Growth monitoring during pulsed laser deposition of oxides using atomic force microscopy

Werner Wessels

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deposition of oxides using atomic force
microscopy

Cover: Illustration of developed experimental setup.

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Growth monitoring during PLD of oxides using AFM

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GROWTH MONITORING DURING PULSED LASER DEPOSITION OF OXIDES USING ATOMIC FORCE MICROSCOPY

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Part I

Background & Motivation

Chapter 1

Growth monitoring during pulsed laser deposition of oxides using atomic force microscopy

Abstract

This chapter gives an introduction to growth monitoring during pulsed laser deposition (PLD) of oxides using atomic force microscopy (AFM). In material science, the growth-structure-property relation is studied. Understanding growth gives access to control and manipulation of material properties. Here, examples of diagnostic tools and studies regarding PLD oxide film growth are described. From there on, a motivation is given how *in situ* atomic force microscopy can have a major contribution to a deeper understanding of oxide thin film growth by PLD. This chapter ends by presenting the outline of this thesis.

1.1 Motivation

One of the meanings of growth is "an increase in size over a certain time of period", while monitoring means "observing, checking, or keeping a continuous record of a systems state" [1]. So, growth monitoring can be translated as the observation or continuous record of a size increase in a system over a certain time of period.

From a materials science point of view, growth monitoring is described as the observation of the growth front of a material system. Many material scientists study artificially fabricated materials with reduced dimensions, such as thin films. Understanding and manipulating thin film growth down to the (sub)nanometer length scale enables the controlled fabrication of novel materials containing new atomic arrangements and accompanying functionalities.

Thin films are material layers with a thickness ranging from (sub)nanometer to several micrometers. These films can be grown on substrates using various deposition methods. In physical vapor deposition (PVD) techniques, material is typically evaporated from a target and subsequently deposited on a substrate surface. In general, nucleation and growth take place on the surface during deposition [2]. Nucleation is the stage where adatoms form islands on the surface. Once a critical nucleation density/size is reached, adatoms diffuse on or in between islands to form new nuclei centers or adatoms become attached to island edges. Understanding of nucleation and growth and the growth front gives access to atomic growth control of thin films.

A fascinating material class are the perovskite oxides due to their wealth in available physical properties, such as superconductivity, ferromagnetism, ferro- and dielectricity [3]. Perovskite oxides, with the ABO_3 crystal structure, can be fabricated with a wide variety of A and B elements. The B cation is surrounded by a six-fold coordinated oxygen octahedra, where the latter is the main building block of this crystal structure. This material class, with similar lattice constants but various physical properties, is suited for fabrication of heteroepitaxial materials [4]. Heteroepitaxy refers to the preferred crystal structure ordering of a different film material with the underlying substrate.

From 1987 on, pulsed laser deposition (PLD) has become a popular PVD thin film growth technique to fabricate high quality (perovskite) oxide materials. The interest in PLD was induced by the discovery of high- T_C superconductors grown by PLD [5, 6]. This technique is unique compared to other PVD techniques, such as molecular beam epitaxy (MBE) and magnetron sputtering due to the pulsed nature of flux [7]. Especially this feature has been used throughout this thesis.

Among the current *in situ* diagnostic tools, reflection high-energy electron diffraction (RHEED) is by far the most commonly applied technique for monitoring *in operando* the oxide thin film growth. The PVD growth of oxides was monitored by RHEED only during (laser-)MBE up to the end at the nineties [9].

"I could not stop looking at the images. It was like entering a new world. This appeared to me as the unsurpassable highlight of my scientific career. Quote Nobel Prize winner Gerd Binnig (one of the inventors of the atomic force microscope), December 1986.

Fig. 1.1 Growth monitoring of perovskite oxides (ABO_3) thin films deposited by PLD, a) RHEED specular spot (spot surrounded by red box) intensity monitoring during 2D / layer-by-layer growth with in the inset the corresponding RHEED diffraction pattern, b) typical *ex situ* AFM images of the surface topography after deposition is stopped at the position of the indicating arrow, c) illustration of the ABO_3 surface at the (I) minimum and (II) maximum of a RHEED oscillation. *In situ* AFM during PLD enables direct measurement of the growth kinetics by monitoring the growth front. Fig. included with permission from Rijnders [8].

At that time, RHEED could only be utilized during oxide deposition at (ultra) high vacuum (UHV) as RHEED is hampered by electron scattering at high oxygen background pressures. In the same period, PLD systems were modified such that they could operate at UHV, sometimes referred to as laser-MBE, enabling RHEED monitoring. Furthermore, low pressures of molecular oxygen [10, 11], NO_2 [12, 13], O_3 [14] and pulsed oxygen sources [15] were applied to incorporate oxygen in the growing film, while being able to monitor growth using a charge particle beam. However, in practice best perovskite oxide PLD growth was obtained at high oxygen background pressure, and therefore a diagnostic tool was required operating at this pressure condition. In 1997, Rijnders *et. al* designed a

high-pressure RHEED-PLD system capable of operating up to pressures of 50 Pa using differential pumping [16]. They were able to monitor the growth of single perovskite oxide unit cell layers [17, 18]. Nowadays, more PLD systems become equipped with RHEED for *in situ* growth monitoring.

The use of high pressure RHEED-PLD systems led to many interesting observations in the field of perovskite oxides. It has for example been shown that an atomically flat single terminated substrate is a requirement for atomic growth control [19, 20]. Next to that, Lee *et al.* found polarization enhancement by growing a superlattice of BaTiO₃, SrTiO₃ and CaTiO₃, each of two unit cells thick, in a controlled manner [21]. Surprisingly, an extreme carrier mobility was observed at the SrTiO₃ / LaAlO₃ interface, two wide band gap insulators, dependent on the exact atomic stacking at the mentioned interface [22]. These examples are just a small selection of growth studies, where RHEED was used to obtain improved or novel material properties having atomically flat surfaces/interfaces.

Although RHEED has become an established research tool to monitor growth of oxides *in operando*, it does not allow to measure the growth of local islands. No direct measurement of the local nucleation density and island radius over time is possible, as the surface reflectivity signal is averaged over a large surface area¹ [18]. In order to study growth kinetics, it would be beneficial to acquire locally growth of islands and the nucleation density. This issue can be overcome by real-space surface monitoring, having high spatial resolution in the order of (sub)nanometers. Examples of real-space growth studies have been demonstrated for metals and semiconductors [23, 24, 25].

Several real-space diagnostic tools are available, each having their own advantages and disadvantages. Scanning probe microscopes (SPM) are the most suitable techniques to monitor growth kinetics as they visualize the surface morphology with (sub)nanometer spatial resolution [26, 27, 28, 29]. SPM enables local monitoring of the growth front over time and therefore growth of islands can be measured [30]. Most perovskite oxides are insulators or have a large band gap, which limits monitoring by utilizing scanning tunneling microscopy (STM), as it is based on a tunneling current flowing between tip and sample [31, 32].

A first design and demonstration of a conventional atomic force microscope (AFM) operating at metal-oxide PLD conditions has been reported [33, 34]. Until recently, the main drawback of AFM was the sample throughput, since real-time monitoring the PLD growth kinetics requires high-speed AFM instrumentation. Conventional AFM's are slow due to the low bandwidth of the cantilever, AFM scanner,

¹ RHEED beam (size $\approx 250\text{ }\mu\text{m}$) under grazing angle of $0.1 - 5^\circ$ results in a beam footprint on the sample surface of a few mm.

AFM electronics and optical detection systems. Many efforts have been made to increase the bandwidth of these components such that the development of high-speed AFM's has been accomplished [35, 36, 37, 38, 39, 40]. These developments could enable monitoring of growth kinetics during PLD using AFM.

In conclusion, RHEED has been mostly applied as a diagnostic tool to monitor oxide thin film growth during PLD. However, *in situ* AFM during PLD opens the opportunity for local measurement of island growth and nucleation density, which is not possible with RHEED. If real-time AFM monitoring the as-grown surface during PLD can be realized, a massive boost can be given to research on the growth of for example (perovskite) oxides and therefore understanding of heteroepitaxial oxides. Throughout this thesis, a new AFM design, containing a high resonance frequency AFM scanner and high bandwidth SPM electronics, is demonstrated with focus on growth monitoring during PLD of oxides.

1.2 Outline

This thesis describes over four years of research and development of an AFM to monitor oxide thin film growth during PLD. The objective is to gain knowledge by real-space observation of initial thin film growth during PLD in order to understand the growth-structure-property relation of (perovskite) oxides in a wider perspective. The described work is subdivided in three parts with each two chapters treating the state-of-the-art on growth monitoring during PVD of oxides, the developed instrumentation and methods and the conducted experimental studies.

In the first part of this thesis, Ch. 1 and 2, the motivation, outline and background of this work are described. A general introduction, motivation and outline are given in Ch. 1. Ch. 2 gives a comprehensive overview of the state-of-the-art on growth monitoring during PVD of oxides. This chapter is mainly devoted to the background on growth monitoring and diagnostic tools, proposed models for nucleation and growth during PVD growth, PVD techniques, such as PLD and MBE, and (perovskite) oxides. Thin film growth during PVD is typically real-time monitored using reciprocal diagnostic tools. However, *in situ* AFM can monitor thin film growth at the local scale in contrast to reciprocal diagnostic tools.

The second part, which covers Ch. 3 and 4, describes the instrumentation and methods used in this work. In Ch. 3, the developed experimental setup is presented, which is used to carry out this research. Here, an *in situ* AFM, containing a high resonance frequency scanner and high-speed AFM electronics, is demonstrated. The concept, specifications, design and performance of the instrument are

presented. It is shown that the developed AFM can operate at temperatures of room temperature - 700 °C and pressures ranging from 10^{-6} - 1 mbar O_2 , which are typical PLD conditions used for oxide thin film growth. Furthermore, the performance in terms of AFM scan speed is shown and discussed. Ch. 4 proposes a fast tip-sample approach method for AFM. The commonly used tip-sample approach of AFM is a tedious procedure resulting in low sample throughput hiding relevant information in the growth front e.g. the nucleation density and island radius. Here, the side approach method is tested using a faster sample transfer showing a reduced tip-sample approach time. Furthermore, it is demonstrated that the side approach can be applied monitoring the same surface location required for studying local nucleation and growth phenomena.

Thereafter, two experimental studies which are described in Ch. 5 and 6 are presented in the third part of this thesis. Ch. 5 is concerned with a perovskite oxide vicinal surface study to extract several energetic parameters, such as the nearest neighbor energy. The nearest neighbor energy is an important parameter in kinetic Monte Carlo (KMC) simulations. In literature, a wide range of nearest neighbor energy values are used to simulate perovskite oxide thin film growth. A similar nearest neighbor energy is found for perovskite oxides. The determination of the nearest neighbor energy is a step forward in avoiding iterative simulation processes of perovskite oxide thin film growth. The final chapter, Ch. 6 describes a growth study with the aim to increase sticking of volatile species. In both growth experiments and KMC simulations, temperature modulation during pulsed laser deposition (TM-PLD) has been applied as method. The results reveal that the step density modulation during 2D growth can be significantly increased compared to deposition at constant temperature. The increased modulation in step density should enhance the probability of sticking. In experiments, an increased sticking coefficient is observed for Pb in $PbTiO_3$ after using TM-PLD.

Chapter 2

Growth monitoring during physical vapor deposition of oxides

Abstract

This chapter gives a comprehensive overview of growth monitoring during physical vapor deposition of oxides. First, the broad spectrum of physical properties of (perovskite) oxides and their reported values are discussed. Then, the basic principles of the physical vapor deposition techniques pulsed laser deposition and molecular beam epitaxy are described. Several examples are shown of diagnostic tools to monitor thin film growth. The chapter continues with the background and theory in literature to describe nucleation and growth during deposition. In the subsequent section, an *in situ* atomic force microscopy is proposed as an complementary diagnostic tool to study the initial growth of complex oxides during pulsed laser deposition. Thereafter, the development of high-speed atomic force microscopes will be addressed, which enables the opportunity to monitor in real-space oxide growth kinetic processes.

2.1 Introduction

The word "oxide" refers to an extremely fascinating material class having a wealth of astonishing physical properties [3]. Besides the wide range of oxide properties in bulk, reducing the thickness down to the atomic scale even opens more phenomena,

such as a 2D electron gas (2DEG) at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface [22]. The variety in physical properties potentially can lead to novel and/or replacement of current electronic devices enabling improved and novel applications for energy harvesting, thermal energy conversion, novel sensors etc. [41]. Analogue to the semiconductor industry, epitaxial strain, doping and confined thickness can be applied to oxides [7, 42].

Functional oxide thin films can be fabricated using various PVD technologies including pulsed laser deposition (PLD) [6, 22, 43, 44, 45], reactive-molecular beam epitaxy (MBE) [46, 47, 48, 49], high-pressure [50, 51, 52] and off-axis sputtering [53, 54, 55]. These PVD techniques enable fabrication of high-quality epitaxial oxide films grown with (sub)nanometer/thickness control and superlattices, abrupt interfaces or construction of new oxide phases can be created. Atomically flat surfaces and interfaces are a requirement for optimization of these oxide heterostructures. This requires *in situ* growth monitoring in order to understand and control the fabrication of novel functional materials [56, 57].

Several diagnostic tools have been adapted to PVD techniques for *in situ* growth monitoring. Reflection high-energy electron diffraction (RHEED) has been utilized in both MBE and PLD to monitor the growth of oxide thin films [9, 16], the particular growth mode and energy activation barrier for diffusion [10, 17, 18, 58]. Other *in situ* diagnostic tools, such as surface x-ray diffraction (SXRD), are used to monitor the nucleation density, coverage and subsequent growth of islands in real-time i.e. during homoepitaxial SrTiO_3 growth [59, 60]. Both diagnostic tools are limited in their applicability as only monocrystalline materials can be studied. Once the growth is polycrystalline, growth understanding is lacking as the diffraction signal becomes diffusive. Real-space diagnostic tools, such as scanning probe microscopy (SPM), can overcome this issue as growth can be studied independent of the crystalline state.

Atomic force microscopy (AFM) has the advantage that it allows monitoring of critical PLD growth parameters, such as nucleation density and island radius evolution over time, independent of the crystalline state. Broekmaat *et al.* showed that AFM imaging can be performed at pressures ranging from 10^{-5} - 1 mbar O_2 and temperatures of 500 - 750 °C [34]. However, typically the maximum AFM acquisition rate is low (in the order of a few min/frame), which makes it unsuitable to follow growing islands. In last decade, a lot of progress has been made in increasing the AFM acquisition rate up to several frames/s in air and liquids [38, 39]. Recent developments in AFM instrumentation enable the possibility to achieve AFM acquisition rates of frames/s under typical metal-oxide PLD conditions [61, 62, 63, 64, 65, 66].

In this chapter, the state-of-the-art on growth monitoring during deposition of oxides using PLD and MBE is presented. First, the diversity in oxide properties are described. In the subsequent section, PVD techniques, such as MBE and PLD and their potential to grow films with atomically flat surfaces and interfaces are discussed. Several growth models have been proposed to describe the thin film growth process which will be presented in the next section. Thereafter, *in situ* reciprocal diagnostic tools are presented, which have been adapted to PVD techniques to enable monitoring and growth control. AFM can overcome the limitations of reciprocal diagnostic tools discussed in the subsequent section.

2.2 Oxides

2.2.1 Metal-Oxides

Many metal-oxides exist in nature, since the free energy state of most of the metals in the periodic table is lower in an oxidized state. Other metal-oxides are artificially fabricated [67]. Among the metal-oxides, several crystal structures exist, such as rock salt (MO), rutile or fluorite (MO₂), antiferite (M₂O), corundum (M₂O₃) and perovskite (ABO₃, A and B are usually a rare-earth and transition metal ion, respectively).

Tab. 2.1 gives an overview of properties with their reported value adapted from Ref. [42]. Schlom *et al.* listed metal-oxides based on exceptional properties in its category. Most of the reported exceptional properties of metal-oxides are found among the perovskite oxide material class, see Tab. 2.1. The wealth in perovskite oxide properties makes them very popular to study. Moreover, the perovskite oxide material class is interesting for applications in next generation devices, such

Property	Value	Oxide	References
Piezoelectricity	$d_{33} = 2500 \text{ pC/N}$	PZNO-PTO	[68]
Ferroelectricity	$P_S = 105 \text{ } \mu\text{C/cm}^2$	PbZr _{0.2} Ti _{0.8} O ₃	[69]
Ferromagnetism	$M_S = 6.9 \text{ } \mu_B/\text{Eu}$	EuO	[70]
Colossal magnetoresistance	$\Delta R/R_H > 10^{11}$	PSCMO	[71]
Metal-insulator transition	$\Delta R/R_{Tlow} > 10^{13}$	EuO	[72]
Spinpolarization	$P > 98\%$	CrO ₂	[73]

Tab. 2.1 Examples of metal-oxide properties with their reported values adapted from Ref. [42]. Abbreviations: PZNO-PTO = PbZn_{1/3}Nb_{2/3}O₃ - PbTiO₃ and PSCMO = Pr_{0.7}Sr_{0.07}Ca_{0.26}MnO_{3-x}.

Fig. 2.1 Schematic presentation of the perovskite oxide ABO_3 unit cell.

as solar-cells, micro-electromechanical systems (MEMS) and organic light-emitted diodes (OLED's) [7].

2.2.2 Perovskite oxides

The perovskite oxide crystal structure is named after Lev Perovski after the discovery of $CaTiO_3$ by Gustav Rose in 1839. The ABO_3 crystal structure of perovskite oxides can accommodate around 30 elements and about half of the periodic table on position A and B, respectively [42]. Most perovskite oxide crystal structures are not perfect cubic resulting in a slight distortion of the BO_6 octahedra. The oxygen ions are relative large in size compared to the metal cations and the crystal lattice parameters of perovskites are determined by the oxygen backbone. Therefore, the lattice parameters of perovskite oxides are quite similar. In Tab. 2.2, the lattice parameters of many perovskite oxides and perovskite oxide-related phases are shown.

