscillations. So all individual layers are defined by a very similar (increased) d-spacing, which means that the assumed point defects related to nonstoichiometry are distributed homogeneously.

Three distinct scenarios can explain the growth and characteristics of the film in relation to the XRD measurements, in which these deviating film thicknesses between experiment and measurement are observed:

- The whole film is thinner then expected from the extrapolated growth speed determined from the first oscillations to obtain 100ML. This means that the growth speed changed over deposition time. This requires a change in particle sticking behaviour for arriving species on the surface during the deposition.

- The film is 100ML thick, but consists of multiple layers with different lattice
4.4 Initial growth; role of substrate oxygenation

constant and crystallinity. In this case, from the simulations it can be determined that in a simplified "two-layer" system, two scenarios are possible:

- First a layer is formed with a thickness equal to the expected amount of monolayers (100ML) minus the amount of monolayer corresponding to the calculated thickness. This layer is indistinguishable from the substrate. This is due to a nearly perfect stoichiometry and corresponding c-axis equal to the substrate. Such a layer would be ‘invisible’ in an XRD measurement, as simply the substrate is marginally thicker. Subsequently, due to a changed growth process, a nonstoichiometric layer with increased c-axis grows. This film gives rise to a film peak in XRD with Laue oscillations, from which the layer thickness is determined.

- First a layer is formed with a thickness and d-spacing determined from the XRD measurement and model. Subsequently, due to a changed growth process, an (near to) amorphous layer is formed on top, barely ‘visible’ in the XRD measurements, as it barely contributes and manifests itself due to a lack of crystallinity.

In the case of the first and last scenario, in which the film is overall thinner, or an amorphous layer is formed on top of the crystalline film, a clear trend should be observed in the thickness of this missing, or amorphous layer, which should increase when film thickness is increased. In the case of a perfect stoichiometric first layer, indistinguishable from the substrate, this layer thickness should be much less depending on the overall grown thickness, as it is formed in the first stages of growth, after which a ‘second’ layer with decreased stoichiometry, and deviating d-spacing is formed.

4.4.3 Growth studies results and discussion

To investigate these possible scenarios, the next section discusses films grown at 10^{-2} mbar partial oxygen pressure, with varying thickness. At this pressure, as shown earlier, SrTiO_{3} films grow nonstoichiometrically, which results in an increase in the c-axis of the film. The growth speed is determined from initial RHEED oscillations and extrapolated to obtain films with varying thickness of 75ML, 100ML and 150ML, where the 100ML sample is equal to the sample as previously discussed.

XRD results for structural characterisation of the films at different thicknesses are shown in Fig. 4.10, with the simulations of the fit model shown in red. The inset shows the expected thickness values \( d_{est} \), 75ML, 100ML and 150ML based on the total growth time divided by the growth speed based on the observed RHEED oscillations, also shown Fig. 4.10. The total film thickness \( d_{fit} \) in ML is derived from the fit model, by dividing film thickness \( d(\text{Å}) \) by the increased out of plane c-axis (c(Å)). \( \Delta d(ML) \) is the difference between these thicknesses. Other corresponding simulation parameter values for the fit are given in table 4.2. The
Controlling stoichiometry in SrTiO₃ thin film growth

Figure 4.10: Left: XRD simulation results shown at three different thicknesses. Aimed thickness derived from initial growth speed is respectively 75ML(a), 100ML(b) and 150ML(c). Right: Corresponding specular RHEED intensities. The insets show the AFM topology of the substrates on which the films are grown.

Simulations show that for all films, the thickness determined from the simulations is lower than the expected thickness from RHEED. The difference $\Delta d$ (ML), or ‘missing’ amount of monolayers is respectively 8, 11 and 7 monolayers. No trend seems present in the relation between ‘missing’ film thickness and increased deposition time. Regarding the possible growth scenarios outlined earlier, this excludes a growth process characterised by an accumulating non crystalline top layer or generally thinner film due to a change in sticking. In Fig. 4.10 the specular spot intensities for the three films for the first 400 seconds of growth are shown. All films show a distinct decay in specular spot intensity after a specific amount of oscillations, indicated with digits. Strikingly, the number of oscillations seems in almost perfect agreement with the ‘missing’ amount of monolayers as determined from the measured and simulated film thickness in table 4.2. This strongly suggests
Table 4.2: C-axis strain of the film with respect to the substrate $da/a(\%)$ ($\text{SrTiO}_3$ lattice constant is 3.905Å), film c-axis $c(\text{Å})$, film thickness $d(\text{ML})$ and thickness difference $\Delta d(\text{ML})$ between expected and actual film monolayer thickness.

<table>
<thead>
<tr>
<th>expected $d(\text{ML})$</th>
<th>$da/a(%)$</th>
<th>$c(\text{Å})$</th>
<th>$d(\text{Å})$</th>
<th>$d(\text{ML})$</th>
<th>$\Delta d(\text{ML})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>1.41</td>
<td>3.960</td>
<td>265</td>
<td>67</td>
<td>8</td>
</tr>
<tr>
<td>100</td>
<td>1.47</td>
<td>3.962</td>
<td>350</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td>150</td>
<td>1.43</td>
<td>3.961</td>
<td>565</td>
<td>143</td>
<td>7</td>
</tr>
</tbody>
</table>

A relation exists between these oscillations and this ‘missing’ film thickness.

More likely the growth is characterised according to the "second scenario". Initially, a $\text{SrTiO}_3$ film is formed with nearly perfect stoichiometry and therefore no significant change in c-axis. This makes the layer indistinguishable from the $\text{SrTiO}_3$ substrate. After a certain amount of layers, the growth process changes into the growth of the ‘second’ layer characterised by an increased c-axis, with a thickness corresponding to the Laue oscillations periodicity, which is thinner than the expected total film thickness. The samples outlined in this section are grown at a partial pressure of $10^{-2}$ mbar of oxygen for which it is shown that plume species are under oxidised and subsequently grown films in the "bulk" of the film are nonstoichiometric. From these measurements and results it is concluded that an initial stoichiometric layer is stabilised, even when nominally depositing under conditions when non-stoichiometry would be expected due to lack of oxygen. The stabilisation apparently occurs with the substrate as the source of oxygen, in the picture of oxidation of surface species being most important to determine sticking as well as diffusivity. In under oxidised conditions with regard to the oxygen in the background gas, during initial growth the arriving species scavenge oxygen from the substrate to replete the lack of oxidation during propagation, necessary to form a stoichiometric film. In addition, the process of bulk oxygen supply is limited by the surface morphology as well as bulk diffusion of oxygen leading to a finite interfacial layer thickness as is seen in both XRD (as ‘missing’ thickness) as well as RHEED oscillations for each individual sample, pointing to a thickness of this layer somewhere between 7 and 11 monolayers.

In this scenario there is no reason for a dependence of the amount of monolayers after which this transition occurs on the deposition time. Therefore the irregularity in amount of monolayers after which this transition occurs might be correlated to the step density of the initial substrate. Namely, for samples with a higher step density the amount of oscillations is lower, as can be seen in the insets of Fig. 4.10. It is speculated that the oxygen exchange possibly depends on surface morphology and substrate-film interface characteristic and morphology.
4.5 Discussion

Based the results, here a model for homoepitaxial growth of SrTiO$_3$ is presented which schematically describes how fluence and pressure affect plume composition and subsequent thin film growth of SrTiO$_3$. Control over film stoichiometry is mainly based on control over species oxidation, rather then control of species kinetics. Although the model is highly oversimplified, this work sheds new light on key mechanisms in the process of ablation, plume propagation and film growth with renewed interpretation of how these mechanisms are affected by these growth parameters.

The effect of fluence on the characteristics of the plasma plume can be understood in roughly three mechanisms. First, fluence affects:

- Ablated volume and flux of material ($[\text{Flux}]$).

Increased fluence results in increased volume ablation. The relation between fluence and ablated volume is not linear as part of the laser pulse energy is absorbed by the formed initial plasma plume. This is supported by the self emission measurements presented in chapter 4, from which it is concluded that the energy is also transferred as:

- Kinetic energy of arriving species ($E_K$), and
- Excitation temperature of species ($K_B T_e$).

The background gas pressure subsequently affects the expanding plume by affecting:

- Propagation dynamics and kinetic energy of species.

It has been shown that the propagation dynamics of the plume are significantly influenced by the background pressure, where in between an absolute background gas pressure of $10^{-2}$ and $10^{-1}$ mbar, the plume propagation dynamics undergo a transition from ballistic to diffuse, thermalised propagation where strong plume confinement occurs. At this point, as schematically outlined in Fig. 4.11 for an absolute pressure $>8 \cdot 10^{-2}$ mbar, species kinetic ($E_K$) and excitation ($K_B T_e$) energy are negligible. Due to the confinement of the plume stoichiometry is maintained, where with the introduction of a partial pressure,

- oxidation and chemical composition of species in the plume

is altered and one could argue, even controlled. Regarding the fluence, in the thermalised pressure regime, it can be concluded that the fluence only affects the flux of species, which are subsequently oxidised to some degree by this partial oxygen pressure.