2.2.3 Perovskite oxide epitaxy

Epitaxy is a Greek word meaning "in ordered manner" or "arrangement". In thin film deposition, it means the ordering of the crystalline structure of a film with an underlying substrate. Two forms of epitaxy are known, namely homoepitaxy and heteroepitaxy. Homoepitaxy refers to an arranged film on a substrate where both exist of the exact same material, while heteroepitaxy refers to the arrangement of a different film and substrate material. The structural compatibility comes from the fact that they exhibit a small range of in-plane lattice parameters a_0 ranging between 0.371 - 0.428 nm, see Tab 2.2, while having a similar ABO_3 crystal structure. The similar lattice constants makes perovskite oxides suitable for fabrication of heteroepitaxial structures limiting effects occurring due to large lattice mismatch between film and substrate. Perovskite oxide heterostructures can be fabricated combining properties of different materials or novel properties

Material	a_0 [nm]	Reference
YAlO ₃	0.371	[74]
LaSrAlO ₃	0.375	[74]
LaAlO ₃	0.382	[74]
CaTiO ₃	0.383	[75]
Bi ₂ Sr ₂ CuO ₆	0.383	[76]
Bi ₄ Ti ₃ O ₁₂	0.384	[77]
LaSrGaO ₄	0.384	[78]
YBa ₂ Cu ₃ O ₇	0.385	[79]
NdGaO ₃	0.386	[74]
LaSrTaO ₃	0.387	[74]
BiCrO ₃	0.390	[80]
LaGaO ₃	0.390	[81]
EuTiO ₃	0.391	[82]
SrTiO ₃	0.391	[74]
SrBi ₂ Ta ₂ O ₉	0.391	[83]
DyScO ₃	0.394	[74]
TbScO ₃	0.395	[84]
BiFeO ₃	0.396	[85]
GdScO ₃	0.396	[74]
SmScO ₃	0.399	[86]
KTaO ₃	0.399	[87]
BaTiO ₃	0.399	[75]
NdScO ₃	0.401	[86]
PbZr _x Ti _{1-x} O ₃	0.404	[88]
BiScO ₃	0.414	[89]
(Ba,K)BiO ₃	0.426 - 0.428	[90]

Tab. 2.2 Pseudocubic or pseudotetragonal a-axis lattice parameter a_0 of different perovskite oxide and perovskite oxide-related phases.

Fig. 2.2 LEGOTM version representing a superlattice structure. Base represents the substrate. Fig. included with permission from Rijnders and Blank (2005) [4].

appear i.e. at the interface between two materials [22]. As an example, Lee *et al.* built such perovskite oxide superlattices containing a repetitive structure of two monolayers BaTiO_3 , SrTiO_3 and CaTiO_3 showing a polarization enhancement [21]. Rijnders and Blank (2005) used the analogy of the fabrication of perovskite oxide single layers, heterostructures and superlattices (repetitive structure of several layers) with building LEGO on the atomic scale [4].

2.3 Physical vapor deposition

Oxide thin films can be grown using a variety of physical vapor deposition (PVD) techniques. In this section, the two commonly used PVD methods and their characteristic properties to synthesize oxide thin films are shown.

2.3.1 Physical vapor deposition

The physical vapor deposition (PVD) method refers to techniques producing a source gas by evaporation, sputtering or other non-chemical methods in a vacuum. In the case of evaporation, the material from the target is transferred into a vapor moving to a substrate surface forming a thin film by condensation. Evaporation is used in several deposition techniques from resistive wire heating to UHV techniques, such as molecular beam epitaxy (MBE) (during evaporation, a target is heated to overcome the binding energy of atoms until they vaporize). The second type of producing a vapor, called sputtering, is the removal of target atoms

into a vapor source by momentum transfer of accelerating ions from the background gas (background ions are accelerated by applying an electric field). Atoms can be removed only when the energy of accelerating ions is a few times larger than the binding energy of the target atoms. Most oxides are sputtered applying a radio frequency (RF) field reducing surface charging of an electrically insulating material. Laser ablation is quite similar to evaporation, but the energy is supplied by a locally heated laser spot instead of heating the entire material. The PVD technique based on laser ablation is known as pulsed laser deposition (PLD).

Two examples of widely used deposition techniques for epitaxial growth of complex oxide thin films are MBE and PLD¹. The conditions in which an oxide thin film is deposited are completely different. In MBE, oxide thin films are deposited at an UHV background pressure range of 10^{-9} - 10^{-4} mbar, while in PLD oxide thin films are typically deposited at oxygen pressures ranging from 10^{-6} - 1 mbar pure O_2 . Another main difference between MBE and PLD is the way stoichiometric transfer is achieved. In PLD, the target contains the same stoichiometry as later on obtained in the film, where oxidation takes place by interaction between plasma plume and oxygen background gas. In MBE, a target with a single element is continuously evaporated forming a so-called molecular beam and oxidation takes place at the surface.

2.3.2 Molecular beam epitaxy

MBE is a PVD technique in which thermal beams of atoms or molecules react with a surface to form a crystalline film. A single-crystalline substrate is positioned in the center of the MBE vacuum chamber. The substrate is heated to the growth temperature to achieve the desired phase of the thin film. Molecular beams are deposited from different effusion cells. Every molecular beam is evaporated from a single effusion cell as multicomponent mixtures rarely evaporate congruently [42]. Shutters are installed in front of every molecular beam to control the deposition interval. Both the shutter time and temperature are parameters to control the layering of heterostructures. This control enables the growth of layers down to a single unit cell thick.

Elemental species in MBE are oxidized after the species reach the substrate. The long mean free path of species should not be destroyed and therefore the pressure (dependent on the oxide material) during oxide deposition is limited to $P \leq 10^{-4}$ mbar. Molecular oxygen has been applied during MBE in order to easily

¹In essence, MBE and PLD are different, but both PVD techniques are unique as they allow fabrication of thin films controlling the film thickness with the precision of a single monolayer.

oxidize metal species, while higher activity oxidants are used for oxidizing species e.g. Bi, Pb and Cu [42]. To prevent inadequate composition control, atomic absorption spectroscopy (AA) has been adapted allowing flux measurements down to an error lower than 1% [91]. A retractable quartz crystal microbalance provides an absolute *in situ* flux measurement at the substrate position.

MBE was developed to deposit GaAs and (Al,Ga)As [92]. This PVD technique allows controlled layering of monolayers in combination with its growth diagnostics and fabrication of thin films has been expanded to other classes of materials, such as metals and oxides [93]. Besides molecular beams emanating by heated crucibles of individual elements, molecular beams of gasses are introduced during oxide deposition. This variant of MBE is called reactive MBE [42]. The growth of oxide heterostructures using reactive MBE started around 30 years ago. In 1985, Betts and Pitt reported on epitaxial growth of LiNbO_3 films [94]. It turned out that LiNbO_3 was more difficult to grow compared to several oxides deposited afterwards [93]. Since the discovery of high temperature superconductivity [5], oxide MBE has been used to grow oxides other than LiNbO_3 , such as superconductors [46, 47, 95, 96, 97, 98], ferroelectrics [49, 94, 99, 100, 101, 102, 103], ferromagnets [104, 105, 106, 107, 108, 109], magnetoelectrics [106], multiferroics [110, 111, 112, 113, 114] and superlattices [100, 115]. The first integration of an oxide (SrTiO_3) on Si was reported in 1998 [101]. Schlom (pioneer in the oxide MBE field) concluded based on literature that epitaxial SrTiO_3 can be grown on Si with a narrow full width at half maximum (FWHM) of 0.008° in its rocking curve, smaller than 0.068° achieved by other deposition techniques [93]. It has to be noted that not every oxide is stable on Si [116]. Besides oxide MBE deposition on Si(001) [99, 107, 117], oxides have been grown on several other semiconductors, namely Ge(001) [118], GaAs(001) [119] and GaN(0001) [120, 121].

2.3.3 Pulsed laser deposition

Before 1986, pulsed laser deposition (PLD) was a rarely used and a somewhat exotic PVD method in thin film laboratories. In the beginning of the sixties, Breech and Cross succeeded to vaporize atoms from a solid surface using a ruby laser. A few years later, Smith and Turner published the first vacuum PLD (using a ruby laser) growth of different solid compounds onto a substrate having stoichiometric transfer [122]. Only a few achievements are reported in the following decades, such as pulsed laser evaporation of powders leading to the thin film growth of SrTiO_3 and BaTiO_3 [123] and i.e. inter-metallic materials were fabricated using a pulsed laser beam [124]. In 1983, superconductivity in pulsed laser evaporated $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ films using a post heat treatment was reported by Zaitsev and their

co-workers [125]. The breakthrough for PLD came by the discovery of the high- T_c (above boiling point nitrogen) superconducting thin films of LaBaCuO [5] and YBaCuO [6] in the period 1986 - 1987². This discovery started massive research efforts with focus on growing high- T_c superconducting cuprates and different other complex oxide phases and materials.

In the nineties, PLD became more established and 2D growth was monitored using reflection high-energy electron diffraction (RHEED) at UHV [9]. PLD at UHV is called "laser-MBE", but MBE in this term is questionable as the plasma plume contains ions, electrons and neutrals. After the introduction of high-pressure RHEED in 1997 [16], several studies focused on PLD growth of oxides, such as SrRuO₃ [18] and superlattices of (Ba,Sr,Ca)CuO₂ [17]. A few years later, Eres *et al.* presented an *in situ* time-resolved surface x-ray diffraction (SXRD) study providing direct physical insight beyond RHEED. In 2004, a 2DEG has been found between the interface of SrTiO₃ - LaAlO₃ grown in a controlled manner using PLD [22]. In this period, production related issues, such as large-area scale-up have been addressed. Nowadays, companies i.e. Twente Solid State Technology (TSST) and SolMates explore the possibilities of integrating oxides on 4 - 8 inch silicon wafers using large-area PLD techniques [7].

The key component of a PLD setup is the pulsed laser. In the field of oxides, mostly an UV laser is used due to the high absorption of laser energy³. Material is ablated from the target forming a vapor. Due to the pressure gradient, the vapor called "plasma plume" moves towards the sample surface. Particles with tunable kinetic energies penetrate typically through an oxygen pressure in the range of 10^{-6} - 1 mbar O₂. Typical kinetic energies of species during oxide PLD varies in a range of few eV - several hundred eV [18]. Particles in the plasma plume interact with i.e. the oxygen molecules in the background gas resulting in oxydation of the ablated species and reduced kinetic energy E_{kin} . Upon arrival of the species at the substrate surface, absorption takes place followed by diffusion and sticking/desorption. The adatom diffusion, absorption and desorption probability are controllable parameters to influence the PLD thin film growth behavior.

PLD has some unique features, namely 1) oxidation of species before reaching the substrate, 2) a high deposition rate R and 3) deposition and growth are separated in time t . Recently, it has been found that surface diffusion is heavily influenced by oxidation [126]. Within the deposition pulse, deposition rates R of 10^2 - 10^5 nm/s can be achieved, while other PVD techniques have typical deposition rates of

² High- T_c superconductors are materials that behave as superconductors at temperatures typically higher than the liquid nitrogen temperature (77 K).

³ A pulsed excimer (ArF, KrF) laser is commonly used to deposit oxides with a repetition rate of 0.1 - 100 Hz.

Fig. 2.3 Typical PLD setup in 2016.

10^{-2} - 10^{-1} nm/s [18]. The high R of PLD induces a very high degree of the supersaturation $\Delta\mu$, which is given by:

$$\Delta\mu = k_B T \ln\left(\frac{R}{R_0}\right) \quad (2.1)$$

where, k_B is the Boltzmann constant, T is the deposition temperature, R is the actual deposition rate and R_0 the equilibrium rate. This high degree of supersaturation $\Delta\mu$ induces on its turn a high nucleation density with small nucleation radius [2]. In contrast to other PVD techniques, the PLD deposition flux is not constant over time causing separation of deposition and growth of islands in time t . The majority of the studies argue that this is the case [7, 18, 44], with the exception of Christen and Eres [127].

Nowadays, a typical PLD setup looks like the schematic illustration in Fig. 2.3. For fabrication of oxide thin films, a KrF excimer laser is typically utilized with a pulse energy of several hundreds of mJ and a pulse width of 25 ns. A mask is placed in the optical beam to select only a homogeneous part of the laser beam. Mostly, the laser beam (guided by an optical focal lens) is focused at an angle of 45° on the target. The energy density of the laser beam is adjustable by the mask size, demagnification and laser energy. A target holder capable of holding several targets and a heater sample holder with heater holder are mounted both on a computer controlled XYZ rotational stage (the heater holder is guided through

a loadlock without breaking the vacuum level ranging from 10^{-8} - 10^{-6} mbar for different PLD systems.

2.4 Nucleation and growth

In this section, the general theory behind nucleation and growth of oxide thin films during PVD techniques, such as MBE and PLD is described.

2.4.1 Thermodynamic equilibrium

In thermodynamic equilibrium, three growth modes are known describing crystal growth, namely Frank-van der Merwe growth [128], Volmer-Weber growth [2] and Stranski-Krastanov growth [2]. The different growth modes are explained by the surface energies of the film (γ_F) and substrate (γ_S) and interfacial tension between film and substrate (γ_I). Frank-van der Merwe growth occurs when a film wets the substrate ($\gamma_S \geq \gamma_F + \gamma_I$) and the preferred growth direction is in-plane. In the Volmer-Weber growth mode, the film does not wet on the substrate ($\gamma_S < \gamma_F + \gamma_I$). Thermodynamic factors, such as misfit strain can induce a growth mode transition from Frank-van der Merwe to Volmer-Weber, so-called Stranski-Krastanov growth mode. At the critical thickness of the film, the misfit strain and interfacial energy become too large resulting in defect formation and change in growth mode.

2.4.2 Growth kinetics

The growth front evolution of thin films during PVD, such as MBE and PLD is assumed to be dominated by growth kinetics (instead of thermodynamics) [127]. For example, homoepitaxial PLD growth experiments revealed that kinetic parameters determine the growth mode [17]. The interlayer mass transport is limited by the adatom diffusion length l_D on the surface and/or kinetic step energy barrier. Due to a limited l_D , roughening of the surface occurs in practice after the deposition of a monolayer (ML) (therefore, damping of the maximum RHEED intensity is observed after every subsequent grown ML, see Fig. 2.5).

The diffusion length l_D scales with diffusion time τ_D and the diffusion coefficient D_S according to $l_D = \sqrt{D_S \tau_D}$, where D_S is given by:

$$D_S = D_0 e^{\frac{E_A}{k_B T}} \quad (2.2)$$

The adatom diffusion length l_D depends on both temperature T and the activation energy barrier for diffusion E_A . Depending on the nucleation density/island radii and diffusion length l_D , several growth modes exist (see Figs. 2.4 and 2.5), which are described below.

1D / Step-flow growth

The 1D (step-flow) growth mode only occurs on vicinal (oxide) surfaces. Typically, oxide surfaces have a certain miscut angle containing unit cell height steps with a characteristic average terrace width $\langle L \rangle$ between the surface steps, see Ch. 5. If $l_D \geq \langle L \rangle$, adatoms diffuse towards step-edges and attach to it. Therefore, adatoms nucleate at step-edges and limited nucleation on terraces takes place or nucleation centers are absent. As a result, steps will effectively move [127].

Due to the spread in kinetic energy of arriving species in PLD (the spread is small in MBE), an effective $\langle D_S \rangle$ has to be considered [127]. In a different approach, the effective $\langle D_S \rangle$ was used as parameter to predict whether 1D growth can be expected. This type of growth is expected when:

$$F < 2N_p \langle D_S \rangle / \langle L \rangle^2 \quad (2.3)$$

assuming that the time between laser pulses is larger than the diffusion time τ_D , where F is the average deposition flux per pulse, N_p is the amount of material per pulse [129]. From this it can be concluded, that the existence of 1D growth depends on average adatom diffusivity, deposition rate and the miscut of the substrate [18]. For MBE, the expression is somewhat different, namely $F < 2D_S a_0^2 / \langle L \rangle^4$, where F has the unit monolayer per second and a_0 is the in-plane lattice constant [129]. As an example, Rijnders *et al.* showed that SrRuO₃ grows 1D after a few monolayers deposited on SrTiO₃(001) using PLD [8].

2D / layer-by-layer growth

The 2D (layer-by-layer) growth mode differs from 1D as $l_D < \langle L \rangle$ and therefore nucleation will take place on a terrace/surface. Nucleation takes place when atoms meet and form clusters on a surface. The characteristic distance between the nucleation of islands is here defined as ρ . This value depends on both the flux F and diffusivity coefficient of adatoms D_S [127]. After nucleation, islands grow in the period $2r_{\text{island}} < \rho$, where $2r_{\text{island}}$ is the island diameter. Under the condition $2r_{\text{island}} \approx \rho$, islands coalesce and then second layer nucleation takes place. This

Fig. 2.4 Schematic illustration of kinetic growth modes.

description represents a perfect 2D growth of thin films. However, perfect layer-by-layer growth will not be observed in experiments [130]. SrTiO₃ homoepitaxy is an example of a model system growing 2D in a wide range of PVD settings [17, 131].

3D / island growth

In the multilevel (island growth) growth mode, the diffusion length $l_D \ll \rho$ and/or kinetic step energy barrier is too high such that 3D islands are formed at the surface. Here, second layer nucleation starts far before islands coalescence as l_D is small. As a consequence, l_D is rapidly smaller than the island radius r_{island} and results in limited interlayer mass transport. The probability for second layer nucleation increases rapidly and leads to multiple level growth [127]. In practice, this growth mode will always be in between the described extreme 2D or 3D growth modes [18].

2.5 Growth monitoring using diagnostic tools

In this section, the most commonly used growth monitoring tools during PVD are described. Many PVD techniques are equipped with reflection high-energy electron diffraction or surface x-ray diffraction in order to monitor oxide growth kinetics.

2.5.1 RHEED

Reflection high-energy electron diffraction (RHEED) is a reciprocal diagnostic tool requiring minimal hardware. It is utilized in the field of surface science because of its high surface sensitivity under grazing angles. A high-energy electron beam (10 - 50 keV) is focused on a surface under a grazing angle of only 0.1 - 5°. Due to the grazing incidence angle, electrons interact with the topmost layer of only 1 - 2 nm at the surface (therefore it's surface sensitive). On a phosphorus screen,

scattered electrons are gathered showing a diffraction pattern characteristic for the crystal structure and containing information about the surface morphology.