Subsequently a SrTiO$_3$ film is formed, for which this work has shown that mainly the oxidation state of species on the surface determines the stoichiometry of the film. Multiple mechanisms that contribute to the oxidation of species and film have been identified. First,
Figure 4.11: Schematic overview on the influence of fluence and background gas pressure on the growth of SrTiO$_3$. At relatively high pressure, fluence only affects ablated volume. Stoichiometry of the SrTiO$_3$ film is determined by the matter of oxidation from either the background gas pressure or oxygen diffusion through the substrate.

- plume oxidation due to background gas pressure,

As thoroughly outlined in this work. But besides the oxidation due to oxygen background gas, also

- species oxidation by oxygen diffusion from the substrate surface

appears to occur. The results of the measurements presented in Fig. 4.10 strongly suggest a stoichiometric reconstruction occurs in ‘nonstoichiometric’ plume conditions, likely explained by this oxygen diffusion. Species arrive under-oxidised, which results in a nonstoichiometric film. However, due to oxygen diffusion from the surface, apparent oxidation occurs, resulting in initial stoichiometric layers. The thickness of this initial layer likely depends on the oxidation state of the arriving species and the surface morphology. Lastly,

- species on the substrate surface can oxidise with oxygen from the background gas.
Besides oxidation of under oxidised species with oxygen from the substrate, (depending on partial oxygen pressure) species can oxidise with the oxygen in the background gas. For these SrTiO$_3$ film growth studies no clear observations have been made that point towards the contribution of this process of oxidation of surface species with the background oxygen gas. Nonetheless, in chapter 5 focussing on YBiO$_3$ growth, it is speculated that due to lacking correlation between plasma and film characteristics, oxidation of species on the surface contributes to the sticking and adsorption of bismuth.

### 4.6 Conclusion

Growth and structural characteristics of homoepitaxial grown SrTiO$_3$ films under different oxidising conditions have been investigated with RHEED, AFM and XRD and related to plasma plume characteristics as outlined in chapter 3. Films have been grown in a pressure regime between $10^{-2}$ and $10^{-1}$ mbar. In chapter 3 it was shown that in this pressure regime, the oxidation of SrTiO$_3$ plume species can be controlled using background gas mixtures of oxygen and argon. Here, a clear dependence of film characteristics on background gas pressure conditions was shown, where both stoichiometry as well as surface diffusivity was controlled by the oxidation of arriving species and not so much their kinetic energy. This oxidation was controlled within the plasma plume before species arrive on the growth surface, in addition to the observed oxygenation by substrate.

From RHEED studies it is observed that with increasing oxygen pressure, layer-by-layer growth is maintained for increasing deposition time, indicating improved surface diffusion and film smoothness. From XRD studies, a decrease in film nonstoichiometry is observed up until near perfect stoichiometry, indistinguishable from the substrate, with increasing partial oxygen pressure from $10^{-2}$ to $6 \cdot 10^{-2}$ mbar during growth. In this pressure regime, the spectroscopic studies in chapter 3 show that with increasing partial oxygen pressure, a decrease of Ti and increase of oxidised species is observed in the plume composition. Also, for a specific pressure condition of $6 \cdot 10^{-2}$ mbar partial oxygen pressure, neutral atomic titanium ceases to reach the substrate. Furthermore, both Ti and Sr reach the substrate in an oxidised state. This strongly suggests that (full) oxidation of plasma constituents is clearly a necessary requirement for stoichiometric growth of SrTiO$_3$.

Next to varying background gas conditions, the effect of fluence on film stoichiometry is investigated. It is shown that the stoichiometry for films grown at absolute oxygen pressure depends on the laser fluence, where for films grown in partial oxygen pressures (at $8 \cdot 10^{-2}$ mbar total pressure) no fluence dependence is observed. It is concluded that in the plume ballistic expansion regime, the fluence likely affects the elemental specific spatial distribution due to mass differences of plume species. This effect is suppressed by the plume confinement in the diffusive regime, where stoichiometry only depends on species oxidation controlled by
partial oxygen pressure.

Finally, from a structural investigation of films grown at varying thickness, it is concluded that an initial stoichiometric layer is stabilised, even when nominally depositing under conditions when non-stoichiometry would be expected due to lack of oxygen and oxidation of species. The stabilisation likely occurs with the substrate as the source of oxygen in the picture of oxidation of surface species being the most important to determine sticking as well as diffusivity. In addition, the process of bulk oxygen supply is limited by the surface morphology as well as bulk diffusion of oxygen leading to a finite interfacial layer thickness of several monolayers.
Chapter 5

Controlling bismuth volatility in YBiO$_3$ thin film growth

Abstract
The relation between the characteristics of YBiO$_3$ plume constituents and grown YBiO$_3$ film characteristics containing volatile bismuth was investigated. The pressure dependent composition of the YBiO$_3$ ablated plasma plume was investigated with OES and LIF. From OES it is shown that Y rapidly oxidises. With LIF the Y, YO, and Bi spatiotemporal distributions in the plasma was mapped. It is observed that little chemical interaction takes place between the plasma plume constituents and the background gas. The spatial distribution of YO depends on the background gas conditions, which appears to result from reactions between the background gas and the target. For grown YBiO$_3$ films a strong dependence on partial oxygen gas pressure is observed in structure and composition. Below $2 \cdot 10^{-2}$ mbar partial oxygen pressure, no YBiO$_3$ structure is formed, but polycrystalline Y$_2$O$_3$, with no bismuth present in the film. Above $2 \cdot 10^{-2}$ mbar, a (near)cubic defective fluorite YBiO$_3$ is formed. These transitions in film growth do not coincide with a significant change in plasma composition. From this it is concluded that the strong influence of the background gas on the film composition is the result from surface chemistry involving plasma constituents at the surface and oxygen from the background gas.

Part of the work discussed in this chapter is published in: Kasper Orsel, Rik Groenen, Bert Bastiaens, Gertjan Koster, Guus Rijnders, Klaus Boller, Laser-induced fluorescence analysis of plasmas for stoichiometric growth of YBiO$_3$ films with pulsed laser deposition, APL Materials 4, 126102, 2016. [34]
5.1 Introduction

Since their recent discovery, topological insulating materials have drawn much attention for their unique quantum mechanical properties. These materials, insulating in bulk, have exotic metallic states present at their surfaces, possibly useful for all sorts of new technological applications in spintronics and quantum computing.[71] Several TI materials have been discovered in recent years such as bismuth telluride and bismuth selenide, both containing bismuth. Particularly promising, based on first principles calculations, is YBiO$_3$.[72] Although YBiO$_3$ thin films have been grown by chemical solution deposition,[73] little is reported on the thin film growth of YBiO$_3$ single-crystalline films using PLD. The volatility of bismuth challenges the stoichiometric growth of YBiO$_3$, especially at high temperatures typically used in PLD growth.[74,75] Obtaining stoichiometry in thin films of these materials often has a purely empirically approach, where a nonstoichiometric target is used with an excess of volatile material to compensate for the reevaporation from the substrate surface.[76]

Within such an approach no effort is made in investigating how growth conditions influence bismuth volatility and sticking. This questions the reliability of optimised growth parameters resulting stoichiometric YBiO$_3$ thin films. In chapter 3 and 4, it is shown that the plume chemistry and oxidation and subsequent characteristics of the arriving species, relate to growth kinetics and stoichiometry of the film. Likely, the volatility and sticking of bismuth depends on its chemical nature and oxidation state, which requires a more detailed understanding of plume characteristics in relation to surface chemistry and film growth.

Here the characteristics and composition of laser ablated YBiO$_3$ plasma is investigated with OES and LIF measurements. With LIF, the spatiotemporal distribution of Y, Bi and YO is investigated and mapped for varying background gas conditions based on the findings outlined in the previous chapters. Similar to the previous studies, a partial oxygen pressure regime between $10^{-2}$ and $10^{-1}$ mbar is investigated. To relate plasma plume composition to film growth characteristics and stoichiometry, YBiO$_3$ films were grown on (LaAlO$_3$)$_{0.3}$(Sr$_2$TaAlO$_6$)$_{0.7}$ (LSAT) substrates in similar pressure conditions. A strong pressure dependence on the structure of grown films was observed, as investigated with X-ray Diffraction, X-ray Reflectivity (XRD, XRR) and X-ray Photoelectron spectroscopy(XPS). This structural dependence is related to the investigated plume characteristics. It is shown that, unlike the correlation between plume chemistry and film stoichiometry presented in chapter 3 and 4, the observed film structural change does not coincide with a significant change in plasma composition. This suggests a relation between oxygen in the background gas and surface chemistry of Bi during growth of YBiO$_3$ films.
5.2 Plume composition

To investigate the composition and chemistry of the YBiO$_3$ ablation plume, OES and LIF measurements have been performed from which the results are outlined in the following sections.\(^1\)

5.2.1 Optical Emission Spectroscopy

The composition of the YBiO$_3$ plume is investigated with OES by imaging the spectrally resolved self emission of the expanding plume at varying delay time. OES images have been obtained by imaging the plume self-emission onto the entrance slit of an imaging spectrograph (300 lines/mm 500 nm blaze grating) coupled to an ICCD camera. Measurements have been performed for varying partial oxygen pressures between 0.00 mbar(pure argon) and 10$^{-1}$ mbar of oxygen for a total pressure of 10$^{-1}$ mbar.