Often RHEED is utilized as it allows monitoring of the sample surface during a deposition experiment and operates at a wide range of background pressures (UHV - 50 Pa) [16, 56]. This diagnostic tool is popular as in combination with PVD techniques intensity oscillations can be observed of the specular intensity during deposition indicative for a layer-by-layer growth front [56]. Material deposited on an atomically flat surface leads to roughening and a decrease in RHEED specular intensity (see Fig. 2.5), while up to the completion of full layer the surface becomes smoother and therefore the RHEED specular intensity increases all influenced by nucleation, growth and coalescence of islands. RHEED can be used as a tool to monitor the film thickness during 2D growth as an oscillation period corresponds to the growth of a single crystal layer. Generally, it is assumed that the maximum of RHEED specular intensity oscillations refers to a completely grown monolayer.

A model to explain the oscillations in RHEED intensity is the step density model. For both MBE and PLD, the step density model is applied to describe the relation between the specular intensity and density of steps on the surface. The idea behind the model is that every step acts as a diffusive scatterer and therefore the RHEED intensity decreases. Stoyanov and Michailov assumed that the nucleation of islands takes place at $t = t_{\text{ML}}$ (the period for one unit-cell layer coverage), then the step density $S(t)$ as function of coverage θ is described by [132]:

$$S(t) = 2\sqrt{\pi N_0}(1 - \theta)\sqrt{-\ln(1 - \theta)} \quad (2.4)$$

where N_0 is the initial number of nuclei at $t = t_{\text{ML}}$. In 2D growth during PLD, $\theta \propto t$ and a maximum S is measured at $\theta = 0.39$, while at constant nucleation and step propagation a maximum S is expected at $\theta = 0.5$ [18]. The RHEED intensity I_{RHEED} is approximately given by:

$$I_{\text{RHEED}} \propto 1 - \frac{S(t)}{S_{\text{max}}} \quad (2.5)$$

where S_{max} is the maximum step density. During PLD, not only surface steps contribute to I_{RHEED} . The relaxation behavior in the RHEED intensity after a deposition pulse can be described by the diffusive atoms, which act as individual scatters [18]. Several studies used this approach to study kinetic factors important in both 2D and 1D growth [8, 17, 18, 44, 58]. These studies evaluated relaxation times from RHEED specular intensity fitting between deposition pulses

Fig. 2.5 Typical RHEED specular intensities and RHEED patterns during kinetic PLD (I) 1D, (II) 2D or (III) 3D growth and the corresponding *ex situ* AFM images taken after PLD growth. Fig. included with permission from Koster and Rijnders (2011).

as a function of coverage, temperature and deposition pressure. Assuming 2D growth, relaxation times are extracted by using the function in Eq. 2.6:

$$I_{\text{RHEED}} \approx I_0[1 - e^{-\frac{t}{\tau}}] \quad (2.6)$$

where τ is the extracted relaxation time. A more detailed description and examples can be found in Refs. [8, 17, 18, 44, 58].

RHEED has been utilized in PVD techniques, such as PLD [16], MBE [56] and (RF) sputtering [133] and is often used to monitor the type of growth mode and number of oxide grown layers during 2D growth [18, 21, 22, 134, 135]. The surface sensitivity enables monitoring of oxide initial layer growth, but also of subsequent layers [9, 18]. Moreover, RHEED was used as diagnostic tool to study oxide growth manipulation [44, 58], oxide growth kinetics [10, 18] and qualitative determination of perovskite oxide surface termination [17].

2.5.2 SXRD

The dynamic scattering effects during RHEED, due to strong interaction of electrons with the surface atoms, makes it hard to describe growth kinetics by kinematic theories. Mostly, RHEED is performed to measure the growth of single monolayers, but rarely it is used to qualitative describe growth kinetics. Other sources, such as X-rays are not applicable in surface studies due to the large penetration depth and low signal intensity. The latter is overcome by the third generation synchrotron as an X-ray intensity of 10^{12} photons/s is available nowadays [127]. The kinematic analysis is a motivation to use synchrotron x-ray diffraction as a tool for monitoring thin film growth. In contrast to RHEED, surface x-ray diffraction (SXRD) enables the quantitative measurement of the surface coverage directly from the measured single scattering intensity.

The formula to describe the SXRD scattering intensity is given by:

$$I_{\text{SXRD}} \propto |F_c(\text{HKL})|^2 / [4 \cdot \sin^2(\pi L)] \quad (2.7)$$

where I_{SXRD} is the scattering intensity, F_c the structure factor containing all atomic coordinates. The so-called crystal truncation rods (CTR) are the scattering intensity rods described by Eq. 2.7, with $|F_{\text{CTR}}(L)|^2 = 1 / [4 \cdot \sin^2(\pi L)]$. CTR are used in measurements providing information about growth kinetics. They are sensitive to both vertical and lateral surface structure. The specular rod intensity

(vertical) describes the layer filling during growth, where the diffusive scattering (lateral) contains information about the lateral island distribution. More detailed descriptions can be found in reviews by Robinson [136], Vlieg [137] and Saldin and Shneerson [138].

SXRD has been applied in both MBE and PLD in order to monitor real-time growth kinetics during PVD [59, 60, 136, 139]. A typical setup contains a MBE/PLD chamber, where the diffractometer is integrated such that the sample can be positioned regarding to a fixed incident X-ray beam. In some setups, Be windows are installed resulting in exit X-rays with minimal attenuation and scattering. Most setups vary in chamber configuration, the geometry of the diffractometer and detection scheme. SXRD is often adapted as complementary diagnostic tool besides RHEED [140].

A few SXRD studies have been performed to extend the understanding about the pulsed nature of PLD. The general accepted picture of PLD is the separation between growth and deposition in time t . However, there is still some controversy in literature as SXRD studies suggest that both crystallization and most of the interlayer transport occur in the μs time scale during deposition instead of directly after deposition [141, 142, 143]. Sullivan *et al.* showed that the maximum RHEED intensity does not match with the maximum coverage of a single monolayer during SrTiO_3 homoepitaxial PLD growth [140]. Besides that, Larsson *et al.* chopped continuous molecular beams to study the influence of flux modulation on the growth [144]. The effect of flux modulation on the growth during MBE is minimal suggesting that a pulsed thermal beam is not the most important requirement for producing smoother films.

2.6 Kinetic Monte Carlo simulations

Weeks and Gilmer introduced a solid-on-solid (SOS) model, which has been frequently utilized to predict thin film growth [145]. The mobility of adatoms on surfaces is often described by SOS based kinetic Monte Carlo (KMC) type models based on activated processes i.e. deposition, evaporation and diffusion⁴. In the KMC model, adatom diffusion is simulated by simultaneously calculating the hopping rates (k_{hopping}) for all adatoms on a simulated two-dimensional grid or lattice. Adatoms are only allowed to diffuse in-plane in the KMC model. In thin film growth it is quite reliable due to the 2D structure of thin films. In the KMC simulations, perfect sticking is assumed resulting i.e. in no re-evaporation.

⁴ For perovskite oxides, it is assumed that ABO_3 unit cells are deposited and diffuse over a simple cubic crystal lattice with the grid size of an ABO_3 unit cell.

Fig. 2.6 KMC simulation of perovskite oxide thin film growth, a) KMC simulated surface topography image after five unit cells of deposited SrRuO₃ on SrTiO₃(001), b) KMC simulated RHEED specular intensity of (I) SrTiO₃ homoepitaxial PLD growth and of (II) SrTiO₃ homoepitaxial pulsed laser interval deposition (PLID) growth. Inset shows a zoom-in on the RHEED specular intensity during both PLD and PLID growth of a single monolayer.

Calculating the hopping rate k_{hopping} for adatoms is performed according to:

$$k_{\text{hopping}} = k_0 \cdot e^{-\frac{E_D + n \cdot E_N}{k_B T}} \quad (2.8)$$

where, k_0 represents the attempt frequency for atomic processes, E_D is the energy barrier on the surface, E_N is the nearest neighbor energy and n the number of neighbors (0, 1, 2, 3, 4). The activation barrier energy for hopping has the form of $E_D + n \cdot E_N$ and scales with the number of neighbor (atomistic) interactions n . The RHEED signal I_{RHEED} scales with the step density of a surface according to Eq. 2.5. The step density model for an $l \times l$ matrix in KMC simulations is calculated according to [146]:

$$S = \frac{1}{l^2} \sum_{i,j} |h_{i,j} - h_{i,j+1}| \cos(\Phi) + |h_{i,j} - h_{i+1,j}| \sin(\Phi) \quad (2.9)$$

where S is the step density, $h_{i,j}$ the step heights on the surface and Φ the azimuthal angle of the electron beam with respect to the principal directions of the matrix.

During several decades, faster Monte Carlo algorithms have been written in order to minimize the simulation time [147]. Furthermore, algorithms have been developed to simulate 3D growth of i.e. SrRuO₃ nanowires, while usually only in-plane diffusion is considered [148]. The main algorithm difference between KMC

simulations of PLD and MBE is the way new deposited material is added on the simulated surface. In PLD, the material on the surface is added in a zero duration "pulsed" manner (dependent on the deposition frequency), while during MBE a continuous flow of new material is added on the surface.

Many studies have been reported to explain oxide thin film growth using KMC simulations [18, 58, 148, 149, 150, 151, 152, 153, 154]. The RHEED intensity is simulated to elucidate the experimental obtained RHEED specular intensity during PVD of oxides. These studies have in common that the KMC surface topography images reveal information about growing islands and other microscopic events, which is impossible with RHEED. Therefore, it will be beneficial to use real-space diagnostic tools during PVD thin film growth [25].

2.7 AFM monitoring of growth kinetics during PLD

This section starts with an overview of real-space diagnostic tools available for growth monitoring and motivates why AFM has been selected. Thereafter, the basics of AFM, the use of AFM during PLD and high-speed AFM under oxide PLD conditions are discussed.

2.7.1 Real-space diagnostics of oxide PLD growth

In PLD, the growth front evolution depends on growth kinetics on the surface and on its turn by the nucleation density and island radius evolution over time. For example, tracking of the island radius over time, is a measure for the lateral growth speed of islands and is therefore a measure for the diffusion length of adatoms. On the other hand, monitoring the nucleation density gives an estimate of the supersaturation in PLD and its dependence on i.e sample temperature, deposition pressure and laser fluence etc. Real-space diagnostic tools have in common that the monitoring performance is independent on the material crystalline state. In addition, topographic features can be imaged down to atomic resolution.

Fig. 2.7 gives a schematic view of the PLD process. Just after the laser pulse, typically 25 ns, the deposition pulse with a duration of several hundreds of μ s takes place. In contrast to other deposition methods, growth can be studied in between these deposition pulses without being disturbed by new deposited material. During PLD, the high supersaturation induces a high nucleation density up to the critical nucleation density. In between the PLD deposition pulses, adatoms

	SEM	TEM	LEEM	STM	AFM
Oxide PLD conditions	-	-	-	-	+
Direct measurement in 3D	-	-	-	+	+
Non-destructive	-	-	-	+	+
(Sub)nanometer resolution	+	+	+	+	+
High temporal resolution	+	+	+	+	-
Electrically insulating film/substrate	+	+	+	-	+

Tab. 2.3 Suitability overview of real-space diagnostic tools to monitor oxide growth kinetic processes during PLD.

diffuse on an island to an island edge (lateral island growth) or form new nuclei centers on top of or in between islands (vertical island growth). Understanding the relation between the critical nucleation density, island radius with the growth front evolution would increase the understanding of oxide PLD thin film growth and thus tunability/control on (nano) functional materials.

A suitable microscopy technique to monitor the nucleation density and island

Fig. 2.7 Schematic view of PLD assuming that deposition and growth are separated in time t . The laser pulse, with a pulse width of typically 25 ns, induces a plasma of ablated species existing for several hundreds of μs . The supersaturated material is deposited on the substrate surface, whereafter growth takes place in between the deposition pulses. Monitoring the decay of the nucleation density and increase of island radius enables the measurement of growth kinetic parameters.

2.7 AFM monitoring of growth kinetics during PLD

Monitoring technique	RHEED	AFM
Area	$> 250\mu\text{m}$	few μm
Parameter	Step density	Nucleation density & radius
Ordering	Only crystalline	(Poly) crystalline & amorphous
Space	Reciprocal	Real
Interpretation	"Indirect"	"Direct"

Tab. 2.4 Overview of (relative) characteristics of RHEED and AFM as diagnostic tools for growth monitoring during PLD.

radius during oxide PLD has to meet all the listed conditions: (1) operating at typical oxide PLD pressures (ranging from 10^{-6} - 10^{-1} mbar O_2) and temperatures (ranging from RT up to 850 °C) (2) non-destructive for the sample surface (3) (sub)nanometer spatial resolution (4) high temporal resolution and (5) operating on electrically insulating films/substrates. Tab. 2.4 gives an overview of real-space diagnostics tools whether they meet the listed conditions. Real-space diagnostics tools, such as SEM, transmission electron microscopy (TEM), low-energy electron microscopy (LEEM) and scanning tunneling microscopy (STM) have been utilized to monitor a surface morphology, but so far none of them have been used under metal-oxide PLD conditions in contrast to atomic force microscopy (AFM) [33, 34].

The main differences between AFM and RHEED are that 1) the probing area of AFM is much smaller compared to RHEED and individual nanometer sized islands can be tracked, 2) The RHEED intensity provides an indirect measurement of the normalized step density S/S_{max} , while AFM enables a direct measurement of the step density S , nucleation density N_s and radius r_{island} evolution, 3) AFM operates with a performance independent of the crystalline state and is even applicable to amorphous materials, 4) real-space data gives a direct measure of length scales and 5) RHEED data is harder to interpreted due to dynamic scattering (complicating interpretation of RHEED patterns). AFM meets all listed conditions with exception of the temporal resolution (based on conventional AFM's). The typical time for an AFM to acquire an image is in the order of minutes, where characteristic times of oxide growth kinetic processes during PLD are in (sub)seconds [17, 18]. Recently, a lot of progress has been made to increase the temporal resolution of AFM, which subsequently will be discussed [39, 62, 63].

2.7.2 AFM in general

The atomic force microscope (AFM) belongs to the class of scanning probe microscopy (SPM) techniques. After the introduction in 1986, the invention of the AFM by Binnig *et al.* resulted in a new powerful microscopy tool for researchers to study materials independent of the band gap [30] as a follow up instrument on the earlier presented scanning tunneling microscope (STM) [31]. Nowadays, AFM has been utilized in various fields to study many processes and mechanisms at (sub)nanometer spatial resolution [39, 155, 156]. AFM enables surface mapping at high spatial resolution of properties, such as the surface topography, in liquid, air and even under vacuum conditions. In addition to imaging, AFM has been used to measure mechanical properties using force spectroscopy and i.e. electrical and magnetic surface properties have been measured.

Fig. 2.8 The concept of AFM.

The basic AFM instrumentation is presented in Fig. 2.8. A sharp tip mounted on an elastically suspended probe, which is called the cantilever, is brought in close vicinity of the sample surface such that there acts an interaction force between tip and sample F_{ts} . The force on the tip results in a vertical probe displacement of the cantilever beam. The sharp tip and high force sensitivity of the beam allow the measurement of small forces enabling sub-nanometer resolution. Deflection of the cantilever beam can be measured by various detection methods, such as optical beam deflection (OBD) and interferometry. In Fig. 2.8, the interferometry detection is illustrated. An optical fiber is aligned above the cantilever in order to detect the cantilever motion properties. Light is emitted from a laser through the fiber onto the cantilever top surface. From the top surface the reflected wave from the cantilever is fed into the optical fiber together with the reflected wave from

the fiber glass-air interface. Both reflected waves are detected by a photodetector in the interferometer. A sinusoidal signal from the photodetector is measured by a deflection (contact mode), amplitude A_{osc} (tapping modulation, TM-AFM) or frequency shift Δf (frequency modulation, FM-AFM) detector to measure one of these modulating cantilever properties. This signal is fed into the height feedback to keep the distance d (and therefore F_{ts}) between AFM tip and sample constant.

The minimum detectable force gradient $\partial F_{\text{tsmin}}$ in both TM-AFM and FM-AFM is given by the subsequent equation:

$$\partial F_{\text{tsmin}} = \sqrt{\frac{2k_c k_B T_c B_c}{f_0 Q_c < A_{\text{osc}}^2 >}} \quad (2.10)$$

where k_c is the cantilever spring constant, $k_B T_c$ the thermal energy, B_c the measurement bandwidth, f_0 the cantilever resonance frequency, Q_c the cantilever quality factor and $< A_{\text{osc}}^2 >$ the mean square cantilever amplitude. From Eq. 2.10, it can be seen that an increase in Q_c results in an increase in force gradient sensitivity.

In AFM, the average tip-sample interaction force $< F_{\text{ts}} >$ increases usually when the distance d between AFM tip and sample surface becomes smaller [157]. San Paulo and Garcia derived an equation showing a relation between $< F_{\text{ts}} >$ and the cantilever oscillation amplitude A_{osc} by taking into account that attractive and repulsive forces are only significant near the lower turning point of the oscillation in TM-AFM [158]:

$$A_{\text{osc}} \approx A_0 \sqrt{(1 - 4(\frac{< F_{\text{ts}} >}{F_0})^2)} \quad (2.11)$$

where, A_0 is the driving amplitude and F_0 is the amplitude of driving force. Typically, a small $A_{\text{osc}} = 0.1 - 10$ nm is used during FM-AFM imaging. An approximation of the relation between Δf and the F_{ts} is given for small A_{osc} according to [157]:

$$\Delta f = -\frac{f_0}{2k_c} \frac{\partial F_{\text{ts}}}{\partial d} \quad (2.12)$$

where f_0 is the cantilever resonance frequency, k_c is the cantilever spring constant. Qualitative force-distance curves can be made by measuring Δf as function of distance d . Both Eqs. 2.11 and 2.12 show that the cantilever oscillation properties A_{osc} and Δf are related to $< F_{\text{ts}} >$ or $\partial F_{\text{ts}}/\partial d$, respectively.

The typical *modus operandi* of an AFM is raster-scanning the AFM tip on the sample surface while monitoring F_{ts} (either in TM-AFM or FM-AFM) and keep

F_{ts} constant using the PID controller. Scanning of the AFM tip is controlled by the piezotube⁵ (separated piezoelements in the X,Y,Z direction). In AFM, the raster scanning is generated by applying a sawtooth signal in the X-direction and a voltage ramp in the Y-direction.