The results presented in Fig. 5.1 show normalised measurements for three different partial background gas pressures, 0.00 mbar, 10$^{-2}$ mbar and 10$^{-1}$ mbar of partial oxygen pressure at three different delay times, respectively 1 $\mu$s, 10 $\mu$s and 20 $\mu$s after ablation.\(^2\) Spectral lines are identified based on databases\(^{[53,77]}\) next to reference measurements in which OES imaging is performed on ablated plasma from targets consisting of the individual elements of yttrium and bismuth. Yttrium has many transitions to the 4d5s ground state in the visible light regime, as is observed in the measurements. No bismuth spectral lines are significantly present, as bismuth has only a few transitions in the measured wavelength range, which are relatively much weaker then Y and YO lines. Therefore, as the spectrum of an YBiO$_3$ plume shows only lines corresponding to Y and YO, the identification of the behaviour of both species is obviously not possible.\(^3\)

Clear differences are observed when comparing the spectra at varying background partial gas pressures. When ablating in pure argon (0.00 mbar partial oxygen pressure), strong lines corresponding to neutral Y are measured propagating towards the substrate over time. A weak YO line at $\sim$610 nm is identified increasing in intensity over time. This implies a certain amount of oxidation of Y.

\(^1\)The overview of the results in this section is based on the results sections outlined in the thesis of Orsel,\(^{[33,34]}\) in which also a detailed overview on the theoretical and experimental background of the measurements can be found.

\(^2\)For optimised signal-to-noise ratio images are taken by integration over 10-20 pulses, with a TTL gate width varying between 20-1200ns, depending on delay time. MCP gain for all measurements is set to a maximum value of 4095 (arb. units).

\(^3\)Bismuth only has a limited amount of transitions in the measured wavelength range. These lines correspond to transitions with high upper level energies, which therefore are not significantly excited and populated at typical plume temperatures. OES reference measurements (results not presented here) on a bismuth target show only one significant spectral line at 472.25 nm is observed, corresponding to the 6p$^2$(5P$_0$)7s to 6p3 2D$^-$ transition. However, this line is not observed in the OES measurements on YBiO$_3$ plasma, shown in Fig. 5.1 due to the relative much stronger Y and YO lines. The reference measurements on the Y target shows this extended spectrum of spectral lines identical to the measurements on ablated YBiO$_3$. 


occurs even without addition of oxygen as background gas. When introducing oxygen background gas, the spectra at higher delay times are significantly different. For both $10^{-2}$ and $10^{-1}$ mbar partial oxygen, over time the self emission of Y spectral lines decay significantly, together with a strong increase in YO line intensity. At 20 μs, spectral lines of neutral Y are hardly present, with mostly lines corresponding to YO visible. In contrast to the characteristics of the SrTiO$_3$ plasma plume, as outlined in chapter 3, no gradual oxidation with increasing partial oxygen pressure is observed. Already at the first pressure increment of $10^{-2}$ mbar partial oxygen pressure, the YBiO$_3$ plume seems to fully oxidise, suggesting that Y oxidises much stronger than Ti. Even in pure argon YO is observed, suggesting that Y oxidises not only by oxygen background gas, but also by oxygen from the target, as is discussed more thoroughly in the next section.

To overview the oxidation of the plume over time at all pressure conditions, figure 5.2 shows the ratio between the relative normalised intensity of a Y line at 464.5 nm ($4d5s(^3D)5p$ to ground level transition with upper level of 2.669eV) and a YO line at 613 nm. For all pressure conditions, immediately after ablation a strong increase in YO/Y ratio is observed, indicating a strong increase in YO species density. Even when ablating in pure argon (purple curve) a strong increase of YO is observed. This suggests that Y species do not oxidise with the oxygen introduced in the background (as non is present in pure argon), but apparently oxidise with the oxygen ablated from the target. Generally for higher partial oxygen pressure, the steepness of the curve increases, suggesting an increase in
5.2 Plume composition

Figure 5.2: Relative intensity ratios between YO (spectral line at 613 nm) and Y (spectral line at 464.5 nm), at varying partial oxygen background gas pressure conditions. Line intensities are determined from the OES measurement presented in Fig.5.1 (in which selected lines are indicated with dashed lines). For all pressure conditions, even in pure argon pressure, a strong increase of the YO line immediately after ablation is observed, suggesting strong oxidation of Y.

oxidation. Around 8 µs, a general change in trend is observed for all pressure conditions, where for $4 \cdot 10^{-2} < 10^{-1}$ mbar and 0.00 mbar, the YO/Y ratio again decreases. The ratio at $10^{-2}$ and $2 \cdot 10^{-2}$ still gradually increases. This could be explained by a reduced density of YO at later stages of plume expansion, but this is highly unlikely considering the observed strong oxidising nature of yttrium. More likely this is the result of the pressure dependent plasma temperature and/or the plume thermalisation, see section 3.4, affecting line intensities and the general accuracy of the measurement. To investigate the composition and chemistry in more detail, the next section outlines LIF measurements to obtain more detailed information about the spatial and temporal distribution of constituents of the YBiO$_3$ plume.

5.2.2 Laser Induced Fluorescence

This section outlines the results from the investigation of the spatial and temporal distribution of plume constituents using laser induced fluorescence (LIF). For the atomic species, Y and Bi, the LIF measurements were calibrated with Absorption Spectroscopy (AS) to obtain absolute densities. Like in the previous studies, the plume composition was investigated at partial oxygen pressure. The ablation laser fluence was kept constant for all measurements at 1.3 J/cm$^2$. To investigate the chemical composition of the plasma plume, the spatiotemporal distribution of expected dominant plasma constituents were mapped, respectively Y, YO, Bi and BiO. Species were mapped in a total background gas pressure of $10^{-1}$ mbar, with partial oxygen pressure increments of $2 \cdot 10^{-2}$ mbar, in order to investigate the
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Figure 5.3: Density distributions of several components of an YBO plasma plume cross-section in the propagation plane from the target ($z = x = 0$ mm) to the center of the substrate position ($x = 0$ mm, $z = 50$ mm). The left part of each picture displays the ground state density in $10^{-1}$ mbar of pure oxygen background gas and the right part displays the density in a $10^{-1}$ mbar pure argon background. All pictures are normalised, with the normalisation factor shown in the bottom. The densities shown are measured at $35 \mu$s delay after ablation. The lack of signal close to the centre of the target ($x = 0, z = 0$) is caused by the target holder obscuring one edge of the LIF excitation beam.

The lack of signal close to the centre of the target ($x = 0, z = 0$) is caused by the target holder obscuring one edge of the LIF excitation beam.

oxidation of Bi and Y in the plasma plume. Unfortunately BiO densities could not be measured, with excitation lines at 338.10 nm, 343.44 nm, 670.88 nm and 693.65 nm.\cite{77} Although several of these transitions are described as strong resonance lines, lacking signal could be explained by low concentrations of BiO present in the plume at any measured condition, resulting in a fluorescence signal below the detection limit of our setup.\footnote{Even an upper limit quantification of population density cannot be given for the BiO density as the detection limit of the measurement setup depends on several species specific factors, such as the strength of the transition being used and the wavelength being detected.}

Figure 5.3 shows the absolute density distribution of Y, Bi and YO for a cross section of the YBiO$_3$ plasma plume in the propagation plane from the target ($z = x = 0$ mm) to the substrate position ($x = 0$ mm, $z = 50$ mm).\footnote{The absolute calibration of LIF with AS to obtain absolute species density maps was only applicable to the atomic species and not to molecules. To calculate the amount of YO present in the plume, it is assumed that the primary oxidation product for Y is YO. This assumption is supported by the fact that the total number of Y-containing particles, i.e., $N_Y + N_{YO}$, remains nearly constant for all oxygen fractions. To determine the total number of possible Y based particles present in the YBiO$_3$ plasma plume with an independent approach, the total amount of ablated material is calculated using a measurement of weight reduction of the target. This measurement yielded a number of $\sim 1 \times 10^{15}$ particles per pulse. Considering the stoichiometry of the sintered $Y_2O_3/Bi_2O_3$ target one fifth of the total amount of elements in the plume is Y, $N_Y + N_{YO} \sim 2 \times 10^{14}$ per pulse.} Two images of half of the plasma plume are shown next to each other for comparison. The left half of each image displays the ground state density distribution as recorded in $10^{-1}$ mbar oxygen background gas pressure whereas the right half displays the distribution is recorded in $10^{-1}$ mbar argon background gas pressure. All measurements were carried out at $35 \mu$s delay after ablation, when already significant interaction of the
5.2 Plume composition

Front of the plume with the substrate occurs. All images are normalised to unity, with the normalisation factor displayed in the bottom.\(^6\)

Figure 5.3(a) shows the Bi density distribution. Although the density distributions in both pressure conditions look quite similar visually, their normalisation factor ratio is 2.5. It can be seen that for both pressure conditions, the highest density of Bi remains close to the ablation target, while all other species that have been studied in this work propagate more towards the substrate, similar to Y. The distribution of Y, as shown in Fig. 5.3(b), shows little difference in relative spatial distribution, but does show a very large difference in absolute density by almost two orders of magnitude. The spatial density distribution of YO shows significant differences when ablating in argon or oxygen as is shown in Fig. 5.3(c). Although the value for maximum absolute density changes only slightly for the two different background gas compositions, in pure oxygen the YO distribution has propagated significantly more towards the substrate location \((z = 50 \text{ mm})\) as compared to the distribution in pure argon. The propagation dynamics of the plasma species are nearly identical in both argon and oxygen background gas pressure and the relatively small amount of Y in argon that oxidises in oxygen shown in Fig. 5.3b does not explain the significant change in distribution of YO in argon compared to oxygen background. Therefore, it is suggested that this difference could be assigned to a change in composition at the surface of the target after repeated ablation in either argon or oxygen background gas as is discussed later.