Two AFM scanning principles can be used, namely constant force and constant height mode. During constant force (closed loop) mode, the AFM feedback regulates the voltage over the Z-piezo to adjust distance d to maintain F_{ts} . The position of the Z-piezo is acquired by the electronics as a function of the X and Y scanner position and translated to a topographical image represented on the PC screen. In constant height (open loop) AFM mode, the position of the Z-piezo is kept constant during raster scanning. Then one of the modulating properties is a measure for the sample surface topography. Constant force mode gives a better Z-resolution, while constant height enables faster AFM acquisition rates [37]. High resolution AFM is only possible if the AFM setup has a sufficiently low vibrational level. In general, this is achieved by an as rigid as possible AFM construction and the use of active and passive damping systems.

2.7.3 *In situ* AFM under oxide PLD conditions

Only a single work has been reported of an AFM operating at typical oxide PLD conditions [33]. This work is mainly focused on the applicability of AFM on ABO_3 crystalline surfaces under oxide PLD conditions and imaging during PLD. To prevent an AFM scanner breakdown of the piezotube scanner, Broekmaat *et al.* placed a macor tube as thermal insulator on top of the piezotube scanner to reduce heating of the piezoelements. Furthermore, a high temperature sample stage has been designed to prevent warming of the piezotube scanner by minimizing the required heater input power to reach a certain ABO_3 sample temperature [34]. They reported that $SrTiO_3(001)$ can be imaged up to at least 750 °C and at 10^{-5} - 10^{-1} mbar O_2 by a proper scanner and heater design [34]. However, they observed an AFM instability (under PLD growth conditions) between AFM tip and sample surface of i.e. $SrRuO_3$, a widely used electrode material in ABO_3 heterostructures. Switching from TM-AFM to contact mode (CM) AFM revealed that blobs have been formed on the surface after so-called "neck formation", where earlier blobs were observed by Kuipers *et al.* during STM at elevated temperatures [159].

An AFM scanning instability is reported for oxides at elevated temperatures⁶,

⁵ Piezoelectric materials can contract or expand by applying a voltage over the material.

⁶ In this work, neck formation has been observed on mixed termination $SrTiO_3$ at $T = 600$ °C and $PO_2 = 10^{-1}$ mbar O_2 . It is explained by the fact that a neck is formed with SrO as $SrRuO_3$ has a SrO terminating layer, see Ch. 3.

Fig. 2.9 Schematic illustration of operation distance d between AFM tip and sample surface in TM-AFM and FM-AFM. The probability of neck formation shows a dependence on the distance d between AFM tip and sample [33, 159]. (1) Approach of the tip, (2) just after the jump into contact, (3) growth of a neck and (4) breaking of the neck.

such as SrRuO_3 ($\geq 500 - 600$ °C), undoped ITO ($\geq 300 - 400$ °C) using a Si AFM tip [33]. Changing the AFM tip material from a bare Si tip to a Pt coated Si tip resulted in an AFM instability temperature above 400 °C on $\text{SrTiO}_3(001)$, while with the bare Si tip it could be imaged up to 750 °C at 10^{-2} mbar O_2 [33]. For metals, an STM instability is observed with a W tip on a Pb(110) surface at a temperature of 45 °C [159]. Thereby, Broekmaat *et al.* used a conventional AFM with a low AFM feedback bandwidth and it is claimed that slow AFM tip velocity increases the probability of neck formation [33].

Several recommendations are given in order to reduce/prevent neck formation on ABO_3 surfaces under oxide PLD conditions. The first recommendation is the use of FM-AFM (attractive force regime) instead of TM-AFM (intermittent force regime). The attractive interaction strength between AFM tip and sample is smaller compared to the intermittent regime as the distance between tip and sample is larger, see Fig. 2.9. Therefore, it is expected that the probability to form a neck will decrease. The operation of FM-AFM under oxide PLD conditions compared to TM-AFM is more complicated. During TM-AFM, A_{osc} is by far the most critical parameter to tune, but in FM-AFM more parameters have to be optimized, such as A_{osc} , Δf and τ_{demod} [155].

Second recommendation is the selection of a suitable tip material/coating. Changing the tip coating and/or film/substrate material affects the conditions at which an AFM operation stability is achieved. Therefore, more understanding has to be gathered about the phenomena (chemical reactions, surface energies), which play a role during AFM imaging under metal-oxide PLD conditions. The third recommendation is the increase of the vertical and lateral tip velocity. Increasing the tip

velocity will reduce the probability to form a neck. It is not only a requirement to prevent neck formation, but also for monitoring of oxide growth kinetic processes occurring at characteristic relaxation times τ [17]. Higher AFM tip velocities can be achieved by the development of high-speed AFM instrumentation.

2.7.4 High-speed AFM under PLD conditions

High-speed AFM (HS-AFM) instrumentation is developed in order to visualize nano-scale dynamics (timescale $\approx$ hundreds of ms) [35, 39, 62, 64, 63, 160]. A lot of progress is made to speed up the AFM acquisition rate. Both the development of HS-AFM instrumentation and the HS-AFM operation under metal-oxide PLD conditions are discussed.

Instrumentation for HS-AFM

The AFM instrumentation consists mainly of four devices namely the cantilever, AFM detection system, an AFM scanner (head) and AFM electronics. All these components are related to the time delays involved in the feedback loop bandwidth described in Eq. 2.18 and Fig. 2.11. To extend the maximum AFM acquisition rate $R_{\max}$, many groups focused on increase of the cantilever resonance frequency f_0 [36, 167, 168], the scanner resonance frequency f_s [40, 61] and increasing the bandwidth of the detection system [167, 169, 170] and AFM electronics [35, 171]. Several research groups demonstrated the possibility of increasing the AFM acquisition rate $R_{\max}$ towards frames/s, see Tab. 2.5.

One way to increase $R_{\max}$ is reducing the cantilever size and therefore increasing f_0 . The resonance frequency f_0 of a rectangular cantilever depends on thickness d_c , width w_c and length L_c according to [39]:

$$f_0 \sim \frac{d_c}{L_c^2} \quad (2.13)$$

and,

$$k_c \sim w_c \left(\frac{d_c}{L_c}\right)^3 \quad (2.14)$$

Typically, d_c , w_c and L_c of cantilevers are reduced to increase f_0 (keeping a similar k_c) and therefore the AFM feedback bandwidth f_B . For example, low stress SiN composite cantilevers with a length of 10 μm and f_0 up to 2 MHz are commercial

Research group	Condition(s)	Scan mode	f_B [kHz]	f_0 [kHz]	f_s [kHz]	R_{max} [frames/s]*	References
Stanford (Barrett <i>et al.</i>)	Ambient	CM-AFM ^(I)	-	78.7	740	3.3	[161]
Stanford (Sulchek <i>et al.</i>)	Water	CM-AFM ^(I)	38	35.0	-	2	[162]
Stanford (Sulchek <i>et al.</i>)	Ambient	TM-AFM ^(I)	-	46.0	-	0.06	[163]
Bristol (Humphris <i>et al.</i>)	Ambient	CM-AFM ^(II)	2000	-	0.030 & 35.0	70	[164]
S. Barbara (Fantner <i>et al.</i>)	Ambient	CM-AFM ^(I)	-	2000	> 10	4	[36]
Bristol (Picco <i>et al.</i>)	Ambient	CM-AFM ^(II)	2000	35.0	0.030 & 20	1300	[37]
Kanazawa (Ando <i>et al.</i>)	Water	TM-AFM ^(I)	110	1200	171 & 20	10 - 30	[39]
Leiden (Rost <i>et al.</i>)	UHV	STM ^(I)	1000	-	38.5	200	[38, 61]
Leiden (Tabak <i>et al.</i>)	Ambient	CM-AFM ^(I)	1000	-	250 - 1500	1	[165]
Cambridge (Fantner <i>et al.</i>)	Water	TM-AFM ^(I)	-	125	-	0.08	[166]

Tab. 2.5 Overview of research groups reporting on the development of HS-AFM (and STM). HS-AFM have been utilized or in (I) closed-loop or (II) open-loop and under conditions, such as ambient, water and UHV. Here, f_B is the feedback bandwidth, f_0 is the cantilever resonance frequency, f_s is the scanner resonance frequency and R_{max} the maximum achievable acquisition rate. *Note that most of the studies present AFM/STM images with a significant lower number of pixels than $256 \times 256 / 512 \times 512$ pixels².

Fig. 2.10 Examples of mechanical AFM instrumentation to increase the maximum achievable acquisition rate $R_{\max}$, a) SEM image of an AC55TN high resonance frequency (small) cantilever of Olympus having a $f_0 = 1.6$ MHz (scale = 10 μm), b) drawing of a flexure scanner design. AFM flexure scanners have been developed to extend f_s .

available [36]. Si cantilevers containing a $f_0 = 2 - 5$ MHz were developed by several research groups [62, 172, 173]. Another way to increase the bandwidth (BW) of an AFM cantilever ($\text{BW} \sim \frac{f_0}{Q_c}$) is increasing the cantilever damping by selecting a different cantilever material and mimic a high Q_c factor [66]. Moreover, $R_{\max}$ has been increased by phase shifting the excitation signal using methods, such as Q_c control [163, 174, 175, 176]. Jaafar *et al.* report that switching the AFM feedback on the drive-amplitude signal (DAM-AFM) (instead of cantilever oscillation amplitude A_{osc} signal) reduces the cantilever response time in vacuum as $\tau_{\text{cDAM}} \approx \tau_{\text{cFM}}$ [177].

Besides achieving a higher $R_{\max}$, cantilevers with a higher f_0 (higher spring constant k_c) have a lower total noise density $\sqrt{k_B T / k_c}$ [178]. The total thermal noise is distributed over frequencies up to slightly above f_0 and therefore thermal noise is lower for higher f_0 cantilevers [167]. It has to be taken into account that cantilevers with $w_c \leq 2$ μm reach the optical diffraction limit to align the optical beam on the cantilever using beam deflection detection method [39].

To detect oscillation properties of small MHz frequency cantilevers, the detector bandwidth should be above f_0 and the optical beam diameter should be smaller than the cantilever dimensions. Schäffer *et al.* were one of the first designers of an optical beam deflection (OBD) detector for small cantilevers [179]. In this design, single lenses are used for focusing the incident beam on the cantilever and reflective beam on the OBD detector. Later on, Ando *et al.* replaced the single lens by an objective lens (working distance = 8 mm) and used a focused spot of 3 - 4 μm in diameter [169]. A four-segment Si PIN photodiode (3 pF, 40 MHz) and a fast amplifier/signal conditioner (≈ 20 MHz) were integrated in a photosensor to detect the deflection of MHz frequency cantilevers [39]. Hoogenboom *et al.*

developed a Fabry-Perot interferometer for micrometer-sized cantilevers [170]. The interferometer has a spot size of only 3 μm in diameter and the photodetector had a noise floor of 1 fm/ $\sqrt{\text{Hz}}$ at 1 MHz. The signal coming from the photodetector is fed into a RMS-to-DC converter, which detects the cantilever oscillation amplitude A_{osc} (DC output voltage is a measure for A_{osc}) or a phase-locked-loop (PLL) outputs a DC signal as measure for the frequency shift Δf .

Detecting the cantilever oscillation amplitude costs at least half an oscillation period according to $\tau_{\text{m}} = 1 / 2f_0$ [39]. Most amplitude detectors (RMS-to-DC converters) require several oscillation cycles to output an accurate RMS value. Groups introduced a 10 MHz peak-hold method (also called peak-detector) and reduced the required cycles to only half a cycle [169] and developed a Fourier method for fast amplitude/frequency shift detection [180]. Recently, Karvinen *et al.* have become inspired by the RF and microwave circuit design and they introduced a phase shift of 90° to the input signal resulting in canceling of the $2\omega_0$ component and no filtering was required (and increase of measurement bandwidth) [181]. Nowadays, PLL demodulator bandwidths are achieved of 0.2 - 5 MHz by the company Zurich Instruments and the research group of Fantner [65, 182]. Next to that, other high bandwidth electronics is needed for acquiring and applying higher frequency AFM scanner signals.

Several groups developed high bandwidth AFM electronics [35, 164, 169, 171, 183]. Rost *et al.* developed a video-rate (≥ 25 frames/s) SPM controller enabling (real-time) monitoring of thin film growth [25, 184] and catalysis [185, 186]. The video-rate controller existed of an MHz bandwidth analog feedback electronics and a piezodriver to reach a tip speed of 0.3 m/s, while obtaining atomic resolution [35]. In the field of biomolecule studies, Ando and coworkers are leading inventors of HS-AFM [39]. After years of pushing the AFM speed limits, Ando *et al.* published high-speed tapping mode AFM (HS-TM-AFM) observations of a walking myosin V biomolecule occurring in hundreds of ms [187]. They designed a dynamic high bandwidth (70 kHz) PID controller to optimize the PID settings continuously during AFM imaging [188]. A dynamic PID controller reduced the feedback saturation and there is a limited bandwidth dependence on cantilever amplitude. Furthermore, it reduced the parachuting time τ_{p} as the gain should be larger at downhill regions compared to uphill regions [39]. Picco *et al.* achieved one of the highest reported AFM acquisition rates (≈ 1000 frames/s) with their developed instrumentation by using contact mode AFM in open loop [37]. In that case, the AFM scan speed is mainly limited by the mechanical microscope/scanner.

Piezotube scanners have low resonance frequencies around several hundreds of Hz due to the elongated tube shape [38]. Other scanner designs have been proposed

in literature in order to extend f_s . Conical piezotubes have a triangular aspect of shape and therefore a higher stiffness design and higher f_s compared to conventional piezotubes [38, 61]. A first resonance f_s has been found at 45 kHz in Ref. [61]. Flexure hinges (see Fig. 2.10 b)) are designed with the desire to increase stiffness and decoupling of the X, Y and Z [39, 40, 62, 189]. Dependent on the required scan range, the first resonance f_s is typically found at tens of kHz. A MEMS design with $f_s = 1.5$ MHz is presented as a Z-scanner, which has a mass of only 10^{-11} kg [165].

Feedback operation of HS-AFM

HS-AFM is defined as AFM imaging with a frame rate beyond 10 frames/s having 256×256 pixels² [38, 171]. Conventional AFM's were slow due to the low feedback bandwidth and therefore it takes a few minutes to record a single AFM image [38]. The AFM feedback bandwidth depends on the bandwidths of instrumentation, such as the AFM scanner, AFM electronics, AFM cantilevers and (optical) detection system. In order to achieve an increase in temporal AFM resolution, the bandwidths of these components have to be significantly increased [36]. All time-constants of the feedback loop have to be as low as possible, see Fig. 2.11. The AFM feedback can be considered as a chain, which is just as strong as the weakest link [190].

As an example, from the AFM image settings and sample surface topography, the required AFM feedback bandwidth f_B can be calculated. Suppose that an AFM image is recorded in time t_{AFM} , over a $W \times W$ scan range with N scan lines. The scan velocity V_s in the x-direction is then given by $V_s = 2 \times W \times N / t_{\text{AFM}}$ [39]. In the case a sinusoidal shape sample surface (periodicity = λ_{surf}) is assumed, the feedback operation frequency $f = V_s / \lambda_{\text{surf}}$ in order to maintain the tip-sample distance. Therefore, the feedback bandwidth f_B has to be equal to or larger than f according to:

$$f_B \geq \frac{2WN}{\lambda_{\text{surf}}t_{\text{AFM}}} \quad (2.15)$$

The expression in Eq. 2.15 describes the relation between the AFM acquisition time t_{AFM} and feedback bandwidth f_B . From Eq. 2.15, it becomes clear that the required f_B is related to spatial frequency in the surface morphology. From this the maximum achievable AFM imaging rate R_{max} ($1 / t_{\text{AFM}}$) can be calculated:

$$R_{\max} = \frac{\lambda_{\text{surf}} f_{\text{B}}}{2WN} \quad (2.16)$$

A $f_{\text{B}} = 110$ kHz is reported by Ando *et al.* and is approximately three orders of magnitude higher than conventional AFM's [63]. Assuming a $\lambda_{\text{surf}} = 100$ nm, $W = 1$ μm and $N = 512$ lines results in maximum achievable AFM acquisition rate $R_{\max} = 10$ frames/s.

TM-HS-AFM under metal-oxide PLD conditions

Dynamic mode AFM is preferred instead of contact mode AFM under metal-oxide PLD conditions as contact mode is more sample destructive due to large shear forces [33]. TM-AFM is easier in use compared to FM-AFM as less parameters need to be adjusted. TM-AFM was proven as AFM scan mode to image $\text{SrTiO}_3(001)$ at $T = 750$ °C and $PO_2 = 10^{-2}$ mbar O_2 [34]. However, TM-HS-AFM under metal-oxide PLD conditions requires an increase in feedback bandwidth f_{B} . Ando *et al.* presented an approximation of f_{B} dependent on various factors under ambient conditions [39]. This approximation can be applied for TM-HS-AFM under metal-oxide PLD conditions as well.

First of all, there is always a phase delay $\phi(\omega)$ in open-loop. A relation of $\varphi(\omega) = 2\phi(\omega)$ ($\varphi(\omega)$ is phase delay closed-loop) is given by satisfactory of the feedback performance and the feedback gain is maintained at ≈ 1 (a detailed description can be found in Ref. [39]). The open-loop phase delay is described by $\phi(\omega) = 2\pi f \Delta\tau$, where $\Delta\tau$ is the total time delay in open-loop. In Fig. 2.11, the main time delays in TM-AFM are indicated, where τ_{cTM} is the cantilever response time in TM-AFM, τ_{m} is the reading time of the cantilever oscillation amplitude (reading of the cantilever oscillation amplitude needs at least a time of $\tau_{\text{m}} = \frac{1}{2f_0}$), τ_{I} is the integral time of error signals in the feedback controller, τ_{z} is the z-scanner response time and τ_{p} is the parachuting time. Parachuting is here described as that the cantilever tip completely detaches from the sample surface at a steeply sample inclined region and then time elapse until it lands on the surface again [39].

The cantilever and z-scanner behave as second-order resonant systems [62]. As a result, the cantilever response time τ_{cTM} (in TM-AFM) is expressed as:

$$\tau_{\text{cTM}} = \frac{Q_{\text{c}}}{\pi f_0} \quad (2.17)$$

where Q_{c} is the cantilever Q factor. The z-scanner response time is given by $\tau_{\text{z}} = \frac{Q_{\text{s}}}{\pi f_{\text{s}}}$, where Q_{s} is the scanner Q factor and f_{s} is the scanner resonance

Fig. 2.11 Feedback loop of TM-AFM and the involved time delays. The height variation of the surface is taken as input for the feedback loop and the latter is controlling the z-scanner as output. The most important time delays in the feedback loop are the cantilever response time τ_{cTM} , parachuting time of the cantilever τ_p , time required to measure the cantilever oscillation amplitude detection time τ_m , the integral time of error signal of the PID controller τ_I and the z-scanner response τ_z .

frequency. An approximation of feedback bandwidth f_B is given in Eq. 2.18, the feedback frequency having a time delay of $\frac{\pi}{4}$:

$$f_B = \alpha \frac{f_0}{8} \left(1 + \frac{2Q_c}{\pi} + \frac{2Q_s f_0}{\pi f_s} + 2f_0(\tau_p + \tau_I + \delta) \right) \quad (2.18)$$

The cantilever resonance frequency f_0 is involved in the feedback delays τ_{cTM} , τ_{cFM} (cantilever response time in frequency-modulation AFM) and τ_m (reading time of cantilever oscillation amplitude TM-AFM) and are inversely proportional to f_0 . Guidelines for developing a TM-HS-AFM are presented [39]:

- Increase of cantilever resonance frequency f_0 . This is the most important parameter to extend the feedback bandwidth f_B .
- Q factors of cantilever Q_c and z-scanner Q_s have to be lowered.
- Resonance frequency of z-scanner f_s should be high. Preferably above f_0 .
- An additional phase compensator that can compensate for the phase delay.
- The free oscillation peak-to-peak amplitude of the cantilever should be a few times larger than the maximum height of topographic features.
- Avoid or shorten parachuting time τ_p .
- Electronic systems should have bandwidths preferably in the order of MHz.

Increasing the scanner and cantilever resonance frequencies (f_s and f_0 , respectively) has the highest priority [39]. Under metal-oxide PLD conditions, another priority is facing a high τ_{cTM} due to the high Q_c . The cantilever Q_c can be $\geq 10^4$ under metal-oxide PLD conditions, while in ambient it is $\approx 10^2$ [178]. Assuming a $f_0 = 190$ kHz results in $\tau_{\text{cTM}} \geq 17$ ms and $\tau_{\text{cTM}} = 0.17$ ms in vacuum and ambient, respectively.

FM-HS-AFM under metal-oxide PLD conditions

An alternative dynamic AFM scan mode is frequency-modulation (FM) AFM [178]. In FM-AFM, the cantilever response time τ_{cFM} is similar under vacuum and ambient conditions. This AFM scan mode uses almost the same feedback scheme as presented in Fig. 2.11. The difference in feedback scheme is the replacement of the amplitude detector by a PLL to measure the frequency shift Δf . Therefore, the AFM feedback is performed at a constant Δf setpoint instead of a constant A . FM-AFM is typically used in vacuum to circumvent the high cantilever response time τ_{cFM} . The cantilever response time for FM-AFM τ_{cFM} in vacuum is independent of the cantilever Q_c :

$$\tau_{\text{cFM}} = \frac{1}{\pi f_0} \quad (2.19)$$

which makes it more suited at UHV pressures. The cantilever response time in FM-AFM $\tau_{\text{cFM}} = 1.7$ μs , using a $f_0 = 190$ kHz. FM-AFM is more difficult to operate as more parameters have to be optimized during AFM imaging, such as A , Δf , τ_{PLL} (time-constant PLL) [155]. Furthermore, the PLL demodulator bandwidth was low until recently and therefore was limiting the maximum AFM acquisition rate R_{max} during FM-AFM. In addition, typically a small full-width half maximum (FWHM) of the amplitude vs. frequency curve (and therefore high Q_c) is used to obtain high resolution AFM images. In order to image with HS-FM-AFM under metal-oxide PLD conditions, the PLL demodulator bandwidth has to be larger than the required pixel rate. In general, *ex situ* AFM images contain 512×512 pixels² when recording perovskite oxide surface topographies. A PLL demodulator bandwidth of 263 kHz is required when AFM images are to be acquired with one frame/s.

2.8 Conclusions

PVD techniques, such as MBE and PLD have been successfully utilized in growing functional oxide materials. Especially, perovskite oxide materials are interesting due to the wide range in properties and their small variety in in-plane lattice parameter. MBE and PLD are popular PVD techniques as they allow growing oxide films with atomically flat surfaces and interfaces. In order to extract the growth behavior, *in situ* diagnostic tools, such as RHEED and SXRD have been adapted on both MBE and PLD. These diagnostic tools reveal the growth speed and growth front evolution only if the film material is nearly perfect crystalline.

AFM has the advantage that it can monitor the growth front evolution independent of the film crystalline state. Furthermore, topographic features with (sub)nanometer resolution can be imaged, while this is not feasible for reciprocal diagnostic tools. However, AFM on the same location as PVD results in hindering of deposition and most likely tip contamination. As deposition and growth in PLD are assumed to be separated in time, it allows to geometrically separate the AFM and PLD target in location. Therefore, growth can be monitored in between deposition pulses. Previously, it has been shown that perovskite oxide surfaces can be imaged using AFM under typical metal-oxide PLD conditions, but the maximum achievable acquisition rate is low. Recently, a lot of progress has been made to extend the maximum achievable AFM acquisition rate to several frames/s enabling the opportunity to monitor the oxide PLD growth kinetics with characteristic times in the order of (sub)seconds.

Part II

Instrumentation & Methods

Chapter 3

The development of an atomic force microscope to study oxide growth during pulsed laser deposition

Abstract

An atomic force microscope (AFM) has been developed to monitor the oxide growth front during pulsed laser deposition (PLD). The AFM scanner and PLD target are integrated in a single support frame such that microscopy can be utilized after subsequent deposition pulses. A sample transfer stage has been developed to transfer the sample back and forth between AFM and PLD. Microscopy can be performed from room temperature (RT) up to 700 °C and at pressures ranging from a base pressure of 10^{-6} mbar up to 1 mbar using gasses, such as O₂ and Ar. The AFM performance is demonstrated by resolving 0.4 nm unit cell height SrTiO₃(001) surface steps and the surface topography of a BiFeO₃ film under typical oxide PLD growth conditions.

W.A. Wessels, T.R.J. Bollmann, G. Koster and G. Rijnders, Real-time monitoring of thin film growth, *NEVACBLAD* **53**, 6 (2015).

3.1 Introduction

Atomic force microscopy (AFM) has been utilized in several research fields to study surfaces under different conditions, such as vacuum, air and liquids, since its invention in 1986 [30]. This popular research instrument enables probing of surfaces with (sub)nanometer resolution in real-space. Example of an AFM application is the imaging of a surface morphology after thin film deposition. Also in the field of oxide surfaces, films are imaged after deposition by applying *ex situ* AFM in air and/or *in situ* AFM at ultra high vacuum (UHV) [17, 18].

In pulsed laser deposition (PLD), deposition and growth are separated in time allowing monitoring of film growth without disturbing the deposition of new material (see Fig. 2.7 and Ch. 2) [33]. Nowadays, reflection high-energy electron diffraction (RHEED) is often utilized for real-time monitoring of oxide thin film growth [18]. However, the diffraction signal contains information especially about the growth mode, but information about e.g. ripening and defect formation is lacking. Studies reveal that real-space surface monitoring during other deposition methods results in increased thin film growth understanding, especially about these effects [25, 184].

Under oxide PLD conditions, AFM is not straightforward as oxide thin films are grown at elevated temperatures (typically $T = 500 - 850$ °C) and at background pressures of ($10^{-6} - 1$ mbar) O_2 [17, 18, 126, 191]. Some AFM considerations have to be made to image an oxide surface under oxide PLD conditions, namely thermal stabilization of the setup and it should operate at a wide range of oxygen background pressures. The stabilization time is the time required before a setup is in a working thermal equilibrium during sample heating [33]. This time depends on the stabilization time of 1) cantilever resonance frequency, 2) heating stage and (3) mechanical setup. Next to that, the breakdown voltage of piezoelectric elements, typically used for cantilever positioning by the AFM scanner, varies with operating (oxygen) background pressure and separation distance between its electrodes according to Paschen's law [192].

A first AFM design and demonstration under typical oxide PLD conditions is reported [33, 34]. Their developed AFM based on a conventional (EBL2#) piezo-tube scanner with a thermally insulating macor tube between piezotube and cantilever holder unit. The macor tube was placed between the piezotube and cantilever holder unit to prevent heating of the scanner piezo elements and therefore avoiding piezo depolarization. Interferometric detection was used to measure cantilever deflection as beam deflection is unpractical under oxide PLD conditions: (1) the AFM scanner has a more compact design and (2) no adjustment of mirrors

3.1 Introduction

needed. Contact mode (CM) and Tapping mode (TM) AFM were performed on SrTiO₃(001) and DyScO₃(110) substrates at controlled vacuum pressures (10^{-5} - 10^{-1} mbar O₂) and up to $T = 750$ °C, which are typical PLD conditions to grow perovskite oxides, such as SrRuO₃, SrTiO₃ and BiFeO₃ [18, 126, 191].

However, an attempt to image a SrRuO₃(001) thin film above $T = 500$ °C at 10^{-2} mbar O₂ revealed that a neck was formed between a Si AFM tip and SrRuO₃ thin film surface [159]. Neck formation causes an AFM operation instability and therefore it was not possible to image SrRuO₃(001) under oxide PLD conditions. When Pt/Ir-coated Si tips were used, it turned out that SrTiO₃(001) and DyScO₃(110) could only be imaged up to $T = 500$ °C using these AFM tips. This study concluded that neck formation can be circumvented by (1) selecting a suitable tip-sample combination, (2) frequency-modulation (FM) AFM instead of TM-AFM or (3) increase of AFM tip velocities during raster scanning, see Ch. 2 [33, 39]. The latter is also a requirement in order to monitor oxide growth kinetic processes during PLD using AFM.

The acquisition rate of the reported AFM operating at PLD conditions is low due to the low bandwidth of its feedback loop [33, 34]. When trying to speed up the AFM acquisition rate, one has to extend the scanner resonance frequency (to avoid excitations) and to increase the AFM electronic feedback bandwidth [39]. Piezotube resonance frequencies are determined to be 300 - 400 Hz in XY and 1.3 kHz in Z¹, while the lowest resonance frequency is in the order of tens of kHz for conical or flexure based scanners [38, 40]. Furthermore, AFM electronics have been developed to extend the acquisition rate to several frames per second [35, 188].

In this chapter, the development of an *in situ* AFM to monitor the oxide growth front under PLD conditions is described. The design of the *in situ* AFM is based on an AFM flexure scanner, typically used in the field of high-speed AFM (HS-AFM), combined with high bandwidth scanning probe microscopy (SPM) electronics from Leiden Probe Microscopy B.V. [35]. First, the specifications and concept of the instrumentation are described. Then, the instrument design is presented followed by the instrument performance and conclusions regarding the instrument performance.

¹ Piezotube resonances of the AFM operating at PLD conditions were analyzed in this work.

3.2 AFM specifications

In general, perovskite oxides (ABO_3) are deposited at pressures ranging from 10^{-6} mbar up to 1 mbar O_2 and sample temperatures from room temperature (RT) up to around 850°C [17, 18, 126, 127, 191]. Typically, AFM's are not capable of working under these conditions. Piezo's typically operate up to temperatures around its Curie temperature T_C and depolarize at higher temperatures. Often PZT^2 is used as piezoelectric material due to their large displacement vs. voltage characteristic and has a $T_C = 150^\circ\text{C}$. Other type of piezoelectric materials, such as LiNbO_3 have a $T_C > 150^\circ\text{C}$, although they are less suited as the displacement is orders of magnitude lower compared to PZT at the same applied voltage.

A Si cantilever becomes $\pm 90^\circ\text{C}$ in close vicinity with a $2 \times 2 \text{ mm}^2$ SrTiO_3 sample at $T = 750^\circ\text{C}$ and $PO_2 = 10^{-2}$ mbar O_2 [33]. Si cantilevers are temperature resistant up to 900°C in an oxygen environment, while Si_3N_4 cantilevers deform under these conditions and metal reflex coated cantilevers start to bend due to the difference in thermal expansion coefficient between silicon and metal coating [33]. Besides that, cantilever properties change by an increasing temperature such that it results in a negative frequency shift Δf .

As ABO_3 samples during PLD are heated to elevated temperatures, thermal drift in the system plays an important role to be able to follow growth at the same surface location using AFM. Thermal drift arises from different thermal expansion coefficients of different materials during heating up of the instrumentation. Typically, $0.5 \times 0.5 \text{ }\mu\text{m}^2$ up to $5 \times 5 \text{ }\mu\text{m}^2$ *ex situ* AFM image sizes are used to visualize ABO_3 islands after deposition is stopped [17, 18, 33]. To follow the growth of ABO_3 islands on μm length scales over hours, thermal drift should be a small fraction of such typical AFM image sizes. As deposition and growth are separated in time, a sample transfer stage can be applied to transfer a ABO_3 sample back and forth in order to prevent hindering of deposition on an as-grown surface. In this case, the sample transfer stage repositioning repeatability should be a small fraction of the AFM image size to visualize / track growth of specific islands. The latter will be more extensively discussed in Ch. 4.

An AFM scanner operating at PLD pressures should be designed such that an piezo electrical breakdown is prevented. At oxygen PLD pressures of 10^{-6} - 1 mbar O_2 , the piezo breakdown voltage varies by a change in piezo potential offset. This breakdown voltage is called spark-potential and depends on background gas, background pressure P , electrode material and separation distance between electrodes

² Abbreviation PZT stands for $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ($0 \leq x \leq 1$), which belongs to the perovskite oxide material class.

3.2 AFM specifications

d. Typically, a voltage range of 330 V is applied over piezo's in an piezotube AFM scanner. The breakdown voltage of a piezotube is equal to 330 V having a $P \cdot d$ value of 10^{-4} cm·atm. For conventional piezotubes, discharge issues at oxide PLD conditions have not been observed [33].

To be able to discriminate individual perovskite oxide (ABO_3) surface steps, the total noise level should not exceed 0.1 nm, which is a fraction of a typically half or one ABO_3 unit step of around 0.2 nm and 0.4 nm, respectively [19]. Both mechanical and electrical noise contribute to the total AFM noise level. Mechanical noise depends on the vibrational level of the system and the mechanical stiffness between AFM tip and sample surface. The electronic noise level is determined by the noise of several electrical components, such as the AFM feedback electronics, low-noise scan generator, data acquisition system and photodetector. Usually, noise of electrical components increases with bandwidth f_{bw} proportional to $\sqrt{f_{\text{bw}}}$ [35, 39].

Growing ABO_3 islands can be monitored when the lateral AFM resolution is smaller than typical lateral ABO_3 island sizes during PLD. Lateral ABO_3 island sizes have been measured using *ex situ* AFM after deposition is stopped at the minimum RHEED specular intensity. These studies have found ABO_3 lateral island sizes varying from 100 - 500 nm [17, 18, 33]. However, ABO_3 lateral island sizes are expected to be even smaller down to a few unit cells at the early growth stage of a monolayer [193]. The minimum island size that can be measured with AFM is limited by the lateral AFM resolution and on its turn by the AFM tip apex size.

A summary of instrument specifications is described below:

- O_2 pressure ranging from 10^{-6} mbar up to 1 mbar.
- ABO_3 sample temperature ranging from RT up to 850 °C.
- Vibrational level < 0.1 nm in X,Y and Z direction.
- Electronic noise floor < 0.1 nm.
- AFM height resolution of 0.1 nm on perovskite oxide surfaces. Lateral AFM resolution ≈ 10 nm.
- Thermal drift in-plane ≤ 20 nm/min and out-of-plane $\leq \pm 700$ nm (Z-range) for one hour AFM imaging.
- AFM acquisition rate $\geq$ one frame/s (512×512 pixels).

3.3 Concept

Fig. 3.1 shows a schematic illustration of a concept of AFM during PLD. In a support frame, an AFM scanner and PLD target are installed and a sample transfer stage is included. The AFM scanner is positioned geometrically separated from the PLD position for a main reason: It prevents blocking of deposition on the as-grown surface and unwanted AFM tip contamination. As deposition and growth in PLD are separated in time, growth can be studied in between subsequent pulses using this concept. A plasma screen between AFM and PLD should prevent any PLD plasma contamination on the AFM scanner.

In this concept, a sample is transferred back and forth between AFM and PLD, where the sample transfer is based on linear motion. A sample heater is mounted on top of a linear motion slider. The concept is such that the side approach can be applied to reduce the time delay τ_{approach} between PLD and AFM monitoring of the sample surface, see Ch. 4 [194].

Fig. 3.1 Conceptual drawing of PLD combined with *in situ* AFM. AFM and PLD are geometrically in position separated to prevent hindering of deposition and tip contamination. A fast transfer stage is moving a sample back and forth between AFM and PLD. 1) support frame, 2) AFM scanner, 3) plasma screen, 4) PLD target and 5) sample/heater transfer stage.

3.4 Design

In this section, the general architecture of the designed *in situ* AFM in a PLD vacuum setup is described together with a more detailed description of all individual parts.

3.4.1 PLD chamber and peripheral equipment

Fig. 3.2 gives a schematic representation of the designed PLD chamber and peripheral equipment. The PLD chamber (dimensions: length×width×height; $4600 \times 3950 \times 6900 \text{ mm}^3$) is a single vacuum system, which differs in shape compared to traditional cylindrical chambers. A low 10^{-7} mbar base pressure is reached after a bakeout at 120°C for 24 h^3 . In the designed PLD system⁴, the base pressure is limited by O-rings of the vacuum door, valve on entrance flange PLD excimer laser and VAT valve to a vacuum level of 10^{-8} mbar. Typical PLD background pressures of 10^{-6} - 1 mbar O_2 are measured by almost closing the VAT valve and varying the oxygen flow between $0 - 100 \text{ ml/min}$. The vacuum chamber is a square-like box design such that a vacuum chamber door is used to open up the system for accessibility to install the AFM-PLD assembly. The vacuum door has a DN100CF flange viewport window, revolves by a shaft and can be closed by two closing knobs. Four airpod damping units are placed on an Al profile system⁵.