Figure 5.4(a) shows the ground state population densities of Y, YO, and Bi along the propagation axis \(z\) (at \(x = 0 \text{ mm}\) in Fig. 5.3), at specifically the position of the substrate \((z=50 \text{ mm from the target})\) as a function of different partial oxygen pressure. The measurements are taken at 35 \(\mu\text{s}\) delay from target ablation, significantly after first interaction of the plume with the substrate occurs (around 20 \(\mu\text{s}\)). It can be seen that the density of Y decreases by almost two orders of magnitude with an increase of oxygen up to \(6\cdot10^{-2} \text{ mbar}\), while the density remains stable with further increasing the oxygen concentration. The density of YO only increases significantly from 0.00 to \(2\cdot10^{-2} \text{ mbar}\) partial oxygen pressure, after which an increase in oxygen has very little influence on the YO density. In contrast, the Bi density is almost independent of the composition of the background gas and shows only a marginal decrease for increasing partial oxygen pressure.

Figure 5.4(b) shows the total (i.e., spatially integrated) amount of Y, YO, and Bi present in the plume as function of partial oxygen pressure measured at 35 \(\mu\text{s}\) delay from target ablation. The total number of particles as presented in Fig. 5.4(b) is determined by spatially integrating the Y and Bi LIF signals over the entire plasma plume, assuming a cylindrical symmetry around the \(z\)-axis \((x = y = 0)\). It is

\(^6\)In these measurements, the heater with substrate is removed as it causes significant unwanted optical reflections affecting measurement accuracy. As explained earlier although a temperature gradient induced by a heater does affect the propagation of the plume, the grown films described later on in this chapter are heated locally with laser heating. It is verified that, unlike resistive heating with a large heated area, this geometry of heating does not significantly affect the plume dynamics.
shown that even in pure argon, a significant amount of Y is oxidised. When more oxygen is supplied via the background gas, the amount of Y further decreases until the oxidation appears to reach a chemical equilibrium between loss to YO and the reverse reaction for $6 \cdot 10^{-2}$ mbar partial oxygen pressure and above. The amount of YO increases from pure argon to $2 \cdot 10^{-2}$ mbar partial oxygen pressure, beyond which it remains the same for higher partial oxygen pressure. The amount of Bi displays a steady decrease with an increase in oxygen to half the amount of Bi in pure oxygen as compared to pure argon. If oxidation of half of the amount of Bi would lead to the formation of BiO, the corresponding BiO density should fall well within the detection limits of the LIF setup. Therefore it is speculated that the formation of BiO is not the primary channel for the loss of Bi, but other $Bi_xO_y$ species are formed.\cite{78}

**Discussion**

The spatiotemporal data presented in Fig. 5.3 and 5.4 could be interpreted such that only limited chemical interaction takes place between the plasma plume and the background gas. This means that the measurements in the YBiO$_3$ plasma show remarkable differences in comparison to oxidation studies on SrTiO$_3$ presented in chapter 3. To better describe the difference to those observations, in the oxidation studies of Ti three distinct features can be identified as characteristic for oxidation of a plasma species by oxygen from the background gas.

- Oxidation should be largely absent from the plasma for ablation in pure argon, only appearing when oxygen is added to the background gas.

**Figure 5.4:** The ground state population densities of Y, YO and Bi measured along the propagation axis, $z$ ($x = 0$), at 50 mm from the target, at different partial pressures of oxygen. (b) Total number of ground state particles of Y, YO and Bi present in the plasma plume at different partial pressures of oxygen. All measurements are performed at a delay of 35 $\mu$s from target ablation and in $10^{-1}$ mbar total background pressure.
• When increasing the oxygen fraction, species should become oxidised primarily on the outer edges of the plume, since in this region the interaction between the plasma plume and the background gas is strongest. Only in a background gas close to pure oxygen, oxidised species can also appear in the center of the plasma plume.

• A loss of the atomic species on the edges of the plasma plume should be accompanied by the appearance of the oxidised species in these regions, following a chemical reaction converting the atomic species (e.g., A) to the oxidised species (A + O₂ → AO + O).

No clear signature of any of these features, typical for oxidation by reactions with the background gas, appears to be present in the oxidation of Y. From Fig. 5.3 it is evident that large amounts of YO are present in the plasma plume when ablating in pure argon, while the oxidised species appear to arise from the center of the plume, and the Y density decreases homogeneously, instead of primarily at the edges.

Therefore is it concluded that in an YBiO₃ plasma the atomic oxygen provided to the plasma from the target during ablation is the primary source of oxygen for the oxidation of Y. The increase of YO with an increase of the oxygen partial pressure might be caused by a compositional change and oxidation of the target surface, depending on oxygen gas pressure, in between ablation pulses. Changing target composition by repeated ablation has been observed in other studies. Here, in the case of an YBO target, repeated ablation in pure argon might have led to partial oxygen depleted surface of the target, resulting in Y in the front of the plasma plume and YO towards the substrate. In an oxygen background, this depletion does not occur, where the top layer reoxidises in between ablation pulses, resulting in full oxidation of Y and a more homogeneous distribution of YO in the plasma plume. This also suggests that the most important oxygen source for oxygenation of Y species is not so much the oxygen in the background, but oxygen from the target. Bismuth appears to hardly oxidise at all, which is consistent with the observation that the reaction between Bi and O₂ is endothermic.

To be able to investigate the relation between pressure dependent plasma composition and YBiO₃ thin film growth, thin films have been grown on LSAT substrates varying partial oxygen pressure for which the results are outlined in the following sections.

5.3 Thin film growth temperature dependence

As this work focusses on investigating specifically the oxygen background gas dependence on YBiO₃ thin film growth, first optimal growth temperature is determined. Therefore, the temperature dependent composition of grown YBiO₃ thin films is investigated with XPS. Namely, generally for arriving species, but
especially for volatile species such as bismuth, the kinetic behaviour and sticking on the substrate surface dependent on the substrate temperature. This relation between the sticking coefficient $\alpha(t)$, or the ratio between incorporated and arriving species, and temperature of the substrate $T_S$ typically follows an Arrhenius type of plot. The sticking coefficient depends on temperature and adsorption energy $E_{ads}$, or the strength of interaction between the adatom and the substrate by $\alpha(t) \sim \exp\left(\frac{E_{ads}}{k_B T_S}\right)$. This shows that with increasing temperature a strong increase in adatom desorption occurs. Here, this work does not focus on relating this model to growth experiments to quantify kinetic parameters, but an empirical determination of the relation between film composition and temperature. The background gas pressure for these films is chosen at $10^{-1}$ mbar oxygen pressure, as the next section outlines the investigation on the role of partial oxygen pressure on film composition, at a total pressure of $10^{-1}$ mbar. For the grown films, growth temperature is varied between 620°C and 720°C. The target-to-substrate distance was set to 50 mm, the laser repetition rate was set to 1Hz. Deposition duration was set to 30min or 1800 pulses for an aimed film thickness of $\sim$30-40 nm. After growth films were cooled down in 100mbar oxygen pressure at 30°C/min cooldown rate.

Figure 5.5 shows the photo-emission spectra measurements on the films at varying growth temperatures. Figure 5.5a shows photo-emission spectra for two films grown at 695°C and 720°C, around Bi 4d (440eV), Y 3s (395eV) and Y 3p (305eV) core levels. Clearly, for the sample grown at 720°C, the yttrium signal relative to the bismuth is much stronger compared to the 695°C grown

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7Due to the lack of RHEED monolayer oscillations, no exact growth speed could be determined during growth. Therefore, for all samples a growth time of 30min or 1800 pulses was chosen roughly based on the growth speed of SrTiO$_3$ films as discussed in the previous chapter.

8Film structure and morphology is discussed in following sections, from the presented results growth temperature for subsequently grown films is defined.
5.4 Thin film growth; partial oxygen pressure dependence

Films have been grown on LSAT substrates at varying oxygen and argon partial pressures at a total pressure of $10^{-1}$ mbar. Samples have been grown at respectively $0, 10^{-2}, 2 \cdot 10^{-2}, 4 \cdot 10^{-2}, 6 \cdot 10^{-2}, 8 \cdot 10^{-2}$ and $10^{-1}$ mbar of partial oxygen pressure. Growth temperature is set to 670°C. The target-to-substrate distance was set to 50 mm, the laser repetition rate was set to 1Hz. Deposition duration was set to 30min or 1800 pulses for an aimed film thickness of $\sim 30-40$ nm. After growth films were cooled down in 100mbar oxygen pressure at 30°C/min cooldown rate. The following sections outline and discuss results on growth characteristics, morphology, structure and composition using in situ RHEED, AFM, XRD and XPS.