Matted corks are placed underneath the Al profile system to avoid system resonances (5 Hz , 11 Hz and 22 Hz) validated by measuring the transfer function in x- and y-direction according to Segerink *et al.* [195]. A homebuilt passive damping stage is connected to both the airpods (reduces vibrational level, especially in the z-direction) and vacuum chamber. The PLD chamber houses an Al tube as connection between an AFM-PLD frame and an active damping stage. The active damping stage is mounted as a lid on this PLD chamber. This damping stage ensures good vibration isolation and consists of two parallel Halcyonics MOD2-S active damping control elements (operational from $10 - 100 \text{ Hz}$).

On top of the active damping stage, a five-way cross has been assembled. Two DN100CF flanges with each two sub-D 25 pins electrical feedtroughs have been installed on this cross. These feedtroughs are needed to send and receive signals from and to the AFM scanner, coarse approach stepper motor, slider piezomotor

³ Bakeout can be performed up to 150°C and the maximum temperature is limited by the active damping control elements.

⁴ A helium leak rate was measured of $3.5 \times 10^{-10} \text{ mbar}\cdot\text{l/s}$ directly after PLD chamber assembly by the factory VDL Enabling Technologies Group Almelo BV.

⁵ Al profiles are ordered from Boikon.

Fig. 3.2 Schematic drawing of PLD vacuum setup and peripheral equipment. 1) PLD vacuum setup, 2) AFM-PLD frame, 3) door PLD chamber, 4) Halcyonics MOD2-S active damping control element, 5) air damped pods, 6) Al profile system, 7) passive damping stage, 8) active damping stage, 9) incoming excimer laser light KrF-ArF wavelength 248 nm, 10) DN100CF five-way cross, 11) fiber feedthrough, 12) electrical feedthrough, 13) mounting unit PLD chamber - passive damping stage, 14) DN40CF flange with Pfeiffer vacuum compact full range pressure sensor ($5 \cdot 10^{-9}$ - 1000 mbar), 15) DN40CF flange reduced to DN16CF with MKS type 626A baratron pressure sensor full-scale pressure/vacuum ranges as low as 0.02 mbar, 16) gasinlet O_2 , Ar and N_2 , 17) DN63CF flange with quartz glass type 420GSG063, 18) VAT valve with adaptive pressure controller PM-5, 19) valve to measure laser energy behind window, 20) closing unit door PLD chamber, 21) Al tube which works as cable feedthrough and it connects the active damping stage with the Al frame, 22) DN200CF flange for a turbopump. The turbo pump is a Pfeiffer turbomolecular pump D-35614 Assler S(N_2) 60 l/s with Pfeiffer TC600 controller.

Fig. 3.3 Photographs of a) AFM-PLD setup and b) Al AFM-PLD frame with installed AFM flexure scanner. 1) PLD vacuum setup, 2) PLD chamber door, 3) air damped pods, 4) Halcyonics MOD2-S active damping control element, 5) VAT valve with adaptive pressure controller PM-5, 6) optical rail guiding (KrF $\lambda = 248$ nm wavelength) laser beam, 7) Al profile system, 8) AFM-PLD Al frame, 9) HR4 vacuum motor, 10) coarse approach stage, 11) mounting bracket, 12) AFM flexure scanner, 13) connection Al tube and the AFM-PLD Al frame, 14) PLD target holder (no PLD target). The AFM position and PLD position are indicated by A and B, respectively.

drive and readout and heater wires. On top of this cross, an APC-DIN optical feedthrough has been mounted to feed and read the optical signal for detecting the cantilever response through. Three DN40CF flange ports are accessible, where two are used with a DN40CF - DN16CF reducer for a MKS type 626A baratron pressure sensor full-scale pressure/vacuum ranges (capable to measure more accurate typical PLD pressures) and the other is connected with a Pfeiffer vacuum compact full range pressure sensor, where the latter is more accurate at high vacuum pressures (10^{-7} - 10^{-3} mbar). On the back side of this PLD chamber, there is a DN63CF flange available for optional equipment.

A KrF excimer laser (LXPROTM from Coherent, Inc) with optical rail is integrated such that a 248 nm pulsed laser beam with a typical pulse duration of 25 ns is focused on the PLD target. As an entrance flange for the PLD excimer laser light, a 15° flange is designed for a 15° incidence of a laser pulse on the PLD target. The flange is integrated with a quartz glass type 420GSG063 window, a valve for measuring laser intensity behind the window and a gasinlet for O₂, Ar and N₂ gasses. A gas manifold has been designed to separately let N₂, O₂ or Ar into PLD chamber *via* its gasinlet. Brooks Instruments flow meters type Brooks 5850TR (0 - 100 ml) O₂ and Ar are integrated in the manifold to control gas flow of O₂ and Ar, respectively.

At the PLD chamber bottom side, a DN200CF flange is connected to a VAT valve typically used for automatic pressure control. On the other side of the VAT valve, a DN200CF - DN63CF reducer has been assembled for connection with a Pfeiffer turbomolecular pump D-35614 Assler S(N₂) 60 l/s (turbomolecular pump is controlled by a Pfeiffer TC600 controller). Vibrational level characterization is performed using three accelerometers from OCEANO Sensor⁶, type TR1BCN, mounted on three directional faces of a small 30×30×30 mm³ Al cube, where the latter is screwed onto the Al support frame. Triggering of PLD laser pulses is controlled by a TSST140103 triggerboard of Twente Solid State Technology (TSST).

3.4.2 AFM-PLD support frame

Fig. 3.4, schematically illustrates the AFM-PLD Al frame (frame dimensions: length×width×height; 180×100×144 mm³). This Al frame, exhibiting a robust and high stiffness design, is attached with an Al connection tube to an active damping stage. This damping stage has the functionality to lower the vibrational level in the mechanical loop of the AFM. The chosen shape and size of the support

⁶ Oceana Sensor, 1632 Corporate Landing Parkway, Virginia Beach, VA 23454.

Fig. 3.4 Schematic drawing of support frame including AFM and PLD. 1) Al frame, 2) AFM flexure scanner, 3) mounting bracket, 4) PLD target 5) coarse approach stage, 6) Vexta 5 phase stepper motor PK545-B, 7) HR4 nanomotion ultrasonic piezomotor, 8) macor heater stage, 9) sample transfer stage, 10) plasma screen, 11) two Kamet HDA pt200 RTD's connected in serie, 12) 5×5 mm² sample on top of an 5×5 mm² Pt plate and 13) location of screwed cube for integration of acceleration level sensors.

frame is based on required sizes and shape of the AFM scanner, PLD plasma and a mechanical stiffness such that the required vibrational level is not exceeded. The Al frame consist of two assembled Al frames, where the top frame is used for integration of both the AFM scanner and PLD target. The bottom frame has the functionality to integrate a sample transfer stage enabling back and forth sample transfer between AFM and PLD.

A HR4 nanomotion ultrasonic vacuum piezomotor with low vibrational level, a repositioning resolution within 20 nm and a maximum speed of 244 mm/s is installed in the bottom frame in order to propel the sample transfer stage. The bottom frame contains an 94 g Al stage to ensure low mass for sample transfer and therefore fast acceleration. Two strips are placed on the bottom side of the Al stage with vacuum-compatible glue, where one ceramic strip is used as piezomotor friction bar and a Renishaw RGS-20 gold strip for position readout by a Renishaw RGH25F UHV optical encoder (resolution of 5 nm). A heater can be mounted on top of the Al stage (using four M1.6 screws).

An Owis LM60 linear coarse approach stage with on top a Vexta 5 phase PK545-B stepper motor (having a step resolution of 100 nm/step) is screwed in the top frame. A homebuilt Al mounting bracket has been designed as connection unit between coarse approach and AFM scanner. The PLD target holder is made out of Al with two screws to adjust its position. The target can be adjusted in height and position along the sample transfer direction. In the direction perpendicular to the sample transfer, the target position is fixed. In this design, the distance between the AFM tip and PLD target center is 57 mm (distance center PLD target to plasmascreen is 25 mm). During sample and cantilever replacement, the Al plasma screen has to be removed to unscrew and uninstall the AFM flexure scanner with mounting bracket. A plasma screen can be mounted to prevent plasma contamination onto the AFM flexure scanner.

3.4.3 AFM flexure scanner

The AFM scanner is based on a flexure, see Fig. 3.5, which is often used in the field of HS-AFM [62]. Flexure scanners are used as an alternative to commonly used low resonance frequency piezotubes to extend the mechanical scanner bandwidth from Hz to the kHz range [40]. In addition, stacked piezo's integrated in a flexure results in less cross-coupling, hysteresis and creep as compared to generally used piezotubes. The AFM flexure in this work has been made out of Ti6Al4V to achieve high stiffness, high resonance frequency and low thermal expansion in order to minimize thermal drift. A calculated lowest resonance of the designed flexure scanner is found of ≈ 19 kHz in XY-direction⁷. The maximum achievable linerate is therefore between 0.19 - 1.9 kHz based on this scanner design. This has been calculated according to 1/100th - 1/10th of its lowest resonance frequency [40].

Double XY stacked PI PL-088.30 piezo actuators from PI company are used to achieve the required scan range. Standard scan range of these piezo's is 4 μm , but strongly reduces to 1.4 μm due to a high preload. The Z-flexure is aligned nearly in the center of XY-flexure and can be positioned by the double stacked XY-actuators in the XY-plane. For Z-actuation and sensing, a PI PD080.30 piezoring is located underneath the cantilever stage with 1.4 μm effective scan range. A counterbalance PI PD080.30 piezo has been integrated in the Z-flexure to counter momentum generated by center of mass movement of the Z-piezo. The whole cantilever unit is displaced by this Z-piezo such that the tip on cantilever chip is effectively moving towards sample surface. This cantilever unit exists of two parts. The bottom part is screwed on top of Z-flexure and is milled under 7° . A ZrO₂ ferrule ($\varnothing = 125$ μm cladding together with a $\varnothing = 9$ μm fiber inside) is glued into

⁷ Simulated using finite element analysis (FEA) with Autodesk[®] Inventor[®].

Fig. 3.5 Schematic drawing of high resonance frequency AFM flexure scanner 1) Ti6Al4V flexure, 2) stacked XY actuators PI PL-088.30 piezo's, 3) cantilever stage, 4) screw holes, 5) connection plate between cantilever base plate and flexure, 6) cantilever base plate 7° angle with respect to connection base plate 7) CuBe electrical contacts dither piezo, 8) ZrO₂ ferrule with 125 μm fiber cladding inside, 9) cantilever chip, 10) chip holder, 11) cantilever clamping spring, 12) dither piezo - PI PL033.30 piezo stack, 13) M1 screws, 14) cantilever, 15) optical fiber end. Distance between fiber end and cantilever $\approx 40 - 50 \mu\text{m}$, where the optimal interference working point distance $d(V_{\text{DC}})$ in the cavity can be tuned with a DC voltage V_{DC} applied to the dither piezo.

the small hole in the bottom part. On top of the bottom part of the cantilever stage, a top part unit is placed existing of a flat plate with on its top a PI PL033.30 piezo stack (dither piezo), cantilever spring and CuBe dither piezo contacts.

Optical interference is used instead of optical beam deflection to detect cantilever modulating properties. Beam deflection requires use and adjustment of optical instrumentation, such as mirrors and is unpractical under PLD conditions, where space is lacking. Therefore, usage of interferometric detection results in a more compact design. A laser beam (wavelength $\lambda = 790 \text{ nm}$, interference period $\lambda/2 = 395 \text{ nm}$) is reflected from the cantilever top plane and fiber-air interface, where the cantilever and fiber are separated by $\approx 40\text{-}50 \mu\text{m}$. A reference wave is reflected by the planar end of the fiber (glass-air interface). The detected wave is reflected by the top face of the cantilever. Both light waves interfere on an 400 kHz photodiode after both are transmitted through a fiber into the Surface Imaging Systems

Fig. 3.6 Photographs of a) AFM flexure scanner, b) a zoom-in of AFM flexure scanner and of c) AFM flexure scanner with Al foil radiation shield. 1) AFM flexure scanner, 2) stacked XY actuators PI PL-0.88.30 piezo's, 3) cantilever stage, 4) mounting bracket, 5) AFM flexure holder unit to exchange cantilever, 6) cables X, Y and Z piezo actuators, 7) cable dither piezo, 8) fiber protective housing, 9) ferrule, 10) cantilever chip, 11) cantilever alignment chip, 12) M1 screw cantilever spring, 13) cantilever spring, 14) dither PI PL-033.30 piezo stack actuator, 15) CuBe electrical contacts dither piezo, 16) radiation shield of Al foil, 17) kapton tape.

GmbH (SIS) electronics⁸. A 10/90 splitter has a functionality to compensate large intensity differences between a $\approx 96\%$ reference and $\approx 4\%$ detection intensity. This interferometer signal depends on the phase difference $\Delta\varphi_{\text{int}}$ caused by optical path length difference $d(V_{\text{DC}})$ between a reference and a detected wave. If A_{int} and B_{int} are amplitudes of a reflected and detected wave **A** and **B** and $\Delta\varphi_{\text{int}}$ is their phase difference equal to $\frac{4\pi}{\lambda}(d_{V_{\text{DC}}} + d_{V_{\text{AC}}})$, then they add up by superposition to a total intensity (**I**) according to Eq. 3.1:

$$I \sim |\mathbf{A} + \mathbf{B}|^2 = A_{\text{int}}^2 + B_{\text{int}}^2 + 2 \cdot A_{\text{int}} \cdot B_{\text{int}} \cdot \cos\Delta\varphi_{\text{int}} \quad (3.1)$$

The optimal interference working point distance of the cavity can be adjusted by the phase difference $\Delta\varphi_{\text{int}}$ between reference and detection wave. Tuning of $\Delta\varphi_{\text{int}}$ is done by applying a DC voltage ($V_{\text{DC}} = 5.9 - 59.6 \text{ V}$) over the dither piezo (measured piezoelectric coefficient = 11.8 nm/V) to regulate the distance $d(V_{\text{DC}})$ between the cantilever top face and fiber end. On top of V_{DC} , an AC voltage

⁸ Company is acquired by Bruker.

(typically $V_{AC} = 1 - 1000$ mV) is applied to oscillate a cantilever at its resonance frequency f_0 in dynamic mode AFM.

3.4.4 AFM electronics

Two AFM scanning modes are demonstrated namely Tapping-Mode (TM) also called Amplitude-Modulation (AM) and true Non-Contact (NC) mode also known as Frequency-Modulation (FM). There is a main difference between both AFM scanning modes. During TM-AFM, the cantilever amplitude A_{osc} is feed into the AFM height feedback, while during FM-AFM the frequency shift Δf is used for height feedback. Typically, A_{osc} is measured by taking an RMS A_{osc} of an modulating wave signal, where Δf is measured using a phase locked loop (PLL) demodulator [62, 157]. Most electronic AFM components are applicable for both AFM scanning modes except the components for either measuring A_{osc} or Δf . Here, A_{osc} is detected from a modulating interferometer signal using a 10 MHz bandwidth peak / phase detector described by Ando *et al.* [39] and Δf is detected from a modulating interferometer signal using an 50 kHz Zurich Instruments (ZI) PLL demodulator.

An SIS electronics box is adapted as detection optics / electronics for measuring the modulating cantilever properties during AFM (originally, this AFM electronics was used as electronics for scanning, interferometric detection and topographical height feedback). Here, the SIS electronics has two functionalities, feedback on the (optimal) interference working point by controlling V_{DC} and the modulating cantilever signal is acquired (from the BNC interferometer out).

The interferometer out is integrated in an electrical circuit such that the properties A_{osc} or Δf from the cantilever can be detected. After measuring A_{osc} or Δf , the signal is used as input for topographic feedback (0 - 10 V) by the AFM electronics. Scanning and topographic feedback is performed using commercial available high-speed SPM electronics from Leiden Probe Microscopy B.V.⁹ [35]. The FM-AFM mode in this work is in Constant-Excitation (CE) FM-AFM as there is only a feedback used on Δf [196].

In both AFM-modes, a cantilever is driven at its $f_0 = 140 - 190$ kHz with an $A_{osc} = 5 - 120$ nm (calibrated by the SIS interferometer) using a signal generator of a ZI HF2LI. A laser beam ($\lambda = 790$ nm) from a laser inside the SIS interferometer is emitted to the cantilever. Its reflection from the surface and from the glass-fiber interface causes interference, where the interference intensity is detected by a 400 kHz bandwidth photodetector. A photodetector noise floor of $38 \frac{fm}{\sqrt{Hz}}$ is

⁹ Video-rate SPM controller

determined from frequency analyzer measurements.

3.4.5 Heater

Different type of heaters i.e. resistive, radiative and laser heating have been applied during PLD of oxides with each their own advantage. Commonly used PLD heaters have a main disadvantage, namely a relative large input power (tens of Watts) is needed to heat an $5 \times 5 \text{ mm}^2$ ABO_3 sample to PLD temperatures of 600 - 850 °C. This results in a large heat radiation power and therefore warming of both the cantilever and AFM scanner. Besides that, thermal heat loss has to be minimized in order to extend the sample temperature avoiding scanner piezo depolarization [33].

Several research groups developed low input power heater stages to extend the sample temperature during SPM [197, 198, 199]. Potentially, these heaters are suitable for heating ABO_3 samples up to elevated temperatures, but many have a disadvantage crucial for a specific experimental purpose. For example, direct current heaters are not applicable as most ABO_3 substrates are insulators. Commercial available heaters, such as Boralelectric heating elements are not designed for heating $5 \times 5 \text{ mm}^2$ samples as they are only applied to much larger sample area's and rarely custom made.

A PLD heater for $2 \times 2 \text{ mm}^2$ samples with an input power of below 2 Watts under metal-oxide PLD conditions has been reported [34]. However, this high temperature stage is only applicable for sample sizes $\leq 2 \times 2 \text{ mm}^2$, where $5 \times 5 \text{ mm}^2$ ABO_3 samples are commonly used in materials science laboratories. A homebuilt heater has been designed to heat $5 \times 5 \text{ mm}^2$ ABO_3 samples up to typical PLD temperatures, see Fig. 3.7. In addition, here it has been proven that the designed heater is sufficient rigid.