5.4.1 In situ RHEED analyses

During deposition RHEED is used to monitor and study the surface structure of the film. The specular spot intensity was monitored over time and the diffraction patterns were recorded before and after growth of the films, shown in Fig. 5.6. In (a) a typical 2D diffraction pattern of the LSAT substrate surface is shown, representing all the used substrates on which subsequent films have been grown. The time evolution of the specular spot intensity is shown in (b), also representative for growth experiments. For all pressure growth conditions no monolayer oscillations were observed, only a gradual decay of the main specular spot intensity, where during initial growth intensity drops corresponding to single pulses were observed. Figs. 5.6(c-h) show the diffraction pattern after growth at three different partial oxygen pressures, $0.00$ mbar (c-d), $10^{-2}$ mbar (e-f) and $2 \cdot 10^{-2}$ mbar (g-h) at two different crystal orientations. The results shown in (g-h) for the $2 \cdot 10^{-2}$ mbar grown film represent the patterns for all films grown at a pressure $>2 \cdot 10^{-2}$ mbar. Clearly for these three bottom partial oxygen pressures, the resulting films show difference in structure.
For the film grown at 0.00 mbar partial oxygen pressure, weak streaky diffraction spots are visible positioned on the Laue circles, indicating a 2D diffraction pattern. The streaky features indicate a textured nature of the crystallinity of the film, corresponding to non-epitaxial random in-plane orientation. The film grown at 10\(^{-2}\) mbar partial oxygen pressure shows clear 3D diffraction spots. The 3D RHEED pattern is the result of transmission electron diffraction through small surface asperities. In this case, tilting of the sample does not alter the diffraction pattern, which also is experimentally verified. The 45 degrees angle of the diffraction spots with respect to the indicated in-plane direction of the LSAT substrate imply a 45 degrees in-plane tilt of the in-plane crystal orientation of the grown film with respect to the LSAT substrate. Furthermore, mainly shown in (e), higher order diffraction spots are observed, indicated with the smaller arrows. This implies higher periodicities in the lattice of the grown film possibly related to defects or non-stoichiometry. The film grown at 2\(\times10^{-2}\) mbar shows similar 1\(^{st}\) order diffraction pattern features compared to the 10\(^{-2}\) mbar grown film. The higher order diffraction spots are significantly weaker, not to be observed at all in the [11] direction indicating a film with a well defined crystallinity. From the RHEED investigation it is concluded that films generally roughen, where with
increasing partial oxygen pressure up to $2 \times 10^{-2}$ mbar the crystallinity significantly improves. In between $2 \times 10^{-2}$ and $10^{-1}$ mbar partial pressure film characteristics are very comparable, likely characterised by small highly crystalline epitaxial surface asperities or grains, with 45 degree rotated in-plane lattice orientation compared to the substrate. The next section outlines a further investigation of the film surface morphology.

### 5.4.2 Morphology

To investigate the morphology and verify the surface roughening and presence of surface asperities, the film surface is investigated with AFM and crosssection HRSEM. The surface topology is imaged using tapping mode AFM from which the results are shown in Fig. 5.7(a). The sample has been grown in $2 \times 10^{-2}$ mbar partial oxygen pressure and is the same sample from the presented RHEED data. Clear round shaped $\sim$50-100 nm sized surface asperities are visible with a typical height of $<8$ nm. Next to these surface asperities occasional much larger particles are observed with feature size of $\sim$200 nm in width and $\sim$50 nm in height. This surface topology represents the surface topology of all other grown films at different background gas pressure.

Fig. 5.6(b) shows the results of cross-section HRSEM imaging of the same sample. Similar morphology is observed when compared to the results in (a). Furthermore, from this cross-section measurement a rough indication of film thickness is obtained which is $\sim$35 nm. Also here, next to small surface asperities,

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9EDX measurements (not presented) during SEM imaging on these particles showed the presence of only yttrium, no bismuth to be present in these particles. Likely these particles are stable yttria, or $Y_2O_3$ given the 3+ oxidation state of yttrium and the general preference of yttrium to oxidise as has been shown earlier.
occasional large particles are observed. Summarising, all films grown at varying partial oxygen pressure show similar morphological characteristics, with a grainy surface with large particulates, without clear differences at varying partial oxygen pressures during growth. The next section outlines the results on film structure and composition.

5.4.3 Structural characterisation

To investigate the crystalline structure of the grown films, results of symmetrical out-of-plane $\theta$-2$\theta$ scans are outlined, as well as asymmetric scans to determine in-plane crystallinity and epitaxy. Subsequently, the results of X-ray reflectivity scans are discussed to investigate film thickness and density. These results are related to photo electron emission spectra with which elemental composition of the films is determined.

Figure 5.8 shows the results for symmetrical out-of-plane $\theta$-2$\theta$ scans for all YBiO$_3$ grown films at varying partial oxygen pressure. The strong peaks visible for all films at 23.0° and 46.9° correspond to respectively the (002) and (004) Bragg reflections of the LSAT substrate. For the films grown at 0.00 and 10$^{-2}$ mbar partial oxygen pressure, a weak Bragg reflection is observed at 29.0°. Additionally, at 2$\cdot$10$^{-2}$ mbar, also peak at 33.7° is observed. These two peaks likely correspond to the (222) and (004) reflections of polycrystalline grown Y$_2$O$_3$.[79][10] For partial oxygen pressures >10$^{-2}$ mbar a remarkable transition in structure is observed, where the previously described peaks are not present anymore, with only a single reflection present at 33.4° for partial oxygen pressures up to 6$\cdot$10$^{-2}$ mbar. At 8$\cdot$10$^{-2}$ and 10$^{-1}$ mbar, a second weaker reflection at 28.8° is present.

To identify peaks and the corresponding crystalline structures, interpretation is based on earlier studies reporting on structural investigation of polycrystalline sintered targets and grown films of (Y$_x$Bi$_{1-x}$)$_2$O$_3$. From theoretical and experimental results it is concluded that (Y$_x$Bi$_{1-x}$)$_2$O$_3$ with $x=0.2$-0.5 has a cubic lattice constant of $\sim$5.4Å, with a defective fluorite type crystal structure with space group Fm$\overline{3}m$.[80–82][11] Therefore the observed peaks at 33.4° and 28.8° are assigned to respectively YBiO$_3$ (002) and YBiO$_3$ (111) reflections assuming this cubic fluorite structure,[12] which translate to an out-of-plane lattice constant of 5.360Å.

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10 This is supported by XPS compositional characterisation discussed in the next section.
11 These studies agree on a stable (Y$_x$Bi$_{1-x}$)$_2$O$_3$ fluorite phase for $x=0.2$-0.5 where the yttrium and bismuth atoms are distributed uniformly on a FCC lattice, with oxygen filling up the tetrahedral holes with a 75% occupancy. For example, $x=0.5$ results in a ABO$_3$ stoichiometry of YBiO$_3$.
12 Although topological insulating behaviour is assigned to cubic perovskite YBiO$_3$, other studies show that this YBiO$_3$ Pm$\overline{3}m$ perovskite form is never stable. Namely, it is reported from band structure calculations that YBiO$_3$ in the cubic perovskite structure with this 4.405Å lattice parameter and Bi at the octahedral site is about 2.50 eV/atom above the lowest-energy structure and therefore unlikely to be stable.[83] This value of 4.405Å is much smaller than the reported value of 5.428Å[82] lacking discussion on the actual crystal structure. This value of 5.428 is subsequently erroneously[84] assigned to a perovskite structure predicting YBiO$_3$ to be a topological insulator.[72]. Therefore, recent studies highly speculate the TI properties of the perovskite phase of YBiO$_3$, but discuss promising properties to the (Y$_x$Bi$_{1-x}$)$_2$O$_3$ cubic fluorite phase due to its large bandgap.[84]
Figure 5.8: XRD scans of YBO grown on LSAT. The vertical black lines indicate several Bragg reflections of the substrate and the thin film. XRD scans are carried out at different partial oxygen pressures while maintaining a total pressure of $10^{-1}$ mbar. At partial oxygen pressures below $2 \times 10^{-2}$ mbar, only peaks corresponding to poly-crystalline Y$_2$O$_3$ are visible. For pressures $>2 \times 10^{-2}$ O$_2$, an epitaxial YBiO$_3$ layer of similar thickness is grown, as indicated by the (200) peak. At pressures $>6 \times 10^{-2}$ mbar, a small amount of YBiO$_3$ appears to grow in a different, non-epitaxial orientation, corresponding to the (111) peak (Bragg reflection at 28.7), indicating an increase in nucleation rate of YBiO$_3$ at the substrate surface.

The presence of only a single YBiO$_3$(002) reflection for the films grown at $2 < 6 \times 10^{-2}$ mbar suggests a well epitaxially oriented crystalline film, where the observed extra YBiO$_3$(111) peak suggests a certain polycrystallinity and reduced film epitaxy.

To investigate the crystalline structure and film epitaxy in more detail, for the $2 \times 10^{-2}$ mbar grown sample reciprocal space maps around the LSAT(113) and YBiO$_3$(204) substrate and film reflections have been measured at four optimised $\phi$-angles of 45°, 135°, 225° and 315° corresponding to the [113], [113], [113] and [113] LSAT reflections for which the results are shown in Fig. 5.9. Values of $Q_X$ and $Q_Y$ for the film peaks are identical, from which it can be concluded that in combination with $\phi$ optimised values of exactly 90° spacing between every scan, the structure of the film is characterised by a cubic in-plane symmetry. From these reciprocal space maps the in-plane lattice parameter is determined to be 5.420Å, slightly larger than the out-of-plane lattice constant of 5.360Å. Furthermore the maps show that the film structure is mostly relaxed, as the in-plane lattice constant of the YBiO$_3$ film is smaller than the in-plane lattice constant of LSAT, namely 5.470Å for the

\[ d = \frac{n\lambda}{2Q_{xy}}. \]
Figure 5.9: (a) XRD reciprocal space maps at four different φ-angles of a YBiO$_3$ film on LSAT grown at $6 \times 10^{-2}$ mbar of partial oxygen pressure. The measured sharp diffraction spot corresponds to the LSAT(113) reflection, where the wider spot corresponds to the YBiO$_3$(204) reflection. Symmetrical $Q_X$ and $Q_Y$ values indicated in-plane cubic symmetry. Differing $Q_X$ values for film and substrate indicate in-plane relaxation of the film with respect to the substrate. These results represent all YBiO$_3$ grown films in the pressure range of $2 \times 10^{-2} \leq 10^{-1}$ mbar. (b) Schematic representation of the structural orientation of the YBiO$_3$ film with respect to the LSAT substrate structure, indicating the 45° rotation of the fluorite YBiO$_3$ film with respect to the perovskite LSAT structure. Although the schematic shows in-plane lattice match, the YBiO$_3$ structure is in-plane slightly smaller, as is shown with the indicated lattice values.

[110] direction. This suggests that the film has a somewhat tetragonally distorted structure, deviating from the reported cubic fluorite structure.\textsuperscript{14}

\textsuperscript{14}A further investigation and explanation for this exceeds this work.
Figure 5.10: (a) low angle X-ray reflectivity scans on films grown in a range of partial oxygen background gas pressure of 0.00-10^{-1} mbar. A transition in film thickness as determined from Kiessig oscillations is observed at a pressure of ≥2·10^{-2} mbar, together with a shift in critical angle θC increasing for higher pressures. (b) shows photo emission spectra for films grown at 10^{-2} mbar (black) and 2·10^{-2} mbar (blue), representing samples grown respectively at pressures <2·10^{-2} and ≥2·10^{-2} mbar. For the low pressure films, no bismuth is observed, where for the films grown at higher pressure a clear Bi 4d spectrum is measured.

Summarising, from the structural XRD characterisation a strong partial oxygen background gas dependence on structure and composition of the grown film ablated from a YBiO$_3$ target is shown. At low partial oxygen pressures of <10^{-2} mbar remarkably only polycrystalline Y$_2$O$_3$ structures are grown. For higher partial pressures of 2·10^{-2}<6·10^{-2} mbar, a crystalline fully relaxed but epitaxial layer of YBiO$_3$ is formed with a (near)cubic, likely fluorite structure. For higher partial oxygen pressure >8·10^{-2} mbar, an additional YBiO$_3$(111) phase is observed, suggesting polycrystalline phases are formed.

To investigate this transition in film structure in more detail, film composition
was investigated with X-Ray Photo-emission Spectroscopy, next to film thickness studies with low-angle X-ray Reflectivity. Namely, the observed Y₂O₃ films at low pressures suggests a fully lacking presence of bismuth, which should affect film thickness and elemental composition. The results of these measurements on the films grown at varying partial oxygen pressure are shown in Fig. 5.10. Figure 5.10(a) shows X-ray reflectivity scans on grown YBiO₃ films for all background gas pressure conditions from 0.00 mbar to 10⁻¹ mbar partial oxygen pressure. Fringe periodicity is indicated with arrows, critical angle θ_C is indicated with dashed lines. Figure 5.10(b) shows photoemission spectra from 270 eV to 480 eV for films grown at 10⁻² mbar (black) and 2·10⁻² mbar (blue). These measurements represent the spectra for films grown at ≤10⁻² mbar and >2·10⁻² mbar, therefore not shown.

The reflectivity scans show a clear transition in characteristics for the films grown above 10⁻² mbar. Below, clear thickness fringes are observed, translated to a film thickness of 23±1 nm and 26±1 nm. For the films grown at a pressure >10⁻² mbar, thickness fringes are much weaker, with a periodicity which translates to a film thickness of 35±3 nm. Also the critical angle θ_C shows a change for these two pressure ranges, increasing in angle for the higher partial pressure range. The critical angle relates to the film density, increasing with increasing angle. The increase in film thickness in combination with changed film density all support a transition of growth of Y₂O₃ to YBiO₃. The changing film thickness is likely related to the reevaporation of bismuth, not incorporating in the lattice. The critical angle is related to the density of the film, where the density of respectively, LSAT and YBiO₃ is respectively is 5.01 g/cm³, 6.74 g/cm³ and ∼7.3 g/cm³. The larger film density of YBiO₃ explains the shift towards a higher value of the critical angle. Also, as the density of the LSAT substrate is more similar to the density of YBiO₃ then Y₂O₃, this results in less pronounced oscillations, as is clearly observed in the measurements.\footnote{Estimated from the measured unit cell volume of ∼157 Å³ with (YBiO₃)₂ stoichiometry and a documented density of 6.77 g/cm³ for a perovskite YBiO₃ cubic unit cell with lattice constant of 4.4Å.}

These interpretations are fully supported by the photo emission spectra that show a similar transition where for growth pressures below 2·10⁻² mbar, no bismuth is measured. For higher pressures, a clear Bi 4d spectrum is measured. Both spectra show a clear Y 3p and Y 3s signal.\footnote{It is noted that the relative elemental concentration ratio Y/(Y+Bi) (%) is ∼60%, higher than the presented results in Fig. 5.5. Next to typical large error margins of ∼5% in these XPS measurements and calculations, here it also concerns a different set of samples than the films presented in Fig. 5.5}

In the next section these growth characteristics are discussed in light of the results on the pressure dependent plasma plume characteristics outlined in the previous sections.

### 5.5 Discussion

The transition from the absence of YBiO₃ growth in 0.00/10⁻² mbar partial oxygen pressure to the growth of an epitaxial YBiO₃ layer in 2·10⁻² mbar partial oxygen pressure can partially be explained by the increase in available YO at the substrate
position, as shown in Fig. 5.4(a). However, already at 10^{-2} mbar a significant amount of YO should be available, although no YBiO_3 is grown. This dependence of structure and composition on oxygen background gas dependent is completely different from the background gas dependent film growth characteristics outlined in the previous chapters. There it was shown that the oxidation state of plasma constituents, controlled by the partial oxygen pressure, influences just the stoichiometry of the film; a more or less defective perovskite SrTiO_3 structure grows in all conditions, as also observed in other studies, see section 4.1. But here it is shown that with increasing partial oxygen background gas pressure, the sticking of bismuth abruptly changes from zero to (near) unity, resulting in films with completely different composition, with or without bismuth. Therefore it may be concluded that here an additional mechanism, related to surface kinetics and/or surface chemistry, is responsible for the abrupt formation of an YBiO_3 film at >2\cdot10^{-2} mbar partial oxygen pressure. Since also Bi appears to arrive largely in its atomic non-oxidised form independent of the oxygen background gas pressure, apparently this additional mechanism is related to the additional source of oxygen, necessary to improve Bi sticking to form YBiO_3. Therefore it is speculated that, as there is no relation between oxygen background gas, plasma constituents and film characteristics, the dependence of bismuth sticking and the oxygen background gas is explained by reactions on the surface between the arrived plasma constituents and (a certain necessary amount of) oxygen from the background gas. This possibly results in oxidation reactions on the surface and in this way improving sticking of bismuth and promoting the structural formation of YBiO_3. This, more generally, indicates that sticking of species depends on not only the chemical nature of the arriving particle, but also on the oxygen environment reacting with the adsorbed (Bi) atom on the surface which prevents reevaporation and promotes nucleation of the present stoichiometry of species into the thin film crystal structure.

5.6 Conclusion

The partial oxygen pressure dependent composition of a YBiO_3 ablated plasma plume was investigated with OES and LIF. From OES it was shown that Y rapidly oxidises, where a full oxidation may be assumed for species arriving at the substrate for the investigated partial oxygen pressure range of 10^{-2} to 10^{-1} mbar. Even in pure argon, significant oxidation of Y is observed. With LIF, the Y, YO, and Bi spatiotemporal distributions in the plasma were mapped. It was observed that little chemical interaction takes place between the plasma plume constituents and the background gas. A significant amount of YO is already present in the plasma plume when ablating in pure argon, where the oxidised species appear to arise from the centre of the plume. Oxygen background gas affects the spatial distribution of YO, which appears not to be caused by a mixing and reaction of the plasma plume with the background gas, but by reactions between the background
gas and the target. It is concluded that in an YBiO$_3$ plasma, the atomic oxygen provided to the plasma from the target during ablation is the primary source of oxygen for the oxidation of Y. The increase of YO with an increase of the oxygen partial pressure might be caused by a compositional change and oxidation of the target surface, depending on oxygen gas pressure.