Here, macor has been used as thermal insulator (thermal conductivity $\lambda_c = 1.46 \text{ W/m} \cdot \text{K}$) to reduce thermal loss by heat conduction to the transfer stage and therefore resulting in heating up of the support frame. Furthermore, macor has a thermal expansion coefficient $\alpha_{\text{lin}} = 1.23 \times 10^{-7} \text{ K}^{-1}$ and can operate up to a maximum temperature $T_{\text{max}} = 1000 \text{ °C}$ (continuous at 800 °C). In spite of its high thermal emission coefficient $\epsilon \approx 0.9$, the thermal radiation is low as the temperature of the macor piece is expected to be significantly lower than the sample temperature.

A custom designed Mo spring is placed on top of the bottom macor part. This spring clamps two Kamet HDA pt200's to an $5 \times 5 \text{ mm}^2$ Pt sample plate. This Pt sample plate fits exactly in the top macor part. Four screws are used to clamp the

Fig. 3.7 Photographs of designed heater a) mounted on transfer stage, b) without macor top part, c) during BiFeO₃ deposition at $T = 650\text{ }^{\circ}\text{C}$ and d) schematic drawing. 1) Al support frame, 2) transfer stage, 3) macor bottom part heater, 4) macor top part heater (top face shaved off $\alpha = 1^{\circ}$, 5) $5 \times 5\text{ mm}^2$ Pt plate, 6) M1.6 screw, 7) screw to connect electrical wires, 8) molybdenum spring for clamping pt-200 heater elements, 9) Pt paint on pt-200 heater elements, 10) electrical wires pt-200's, 11) BiFeO₃ PLD target, 12) PLD plasma, 13) heated SrTiO₃(001) substrate with as-grown BiFeO₃ film on top.

top macor part on the bottom macor part. By screwing this top macor part on the bottom macor part, a force is load on the Mo spring to clamp the pt-200's. The two Kamet HDA pt200's are connected in serial by using spot welding to reduce contact resistance.

A Delta ES 150-0300-0.45 is used as power supply and current read-out. To measure the serial pt-200's resistance, a Fluke 115 multimeter is placed in parallel to measure ohmic resistance over two serial pt-200's. Calibration of the sample temperature was done by measuring the sample plate with another pt-200 thermal resistor. The pt-200 temperature accuracy is $\pm 15\text{ }^{\circ}\text{C}$ and its temperature is

constant over time. Thermally conducting Pt paint¹⁰ (melting point > 850 °C) is used instead of commonly used Ag paint due to the low sublimation temperature of Ag ≈ 500 °C in vacuum [33]. Furthermore, the Pt paint improves the temperature homogeneity and has a lower temperature gradient between heating elements and ABO_3 substrate.

3.5 Performance

The most important aspects of the AFM-PLD setup are presented. After demonstrating the vibrational level and PLD characteristics, the AFM imaging performance is demonstrated by imaging a $\text{SrTiO}_3(001)$ substrate under different conditions, such as under vacuum and typical PLD conditions. Furthermore, the AFM imaging performance is demonstrated on a BiFeO_3 film deposited on $\text{SrTiO}_3(001)$ under its PLD growth conditions.

3.5.1 Vibrational level and stage translation

Fig. 3.8 shows the X,Y,Z acceleration levels of the AFM-PLD setup operating at $PO_2 = 0.1$ mbar O_2 and acceleration levels of a commercial AFM setup¹¹ operating in air. Both systems are placed on a VC-G classified floor¹² [195, 200]. The vibrational level sensors are positioned in the mechanical loop from tip to the sample, see Fig. 3.4. The passive damping system suppresses the higher frequencies ≥ 100 Hz, whereas the active damping stage significantly decreases acceleration levels from 10 - 100 Hz. Damping of the system by the airpods is mainly done in the Z-direction. At $PO_2 = 0.1$ mbar O_2 , the pre- and turbopump, VAT Valve and mass flow controllers are running, but no significant increase in acceleration levels is observed. Acceleration levels of the AFM-PLD setup are similar to the commercial AFM, where in the AFM-PLD setup some system resonances are visible in the frequency range from 100 - 500 Hz. Resonance peaks of 11, 22 and 32 Hz are only appearing in the frequency spectrum without active damping. Resonance frequencies of the Al support frame are found at 140, 190 and several peaks between 300 - 400 Hz. These resonance peaks are indicated by arrows in Fig. 3.8.

During stage transfer experiments, the time domain signal was recorded in parallel to acceleration levels measurements. The vibrational decay time τ_{delay} of the me-

¹⁰ SPI platinum paint, SPI supplies division of structure probe, Inc. P.O. Box 656, West Chester, PA 19381-0656 USA.

¹¹ Bruker Dimension Icon.

¹² Vibration criteria (VC) curves are a definition of floor vibrations to meet the required vibrational level of equipment.

Fig. 3.8 Vibration spectra by measuring the acceleration levels of the, a) AFM-PLD setup at a typical oxygen PLD pressure of 10^{-1} mbar O_2 and active damping halcyonics control elements turned on (system placed on a VC-G floor) and of a b) Bruker Dimension Icon AFM as reference system (specification AFM height resolution < 0.1 nm). The peaks at ≈ 140 , 190 Hz and between $300 - 400$ Hz (indicated by the arrows) are resonance frequencies of the Al support frame.

chanical AFM tip-sample loop is determined from the time domain signal from the moment that the transfer stage velocity is zero at the AFM position after sample transfer from PLD to AFM, for more details see Ch. 4. Using active damping, a τ_{delay} time is found of 0.4 s, while without active damping $\tau_{\text{delay}} = 1.0$ s. In the parallel acceleration level measurements, resonance peaks are observed at 140 and 280 Hz directly after stage deceleration. Back and forth sample transfer between AFM and PLD is possible in 0.5 s at the HR4 motor maximum acceleration and velocity.

Some unwanted resonance peaks were observed in the X,Y transfer functions of the passive damping stage [195]. The X- and Y-acceleration transfer function showed several low resonance frequencies at 5 , 11 and 22 Hz. These harmonic X,Y passive stage resonances are damped such that the acceleration levels were decreased by almost an order of magnitude by placing matted corks underneath the Al profile frame (initially, Al profile legs were used)¹³. Furthermore, four small Viton 009 O-rings are placed between the Al support frame and Al tube to strongly damp a resonance at 140 Hz. Without Viton 009 O-rings, the resonance peak is appearing in the frequency spectrum only when active damping is utilized. During AFM measurements, the coarse approach stepper motor is switched off to prevent resonances at 50 Hz and its harmonic modes degrading the AFM performance.

¹³ The acceleration levels are decreased to $\approx 10^{-5} \frac{m}{s^2 \sqrt{Hz}}$ using active damping control units. Here, the acceleration levels were measured at $PO_2 = 10^{-1}$ mbar O_2 , which is a typical PLD oxygen background pressure to deposit ABO_3 thin films.

3.5.2 AFM - PLD characteristics

The cantilever resonance frequency f_0 and the cantilever quality Q_c factor are nearly constant at pressures ranging from 10^{-6} - 0.1 mbar O_2 [201]. However, Q_c increases from a few hundred to tens of thousands in the pressure regime 1 bar - 0.1 mbar and therefore the FWHM of the amplitude vs frequency curve decreases strongly ($Q_c = f_0 / \text{FWHM}$) [33]. Another influence on drift in f_0 is a change in cantilever temperature. AFM on a sample at elevated temperatures results in warming of the cantilever. The cantilever temperature increase results in a negative frequency shift as the cantilever expands and the Young's modulus of a silicon cantilever (without coating) decreases with temperature as:

$$\Delta T_c = \frac{2\Delta f}{f_0(\alpha_{lin} - \alpha_E)} \quad (3.2)$$

where ΔT_c is the temperature shift of the cantilever, Δf the cantilever resonance frequency shift in Hz, f_0 the cantilever resonance frequency in Hz, α_{lin} the linear thermal expansion coefficient $\frac{ppm}{K}$ and α_E youngs modulus in $\frac{ppm}{K}$. According to equation 3.2, the calculated frequency shift temperature coefficient of the used silicon cantilever is -4.6 Hz/K. Here a $\Delta f = 200$ Hz is measured resulting in a cantilever temperature ≈ 70 °C ($\approx RT + \Delta T_c$) at a sample temperature $T = 600$ °C and $PO_2 = 10^{-1}$ mbar O_2 .

Moreover, sample heating results in a cantilever stage temperature increase due to thermal radiation of the heater. This temperature increase affects the optimal interference working point distance $d(V_{DC})$ of the cavity by the different thermal expansion rates of the different materials. The expansion is in the order of several interference fringes (several hundreds of nanometers) under typical PLD conditions. This drift can be reduced by preventing warming up of the AFM flexure scanner. At $T = 600$ °C, thermal radiation ($\sim T^4$) dominates causing a temperature increase of the whole AFM scanner. In this work, a piece of Al foil (thermal emissivity $\epsilon = 0.04$) was placed around the AFM scanner as radiation shield (see Fig. 3.6 c)). After placing a radiation shield around the AFM scanner, the DC drift strongly decreased without exceeding a single interference fringe during warming of $SrTiO_3(001)$ from RT up to 600 °C at a background pressure of $PO_2 = 10^{-1}$ mbar O_2 .

Fig. 3.9 a) shows the heater input power versus sample temperature of a $SrTiO_3(001)$ substrate measured in various oxygen pressures. The difference in required heater input power is negligible to reach the same sample temperature in the pressure regime $PO_2 = 10^{-2}$ mbar O_2 - 10^{-6} mbar O_2 , whereas at $PO_2 = 10^{-1}$ mbar O_2 the

Fig. 3.9 Heater characteristics and force-distance curve. a) Input power vs. sample temperature in different pressures using an 5×5 mm² SrTiO₃(001) substrate, b) force-distance curve between AFM tip and SrTiO₃(001) substrate at RT and $PO_2 = 10^{-1}$ mbar O₂. Free oscillation amplitude is 120 nm of SSS Si cantilever (force spectroscopy can be used to study neck formation between tip and sample under PLD conditions [33]).

heater input power (> 1 W) to reach the same sample temperature ($T > 200$ °C) starts to deviate significantly. Increasing the pressure up to 1 bar results in a much larger required input power to heat a sample to the same temperature compared to vacuum conditions. For example, a sample temperature of 400 °C requires a heater input power of 2.4, 2.6 and 4.5 W at 10^{-2} mbar O₂, 10^{-1} mbar O₂ and in air, respectively. At 10^{-1} mbar O₂ - 10^{-6} mbar O₂, the thermal heat loss contribution of convection is small [33]. The difference in heater input power (and heat loss) is therefore contributed by a change in convection behavior at 1 atm - 10^{-2} mbar O₂. The temperature gradient of 150 °C between pt-200's and the SrTiO₃(001) sample at 10^{-2} mbar O₂ to 10^{-6} mbar O₂ at PLD temperatures. The same temperature gradient is measured between Pt200 elements and a SrTiO₃(001) sample at 10^{-1} mbar O₂ and $T = 600$ °C. Therefore, the maximum reachable SrTiO₃(001) substrate temperature is limited to 700 °C due to the temperature gradient of 150 °C. From these experiments, it was found that the serial pt-200's gets a breakdown exceeding a resistance $R_{2pt200} = 1600 \Omega$ corresponding to an input power of 6.0 W, which limit the maximum pt-200 temperature. When the AFM-PLD setup is temperature stabilized after 1.5 - 2 h with a sample temperature of $T = 600$ °C at 10^{-1} mbar O₂, the scanner and support frame temperature $\approx 30 - 40$ °C, which is below the HR4 maximum operating temperature of 50 °C¹⁴.

An issue at elevated sample temperatures is neck formation between AFM tip

¹⁴ Specs are only given for ambient.

and sample surface [33, 159]. Previously, force spectroscopy has been used as a method to study neck formation [33]. Qualitative force-distance curves can be made as Δf is proportional to the interaction force F_{ts} between AFM tip and ABO_3 sample [155, 157]. Here, Δf from the HF2LI auxiliary output is fed into a LPM controller channel for read-out and the X-generator signal is connected to the Z-driver (a force-distance curve can be plotted by taking a line profile of an AFM image of that specific channel). Fig. 3.9 b) shows a force-distance curve measured between a SSS Si AFM tip and $\text{SrTiO}_3(001)$ surface at RT and $PO_2 = 10^{-1}$ mbar O_2 . The measured force-distance curve shows a qualitative agreement with force-distance curves reported in previous work [33].

It should be noted that the cantilever temperature shows a strong dependence on its distance from the heated sample surface. Therefore, a shift in f_0 is observed during the tip-sample approach. Once the cantilever amplitude is below the amplitude setpoint during tip-sample approach, it is assumed that the AFM tip is in close vicinity of the substrate surface. From the SPM electronics channel read-out, it was deduced that the SSS cantilever oscillation amplitude A_{osc} decreases in a time frame of ≈ 0.1 s, when the tip comes in close vicinity of the sample surface at RT. The same experiment was repeated at $T = 600$ °C and $PO_2 = 10^{-1}$ mbar O_2 revealing that the A_{osc} is decreasing in a time frame of ≈ 10 seconds before it is in close vicinity of the sample surface. In the latter case, $-\frac{dA_{\text{osc}}}{dd_{\text{tip} \rightarrow \text{sur}}}$ increases gradually when the distance $d_{\text{tip} \rightarrow \text{sur}}$ between AFM tip and sample surface becomes smaller. Here, the coarse approach stopped without having the AFM tip positioned on the $\text{SrTiO}_3(001)$, since A_{osc} crosses the setpoint A_{set} .

During thermal stabilization, a negative f_0 drift has been observed for a Si cantilever. Fig. 3.10 a) shows results of an experiment, where a $\text{SrTiO}_3(001)$ substrate was heated from RT up to $T = 600$ °C at $PO_2 = 10^{-1}$ mbar O_2 and at an AFM tip - substrate distance = 19 μm . Thereafter, the AFM tip was brought closer to the $\text{SrTiO}_3(001)$ surface in 5 μm steps and an amplitude vs. frequency curve was measured waiting for each step 30 min. This was repeated up to the AFM tip was in close vicinity of the surface. In this experiment, an SSS Si cantilever $f_0 = 156.865$ kHz containing a FWHM = 22 Hz was used.

In Fig. 3.10 a), the drift in f_0 is larger in case the AFM tip is closest to the heated surface. In addition, it can be seen that f_0 drift is larger than FWHM of the cantilever extracted from amplitude vs. frequency curve. Therefore, the cantilever amplitude gradually decreases during the coarse approach when kept the same selected f_0 . To solve this issue, AR5 Si cantilevers are used as their FWHM ≈ 200 Hz is an order of magnitude larger, see Fig. 3.10 b). It turned out that a cantilever with a FWHM = 201 Hz could be successfully used to approach

Fig. 3.10 Amplitude vs. frequency cantilever curves at $PO_2 = 10^{-1}$ mbar O_2 , a) curves at different distances between AFM tip and $SrTiO_3(001)$ surface $d_{tip \rightarrow sur}$ (1) RT, (2) after 2 h thermal stabilization at 600 °C at $d_{tip \rightarrow sur} = 19 \mu m$, (3) after 30 min at 600 °C at $d_{tip \rightarrow sur} = 14 \mu m$, (4) after 30 min at 600 °C at $d_{tip \rightarrow sur} = 9 \mu m$, (5) after 30 min at 600 °C at $d_{tip \rightarrow sur} = 4 \mu m$, (6) after 30 min at 600 °C at $d_{tip \rightarrow sur} = 1 \mu m$ and (7) after 30 min at 600 °C AFM tip on surface. Frequency shift $\Delta f \approx 200$ Hz of the cantilever during warming up of the $SrTiO_3(001)$ sample (1) from RT to (2) 600 °C and waiting for 30 min after approaching AFM tip to sample surface, b) curves of SSS ($Q_c = 12k$) and AR5 ($Q_c = 1k$) Si cantilever at RT. The FWHM of the cantilever is an important parameter for the AFM operation stability and coarse approach.

the AFM tip in close vicinity of the sample surface and stable AFM imaging could be performed at $T = 600$ °C and $PO_2 = 10^{-1}$ mbar O_2 .

3.5.3 AFM imaging

Here, the AFM imaging performance in air, under PLD conditions and while growing a PLD thin film is demonstrated and discussed.

AFM scan speed under air and PLD conditions

First, TM-AFM measurements are performed to test the AFM scan speed performance in air¹⁵, see Fig. 3.11. The scan speed is increased going the Fig. 3.11 from left to right illustrating the AFM performance by imaging $SrTiO_3(001)$ substrate steps of 0.4 nm. At conventional AFM scan speeds, with a 2 Hz line rate having an acquisition time of 256 s/frame, the subnanometer $SrTiO_3$ substrate steps are clearly resolved. The 0.4 nm $SrTiO_3(001)$ steps are visible in the AFM height profile. From this profile, a peak-to-peak z-noise was found < 0.1 nm at a

¹⁵ The vibrational level is lower under vacuum conditions than in air as active damping control units only can be used under vacuum conditions.

Fig. 3.11 TM-AFM $1 \times 1 \mu\text{m}^2$ 512×512 pixels² images of a $\text{SrTiO}_3(001)$ substrate in air at RT with in the bottom panels the corresponding height profiles. The scan speed is increased from left right from 256 s/frame to 20 s/frame. The resolution decreases significantly at a scan speed of 20 s/frame due to the limitation of the cantilever resonance frequency f_0 . The AFM flexure scanner is not the limiting factor in terms of speed. A resonance frequency of 1.6 kHz appears caused by the mounting bracket connection with the coarse approach stage.

bandwidth of 2.0 kHz, see Fig. 3.11 a). The AFM resolution slightly decreases as the acquisition time is reduced to 39 s/frame (bandwidth 13.4 kHz) due to a pixel dwell time decrease. An increase in peak-to-peak z-noise has been observed for 39 s/frame compared to 256 s/frame. Furthermore, a smaller AFM acquisition time per frame of 20 s/frame (bandwidth = 26.2 kHz) results in a even larger increase of peak-to-peak z-noise. At this AFM image acquisition time, a peak-to-peak z-noise ≈ 0.3 nm has been measured. In addition, a resonance frequency of 1.6 kHz is appearing, a vibrational mode of the mounting bracket connection with the coarse approach stage.