Subsequently films have been grown in similar partial oxygen pressure conditions and investigated on morphology, structure and composition. A strong dependence on partial oxygen pressure was observed in the structure and composition of the formed thin film ablated from a YBiO$_3$ target material. Below 2·10$^{-2}$ mbar partial oxygen pressure, no YBiO$_3$ structure is formed, but polycrystalline Y$_2$O$_3$, with no bismuth. Above 2·10$^{-2}$ mbar, a (near)cubic defective fluorite YBiO$_3$ is formed. At 8·10$^{-2}$ mbar and 10$^{-1}$ mbar oxygen pressure, additional polycrystalline YBiO$_3$ phases appear, suggesting that the oxygen fraction can be used to control crystallinity and epitaxy of the grown film. Remarkably, these transitions in film growth do not coincide with a significant change in plasma composition. From this it is concluded that the strong influence of the background gas composition seen in the structural and compositional characteristics of the film enters via surface chemistry, from the plasma constituents at the substrate surface, and not so much via the plasma plume composition. Oxygen from the background gas appears to be a crucial building block for forming YBiO$_3$ from the Bi and YO provided by the plasma plume.
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Summary

A widely investigated group of materials are the (perovskite) complex metal oxides. These materials are highly interesting for their rich variety of physical properties such as ferroelectricity and magnetism and superconductivity. The term ’perovskite’ is used to describe the family of crystals with an ABO$_3$ stoichiometry. The unit cell of a perovskite has rare-earth or metal A and B cations and six oxygen atoms, forming a BO$_6$ oxygen octahedra in the centre of the cubic, with the A cation in its corners. The properties of (perovskite) complex metal oxides are highly sensitive to slight deviation from the ideal crystal stoichiometry. Therefore, a general challenge in the synthesis of complex oxide nanostructures and thin films is the control of the stoichiometry and herewith control of thin film properties. Pulsed Laser Deposition (PLD) has shown in potential for growing near stoichiometric highly crystalline complex metal oxide thin films. Several growth parameters in the PLD thin film growth process can be set to influence the deposition and growth processes, including laser fluence, laser spot-size, target-substrate distance and background gas mixture and substrate temperature. Typically by optimising these settings, a high quality epitaxial thin film can be obtained.

In the laser ablation process, the importance of having control over the uniformity of the laser intensity on the target as well as the pulse to pulse stability is widely accepted. Next to laser parameters, also the background gas conditions affect the ablation process, plume characteristics and film growth. Strong interaction occurs between the laser ablated plasma and the background gas, which affects the physical and chemical characteristics of the plasma constituents and subsequently grown film composition, structure and therefore film properties. Specifically oxygen plays an important role in these processes, where the oxygen in the grown film, depending on background gas conditions, originates from the target, the background gas and/or substrate. Nonetheless, still limited are detailed studies on plume chemistry and composition in relation to surface growth characteristics and chemistry, resulting in specific film characteristics. Especially required is a focus on the sources and role of oxygen and species oxidation. Furthermore, many studies have focussed on investigating the composition of the plume with Optical Emission Spectroscopy (OES). These measurements rely on spontaneous emission spectroscopy and can deliver valuable information. However, the analysis of spontaneous emission yields reliable results only in the early stages of plasma
expansion when the plasma is still very hot. Interpretation of results in later stages of propagation is difficult, especially at higher background gas pressure when the plume thermalises and the plume self emission is significantly reduced.

In this thesis, an investigation on the propagation dynamics and composition of laser ablated SrTiO$_3$ and YBiO$_3$ plasmas is outlined. Results are related to an investigation of PLD film growth and structural characteristics of thin films of these materials. SrTiO$_3$ was chosen as it is widely used as model material system for fundamental studies on the influence of growth parameters on oxide thin film characteristics. Results are subsequently extrapolated to material system containing a volatile element, by investigating the relation between plume and film characteristics of grown YBiO$_3$ thin films, containing volatile bismuth.

In chapter 3, the propagation dynamics and spatiotemporal element specific composition of laser ablated SrTiO$_3$ plasmas was investigated with Optical Emission Spectroscopy (OES) and Laser Induced Fluorescence (LIF). The propagation dynamics undergo a transition from ballistic to diffuse and thermalised propagation which occurs in a relative small pressure regime between $10^{-2}$ and $10^{-1}$ mbar. In this regime, a strong dependence of oxidation of plume constituents on background gas pressure conditions is observed. With LIF, the spatiotemporal element specific distribution of titanium, titanium oxide and strontium oxide is mapped. Oxidation of species occurs especially in the front edge of the plume. For titanium, a gradual oxidation occurs with increasing partial oxygen pressure, which is absent for strontium which appears to oxidise strongly. The oxidation from the background gas, not so much the target, is responsible for species oxidation.

Structural and kinetic growth studies with X-ray Diffraction (XRD) and Reflection High Energy Electron Diffraction (RHEED) analysis of homoepitaxially grown SrTiO$_3$ films have been performed and outlined in chapter 4. It is shown that both film stoichiometry as well as surface diffusivity is determined by the oxidation of arriving species, instead of the commonly assumed mass distribution in the plasma plume and the kinetic energy of the arriving species. It is observed that the film stoichiometry depends on the composition of the background gas during deposition, where in a relative small pressure range between $10^{-2}$ mbar and $10^{-1}$ mbar partial oxygen pressure, the resulting film becomes fully stoichiometric. In relation to the results from chapter 3, at a partial pressure condition of $8\cdot10^{-2}$ mbar at which full oxidation of titanium occurs, stoichiometric growth is observed, coinciding with a transition in kinetic growth characteristics from 3D to 2D atomically smooth growth. Furthermore, from an investigation on the initial growth at specific underoxidised conditions, the role of oxygenation through the surface is discussed. Generally it is concluded that the strong relation between sticking and mobility of species at the growth surface and their oxidation state is the result of an intricate balance between oxidation during the propagation towards the substrate by interactions with the oxygen background gas and oxygen scavenging from the oxide substrate.

The relation between the characteristics of YBiO$_3$ plume constituents and grown YBiO$_3$ film characteristics containing volatile bismuth was investigated
and is outlined in chapter 5. The pressure dependent composition of laser ablated YBiO$_3$ plasma was investigated with OES and LIF. From OES it is shown that yttrium rapidly oxidises already at relatively low oxygen background gas pressure conditions, unlike the gradual oxidation as observed for titanium. With LIF the yttrium, yttrium oxide, and bismuth spatiotemporal distributions in the plasma was mapped. It is observed that little chemical interaction takes place between the plasma plume constituents and the background gas. The spatial distribution of yttrium oxide depends on the background gas conditions, which appears to result from reactions between the background gas and the target. For grown YBiO$_3$ films a strong dependence on partial oxygen gas pressure was observed in structure and composition. Below $2 \cdot 10^{-2}$ mbar partial oxygen pressure, no YBiO$_3$ structure is formed, but polycrystalline Y$_2$O$_3$, with no bismuth present in the film. Above $2 \cdot 10^{-2}$ mbar, a (near)cubic defective fluorite YBiO$_3$ is formed. This transition in grown film structure does not coincide with a significant change in plasma composition. From this it is concluded that the strong influence of the background gas on the film composition is the result from surface chemistry involving plasma constituents at the surface and oxygen from the background gas.
Samenvatting


Samenvatting

Bovendien richten veel studies zich op het onderzoeken van de samenstelling van de pluim met optische emissie-spectroscopie (OES). Deze metingen zijn gebaseerd op spontane emissie spectroscopie en kunnen waardevolle informatie opleveren. Echter levert de analyse van spontane emissie alleen betrouwbare resultaten op in een vroeg stadium van de expansie van de plasma pluim, wanneer het plasma nog heet is. Interpretatie van resultaten in latere stadia van de pluim expansie is moeilijk, vooral bij hogere achtergrondgas druk, wanneer de pluim thermaliseert en de spontane emissie van de pluim aanzienlijk verminderd is.

Dit proefschrift beschrijft het onderzoek naar de propagatie dynamiek en samenstelling van laser-geableerde SrTiO$_3$ en YBiO$_3$ plasma’s. Resultaten zijn gerelateerd aan de groei karakteristieken, structuur en samenstelling van gegroeide dunne films van deze materialen met PLD. Voor deze studies is SrTiO$_3$ gekozen als materiaalsysteem omdat het op brede schaal wordt gebruikt als modelsysteem voor fundamentele studies naar de invloed van groeiparameters op de eigenschappen van gegroeide oxide films. De resultaten worden vervolgens geëxtrapoleerd naar een materiaalsysteem dat vluchtig bismut bevat. De relatie tussen de ablatie pluim en film eigenschappen van gegroeide YBiO$_3$ dunne films is onderzocht.

In hoofdstuk 3 is de propagatie dynamica en de ruimtelijke en tijdsopgeloste element specifieke samenstelling van geableerde SrTiO$_3$ plasma’s onderzocht met optische emissie spectroscopie (OES) en laser-geïnduceerde fluorescentie (LIF). De propagatie van de pluim ondergaat een overgang van een ballistische naar diffuse en gethermaliseerde propagatie. Deze overgang treedt op in een relatief klein druk bereik tussen $10^{-2}$ en $10^{-1}$ mbar. In dit druk bereik is een sterke afhankelijkheid tussen de oxidatie van componenten in de pluim en zuurstofdruk geobserveerd. Met LIF is de ruimtelijke en tijdsopgeloste verdeling van titanium, titaniumoxide en strontiumoxide in kaart gebracht. Oxidatie van componenten vindt vooral plaats aan de voorkant van de pluim. Voor titanium treedt een geleidelijke oxidatie op met toenemende partiële zuurstofdruk. Deze oxidatie is afwezig voor strontium, dat sterk lijkt te oxideren in alle gasdruk condities. De oxidatie van het achtergrondgas, niet zozeer het target, is verantwoordelijk voor oxidatie van componenten in de pluim.

De structuur en groei kinetiek van homoepitaxiaal gegroeide SrTiO$_3$ films is bestudeerd met behulp van röntgen diffractie (XRD) en reflectie hoge energie elektronen diffractie (RHEED) en beschreven in hoofdstuk 4. Hier is aangetoond dat zowel stoichiometrie van de film als diffusiviteit aan het oppervlak van de film worden bepaald door de oxidatie toestand van componenten die aankomen op het substraat oppervlak, in plaats van afhankelijk te zijn van de element specifieke massaverdeling in de pluim en de kinetische energie van de aankomende componenten. Uit observatie blijkt dat de stoichiometrie van de film afhangt van de samenstelling van het achtergrondgas tijdens depositie, waarbij stoichiometrische groei plaatsvindt in een relatief klein druk bereik tussen $10^{-2}$ mbar en $10^{-1}$ mbar partiële zuurstofdruk. In hoofdstuk 3 is waargenomen dat bij een partiële zuurstofdruk van 8-10$^{-2}$ volledige oxidatie van titanium optreedt. Tevens vindt bij deze druk stoichiometrische groei plaats. Dit gaat samen met een overgang in de
kinetische groei karakteristiek van 3D naar 2D atomair vlakke groei. Verder wordt aan de hand van een studie naar de initiële groei bij specifieke ondergeoxideerde condities de rol van oxidatie door het oppervlak besproken. In algemene zin kan worden geconcludeerd dat de sterke relatie tussen de hechting en mobiliteit van componenten aan het groeioppervlak en hun oxidatietoestand het resultaat is van een balans tussen de zuurstof uit het target, oxidatie van componenten tijdens de propagatie naar het substraat door interacties met het zuurstof achtergrondgas en zuurstof uit het oxidische substraat.

De relatie tussen de kenmerken van de componenten in de YBiO₃ pluim en de eigenschappen van gegroeide YBiO₃ films is onderzocht en uiteengezet in hoofdstuk 5. De drukafhankelijke samenstelling van geableerd YBiO₃ plasma is onderzocht met OES en LIF. Uit OES metingen is gebleken dat yttrium snel oxideert bij relatief lage zuurstofdruk, in tegenstelling tot de geleidelijke oxidatie zoals waargenomen voor titanium. Met LIF zijn de ruimtelijke en tijdsopgeloste yttrium-, yttriumoxide- en bismut verdelingen in de plasma pluim in kaart gebracht. Er is waargenomen dat weinig chemische interactie plaatsvindt tussen de plasma pluim componenten en het achtergrondgas. De ruimtelijke verdeling van yttriumoxide hangt af van de omstandigheden van achtergrondgas, wat het gevolg lijkt te zijn van reacties tussen het achtergrondgas en het target materiaal. De structuur en compositie van gegroeide YBiO₃ films is sterk afhankelijk van de partiële zuurstofdruk. Beneden $2 \cdot 10^{-2}$ mbar partiële zuurstofdruk vormt zich geen YBiO₃ structuur, maar polykristallijn Y₂O₃, waarbij geen bismut aanwezig is in de film. Boven $2 \cdot 10^{-2}$ mbar vormt zich een YBiO₃ film met een (bijna) kubische, defecte fluoriet kristalstructuur. Deze overgang in de structuur van de gegroeide film valt niet samen met een significante verandering in samenstelling van het plasma. Hieruit kan worden geconcludeerd dat de sterke invloed van het achtergrondgas op de samenstelling van de film resulteert uit oppervlakte chemie waarbij de plasma componenten aan het oppervlak en zuurstof uit het achtergrondgas betrokken zijn.
Dankwoord

Vele mensen zijn op allerlei vlakken betrokken geweest bij het tot stand komen van dit proefschrift. Hier zou ik graag een kort moment bij stil willen staan en terug willen blikken op het proces en de bijdragen van deze mensen willen toelichten.

Het is nu ruim drie jaar na het officieel aflopen van mijn tijd als promovendus binnen de Inorganic Materials Science vakgroep aan de UT. Vanzelfsprekend een ietwat minder conventionele manier van het afronden van een promotietraject zo drie jaar na dato, bijzonder af te raden ook, echter was het onvermijdelijk en het vertaalde zich de afgelopen jaren naar een bron van vele discussies, zelfreflectie en character building. Het mocht niet anders zijn, de wetten der natuur dicteerden dat resultaten en succes zich niet altijd laten leiden door planning. Na het aflopen van mijn contract aan de universiteit Twente ben ik aan de slag gegaan bij Twente Solid State Technology B.V., waardoor ik gelukkig een sterk contact heb kunnen houden met IMS en mijn onderzoek, waarvan hier het resultaat, ik kan niet trotser zijn.

Allereerst wil ik beginnen met het bedanken van mijn promotor Gertjan. Ik koester onze altijd vriendschappelijke en gelijkwaardige verstandhouding, boeiende gesprekken en vaak scherpe discussies, binnen het veld maar ook daarbuiten. Veelvuldig storm ik nog steeds je kantoor binnen, veel te ongeduldig op zoek naar een sparringpartner waar je altijd voor open staat, resulterend in mooie discussies die vaak totaal ergens anders eindigen dan waar ze begonnen. Je hebt me alle facetten van de wetenschap enthousiast bijgebracht, wat me altijd heeft gemotiveerd en definieert wie ik ben. Ik kijk uit naar onze continueerde samenwerking. Dit geldt ook voor Guus, ik bewonder je inzicht en overzicht in het vakgebied en als mens. 'Neem jezelf niet te serieus, neem je werk serieus,' een leus waarin ik mijn persoonlijke blik op het leven bijzonder herken.

Verder natuurlijk de hele vakgroep van weleer en nu, alle mensen die direct en indirect hebben bijgedragen aan dit proefschrift. Ik wil graag Kasper bedanken, we werkten samen binnen dit project waar onze beide proefschriften het resultaat van zijn. Dank voor alle al dan niet inhoudelijke discussies en gezellige onnozelheid in het lab. Dit werk is, zeker wetenschappelijk, een team effort geweest. Dank ook aan Evert voor de vele inhoudelijke discussies, frisse inzichten in de materie en daaruit volgende bijdrage aan dit werk. Natuurlijk ook dank aan al mijn collega’s bij TSST, binnen onze vriendschappelijke sfeer op de werkvloer heb ik altijd begrip...
gevoeld voor de spagaat waarin ik me bevond tussen proefschrift en werk.
Daarnaast natuurlijk alle vrienden en familie die me erg dierbaar zijn. Ik ben trots op alle vriendschappen die ik heb opgebouwd tijdens mijn studententijd, promotie en daarna. Ramy, Maarten, Frerik, ons sporadisch samenkomen is altijd een waardevol moment van thuiskomen, waar ik mezelf kan zijn. De Bracque, Jasper, Maurice, Vincent, dank voor alle sociale, intellectuele, sportieve en muzikale belevenissen die bij hebben gedragen aan het vormen van mijn leven. Een rode draad door mijn leven is de muziek, een fantastische ervaring is onze New Sound Jazz Machine bigband, dank voor alle gezelligheid en muzikale uitdaging. Ward, de band is voortgekomen uit een van de vele waardevolle avonden waarop we quasi filosofisch de wereld proberen te begrijpen en verbeteren, ik ben trots dat je mijn paranimf bent. Tot slot mijn familie, mijn broer en paranimf, Bas, ondanks de afstand tussen onze levens geniet ik van ieder moment samen. En natuurlijk mijn ouders, jullie onvoorwaardelijke steun en liefde is iets waar ik mijn hele leven al op terug heb kunnen vallen, een bron van inspiratie, motivatie en trots. Lieve Nadya, de vele kopjes thee die je me bracht in de lange avonden zijn tekenend voor je steun en liefde, ik kijk uit naar het samen delen van alles wat de toekomst ons gaat brengen.

Rik Groenen
Enschede, 2017