The increase in peak-to-peak z-noise can be attributed to two sources; (1) the electronic noise increases proportional to $\sqrt{f_{\text{bw}}}$, whereas the LPM electronics has been proven as a suitable SPM electronics system for resolving surfaces with atomic resolution at acquisition rates up to 80 frames/s (128×128 pixels, maximum tip velocity = 0.3 mm/s) on the one hand [35, 185, 186]. On the other hand, the SIS electronics bandwidth is limited to 400 kHz due to its photodetector. Therefore, only cantilevers with a $f_0 < 400$ kHz are applicable. A reduced pixel dwell time results in less oscillations used to determine a RMS value for every single pixel.

To reduce the AFM z-noise at low acquisition times per frame, a high bandwidth detection system needs to be developed with a peak-to-peak z-noise < 0.1 nm such that MHz frequency cantilevers can be used. In addition, (2) a mechanical resonance appearing from the mounting bracket / coarse approach connection increases the peak-to-peak noise in Fig. 3.11 c). A re-design of the mounting bracket with focus on more symmetric positions of its screw holes can reduce the vibrational strength and therefore extending the AFM scan speed without exceeding a peak-to-peak z-noise of 0.1 nm.

Secondly, the AFM scan speed has been tested at $PO_2 = 10^{-1}$ mbar O_2 . Step resolution is hardly visible after a decrease in acquisition time from 256 s/frame to 39 s/frame under these conditions. A significant increase of cantilever quality factor Q_c from several hundred in air to tens of thousand at $PO_2 = 10^{-1}$ mbar O_2 has been reported [33]. The transient time τ_{cTM} is proportional to Q_c and therefore decreases the cantilever bandwidth $\frac{f_0}{Q_c}$. The maximum achievable AFM scan speed can be extended by both (1) using high frequency cantilevers in the order of MHz and (2) increase of detector bandwidth (in this system especially the bandwidth of the photodetector without noise increase). Furthermore, FM-AFM is more favorable to extend the AFM scan speed and is typically applied under vacuum conditions. In FM-AFM mode, the transient time τ_{cFM} is nearly independent of Q_c , but then the bandwidth of PLL demodulator is limiting the AFM scan speed. As mentioned in Ch. 2, a lot of progress has been made recently to extend the demodulator bandwidth enabling real-time FM-AFM [65, 182].

AFM imaging under PLD conditions

In situ AFM images shown in Fig. 3.12 are recorded under typical PLD conditions. In Fig. 3.12 a), an FM-AFM image is depicted of a $SrTiO_3(001)$ substrate containing unit cell vacancy islands of 0.4 nm deep recorded in a background pressure of 10^{-6} mbar at RT [19]. In this FM-AFM image, the vertical resolution is similar to the z-noise level (< 0.1 nm) and unit cell (0.4 nm) deep vacancy islands are obtained. Lateral vacancy island sizes of ≈ 20 nm are visible and measured. In the lateral direction, the AFM resolution was determined to be ≈ 10 nm similar to the tip apex. Lateral AFM resolution is determined by measuring $SrTiO_3(001)$ step-edge broadening [186]. In this pressure regime, the FM-AFM imaging mode is typically used due to the high Q_c for image stability reasons and lower transient time compared to TM-AFM [157, 178]. In this work, TM-AFM imaging on a $SrTiO_3(001)$ substrate at 10^{-6} mbar and RT has a similar lateral AFM resolution

Fig. 3.12 *In situ* AFM $1.2 \times 1.2 \mu\text{m}^2$ (512×512 pixels²) images of $\text{SrTiO}_3(001)$ substrates under different conditions (and different miscut angles) recorded with an acquisition time of 256 s/frame. a) FM-AFM image, $\Delta f = -28$ Hz, $A_{\text{osc}} = 10$ nm, at RT and $P = 10^{-6}$ mbar, b) TM-AFM image, $A_{\text{osc}} = 44$ nm, at RT and $PO_2 = 10^{-1}$ mbar, c) TM-AFM image, $A_{\text{osc}} = 44$ nm, at $T = 600$ °C and $PO_2 = 10^{-1}$ mbar O_2 , d) TM-AFM image, $A_{\text{osc}} = 44$ nm, at $T = 600$ °C and $PO_2 = 10^{-1}$ mbar O_2 after 30 min AFM imaging. Circle markers surround unit cell vacancy islands with a depth of 0.4 nm and square markers surround etch pits of several unit cells deep.

and operating stability compared to FM-AFM¹⁶.

In Fig. 3.12 b), a TM-AFM image is depicted of a $\text{SrTiO}_3(001)$ substrate at $PO_2 = 10^{-1}$ mbar O_2 , which is a typical PLD pressure to deposit perovskite oxide films ensuring good crystal quality, properties, stoichiometric transfer and 2D growth [126]. At $PO_2 = 10^{-1}$ mbar O_2 , the free cantilever amplitude A_{osc} was set to 120 nm and is the most critical parameter for AFM imaging. The lateral AFM resolution on terraces is lowered compared to 10^{-6} mbar O_2 as a $\text{SrTiO}_3(001)$ step broadening is ≈ 20 nm at $PO_2 = 10^{-1}$ mbar O_2 . A smallest lateral vacancy island size of ≈ 34 nm was found in the AFM image in Fig. 3.12 b). An average in-plane drift of 2 nm/min is measured over a period of 3.5 h

¹⁶ In FM-AFM and TM-AFM measurements at 10^{-6} mbar and a sample temperature $T = \text{RT}$, SSS Si cantilevers of 190 kHz were used with a tip apex of ≈ 10 nm.

under these conditions.

The same AFM settings have been used at $T = 600$ °C compared to RT. Due to thermal drift, a lower f_0 has been found, where Δf is typically -200 Hz. Vacancy islands are still obtained at $PO_2 = 10^{-1}$ mbar O_2 and $T = 600$ °C. The AFM noise increase due to temperature is negligible based on the fact that z-noise level and $SrTiO_3(001)$ step broadening remained at $T = 600$ °C [33]. In Fig. 3.12 c), a minimum vacancy island of 40 nm in diameter was found. It was noticed that AR5 Si cantilevers operate more stable at $T = 600$ °C compared to SSS cantilevers due to an order of magnitude larger FWHM in amplitude vs. frequency curve, see Fig 3.10. Using only a power of 5 Watt, the sample temperature is $T = 400$ °C in air and $T = 600$ °C at $PO_2 = 10^{-1}$ mbar O_2 . Under these conditions, a drift of 9 nm/min and 15 nm/min is measured in-plane, respectively. After hours of stable AFM imaging under oxide PLD conditions, the z-piezo stayed within range (± 700 nm).

AFM during and after PLD

$BiFeO_3$ has been deposited as prototypical ABO_3 film using the described PLD system. This material has multiferroic properties and its growth and property relation is intensively studied [191, 202, 203, 204, 205]. It is reported that $BiFeO_3$ tends to grow in several type of domains (71° and 109°) by modifying the $SrTiO_3(001)$ termination [191]. Dependent on the substrate termination, $BiFeO_3$ grows either 1D/2D or 3D. Here, $BiFeO_3$ films have been grown on TiO_2 terminated $SrTiO_3(001)$ substrates expecting 3D growth. $BiFeO_3$ was deposited with a laser fluence of 2.0 J/cm^2 , $PO_2 = 0.3$ mbar O_2 , $T = 600 - 670$ °C, repetition rate $f_{rep} = 0.5$ Hz all settings similar to previous work where only a target-substrate distance¹⁷ of 45 mm is used instead of 55 mm [191].

Fig. 3.13 shows AFM images obtained after and during $BiFeO_3$ deposition. In Fig. 3.13 a), an *ex situ* AFM image¹⁸ is depicted of a $BiFeO_3$ film after deposition of 1000 pulses at 670 °C¹⁹. This $BiFeO_3$ film was deposited as a reference to reported literature [191]. It is reported that $BiFeO_3$ grows 3D on TiO_2 terminated $SrTiO_3(001)$, which is similar to the results obtained here. Terraces with on top 3D islands are visible after 1000 PLD pulses of $BiFeO_3$ deposited on TiO_2 terminated $SrTiO_3(001)$. The 3D $BiFeO_3$ islands on top of the terraces suggest that next layer nucleation starts before a previous layer is completely covered. Island step

¹⁷ Target-substrate distance was here limited to 45 mm due to a irregular thickness of the rod on the $BiFeO_3$ target holder.

¹⁸ After $BiFeO_3$ deposition, *ex situ* AFM images were taken with a Bruker Dimension Icon.

¹⁹ The thickness of the $BiFeO_3$ film d_{film} is expected to be $d_{film} \approx 3\text{-}4$ nm.

Fig. 3.13 TM-AFM $1.2 \times 1.2 \mu\text{m}^2$ (512×512 pixels²) images, acquisition time = 256 s/frame, after 1000 pulses of BiFeO₃ deposited on SrTiO₃(001) a) *ex situ* at RT and in air after deposition at $T = 670^\circ\text{C}$, b) *in situ* at $T = 600^\circ\text{C}$ and $PO_2 = 0.3$ mbar O₂ after 1000 pulses of BiFeO₃ deposited on SrTiO₃(001), c) *ex situ* at RT and in air after deposition at $T = 600^\circ\text{C}$. Square markers point to 3D BiFeO₃ islands, circle markers point to small BiFeO₃ islands and polygon markers point to larger islands.

heights are found of 0.2 nm, 0.4 nm and its multiples up to a maximum peak-to-peak height of 3 nm. Islands of 25 - 30 nm in lateral size are obtained on top of random shaped islands. From these results, it is expected that BiFeO₃ growth will continue 3D, similar to what has been reported [191].

In Fig. 3.13 b), an *in situ* AFM image is presented, which was recorded at $T = 600^\circ\text{C}$ and $PO_2 = 0.3$ mbar O₂ after 1000 pulses of BiFeO₃. The AFM image was taken after BiFeO₃ deposition, sample transfer from PLD to AFM and an AFM stabilization time of 2h at the AFM position. After thermal stabilization, AFM was started with similar settings used for imaging of a SrTiO₃(001) substrate. It became clear that due to an increase in surface roughness after deposition, the integral gain of AFM electronic feedback had to be increased strongly to visualize the smallest BiFeO₃ islands. Stable AFM imaging was continued for several hours on BiFeO₃ without thermally drifting out of the Z-range. Thermal drift causes small distortions at AFM image edges. Smallest lateral BiFeO₃ island sizes of 20 - 30 nm have been measured, similar to the results obtained with an *ex situ* AFM on BiFeO₃ after deposition at $T = 670^\circ\text{C}$ [191]. Some of these small islands are surrounded by a white circle marker in Fig. 3.13. The same lateral island sizes have been found after a zoom-in from $1.2 \times 1.2 \mu\text{m}^2$ to $0.8 \times 0.8 \mu\text{m}^2$. In Fig. 3.13 b), the square white marker representing a zoom-in of a BiFeO₃ taken from an $0.8 \times 0.8 \mu\text{m}^2$ AFM image.

Afterwards, the BiFeO₃ film grown on SrTiO₃(001) at $T = 600^\circ\text{C}$ had a cooldown of $\approx 15^\circ\text{C}/\text{min}$ in its deposition pressure of $PO_2 = 0.3$ mbar O₂. Once the sample

reached RT, it was exposed to an maximum O_2 flow up to atmospheric pressure. In Fig. 3.13 c), an ex-situ AFM image is depicted of $BiFeO_3$ after O_2 exposure up to atmospheric pressure. The AFM image in Fig. 3.13 c) is slightly different compared to Fig. 3.13 b). One difference is that $BiFeO_3$ islands of $\approx 20 - 30$ nm are hardly visible in *ex situ* AFM image. Both AFM images have in common that $BiFeO_3$ islands within polygon markers are similar in size. Most likely, the AFM tip apex could be different as a Bruker 320 kHz cantilever has been used during *ex situ* AFM. Moreover, Q_c decreases more than an order of magnitude from $PO_2 = 10^{-1}$ mbar O_2 up to atmospheric pressure.

This study reveals that $BiFeO_3$ can be imaged using a Si AFM tip at $T = 600$ °C and $PO_2 = 0.3$ mbar O_2 after deposition on a TiO_2 terminated $SrTiO_3(001)$ substrate. Neck formation has not been observed using this tip-sample combination under these conditions. One of the ideas is to deposit $BiFeO_3$ on mixed terminated $SrTiO_3(001)$ in order to study growth (front evolution) differences on both SrO and TiO_2 termination. However, AFM imaging (Si tip) on mixed terminated $SrTiO_3$ substrates results in neck formation at $T = 600$ °C and $PO_2 = 0.1$ mbar O_2 , while stable AFM imaging was achieved on a TiO_2 deposited film on TiO_2 terminated $SrTiO_3(001)$ under the mentioned conditions. From the described measurements and the neck formation of a Si AFM tip with a $SrRuO_3$ film (SrO termination) at $T = 600$ °C and $PO_2 = 0.1$ mbar O_2 , it seems plausible to argue that a Si AFM tip forms a neck if the surface contains a SrO top layer [8, 33]. For this tip-sample combination, an other tip material/tip coating needs to be selected.

3.6 Conclusions

The designed AFM integrated in a PLD system enables *in situ* oxide PLD growth studies on a microscopic scale. The following specifications have been fulfilled:

- The AFM operates at sample temperatures from RT up to 700 °C and at pressures ranging from 10^{-6} to 1 mbar O_2 .
- Subnanometer resolution is demonstrated on a $SrTiO_3(001)$ substrate and on a $BiFeO_3$ film deposited on $SrTiO_3(001)$ at $T = 600$ °C and $PO_2 = 10^{-1}/PO_2 = 0.3$ mbar O_2 , respectively. A bare Si AFM tip was used in this experiment and no neck formation was obtained.
- A similar XYZ vibrational level has been measured under PLD conditions compared to a standard commercial available AFM having a < 0.1 nm height resolution.

- AFM imaging on a PLD grown BiFeO_3 film revealed that BiFeO_3 islands can be measured at least down to lateral sizes of 20 nm at $T = 600^\circ\text{C}$ and $PO_2 = 0.3$ mbar O_2 .
- A thermal in-plane drift has been found of 15 nm/min during AFM imaging at $PO_2 = 10^{-1}$ mbar O_2 and $T = 600^\circ\text{C}$.
- Stable AFM imaging is performed under metal-oxide PLD conditions for a few hours without exceeding the Z-piezo range of ± 700 nm.

However, the maximum achievable line rate of the designed AFM is limited to few Hz under PLD conditions without exceeding a peak-to-peak z-noise of 0.1 nm. In order to extend the AFM scan speed to monitor oxide growth kinetic processes under PLD conditions, the cantilever and detection bandwidth have to be increased to the order of MHz or FM-AFM needs to be applied with a PLL demodulator bandwidth in the order of several hundreds of kHz.

Chapter 4

Fast side approach for atomic force microscopy

Abstract

The commonly used tip-sample approach in atomic force microscopy (AFM) is a time-consuming procedure resulting in low sample throughput needed for studying the growth front during pulsed laser deposition (PLD). Therefore, monitoring the nucleation density and growth of islands within subseconds after a deposition pulse requires a different tip-sample approach, decreasing the approach time. In this chapter, a fast tip-sample approach method is proposed in order to image a specific sample surface location after back and forth sample transfer between monitoring and deposition. This approach enables "quasi" real-time AFM monitoring of the growth kinetics during PLD thin film growth.

W.A. Wessels, J.J. Broekmaat, R.J.L. Beerends, G. Koster and G. Rijnders. Fast and gentle side approach for atomic force microscopy, *Review of Scientific Instruments* **84**, 123704 (2013).

4.1 Introduction

The latest developments in atomic force microscopy (AFM) [30] are aimed at decrease in acquisition time, which is defined here as the time to measure the surface topography with 256x256 pixels per frame [38], and to operate in dynamic mode instead of contact mode. The dynamic operating mode is considered non-destructive as compared to the contact operating mode and is therefore often the preferred imaging method. Currently, the time to capture a topographical image is reduced from minutes towards (sub)seconds in contact as well as dynamic operating modes [36, 37, 39, 61]. These developments have resulted in the first commercial instruments capturing images at a rate of several frames per second [35]¹. The realization of high-speed AFM's (HS-AFM) is an important step in enabling real-time monitoring of surface dynamics, such as growth kinetic processes. For example, real-time AFM monitoring would increase the understanding of oxide thin film growth during pulsed laser deposition (PLD).

AFM and PLD are preferably positioned at a geometrically different position to prevent significant tip degradation and hindering of deposition on the as-grown surface. The sample surface can be monitored after e.g (1) the temporarily AFM scanner transfer towards the sample surface between deposition pulses or (2) using a lateral sample transfer back and forth between AFM and PLD [33]. In this work, the back and forth sample transfer has been chosen based on lower inertia. Using a sample transfer mechanism, surface monitoring can be continued only after deposition pulses if (1) the sample is repositioned at the AFM position and (2) the AFM tip has approached the sample surface. Both procedures should be fast in order to monitor growth kinetics with characteristic relaxation times of (sub)seconds [17, 18]. Regarding the sample transfer, some vacuum compatible motors² enable sample transfer times in the order of subseconds (over 60 mm)³. However, the commonly used tip-sample approach is still the bottleneck as this tedious procedure takes (sub)minutes.

Among tip-sample approach methods, the proposed side approach is one of the few methods showing a significant decrease in tip-sample approach time [33, 206]. Its principle differs from the commonly used tip-sample approach as the sample is transferred lateral towards the AFM tip instead of e.g. perpendicular to the tip. The strength of the side approach can be attributed to the fact that the tip-sample

¹ Bruker Dimension Fastscan and Cypher S AFM.

² PI ultrasonic piezo motors and Nanomotion motors drive stages with a speed of ≈ 250 mm/s. These motors exhibit reposition repeatability errors of around hundred nm.

³ Vacuum compatible linear electro motors can drive stages even up to speeds of several m/s. The implementation has been considered. However, it uses dynamic instead of static repositioning.

approach is part of the sample transfer. The side approach is suited as approach mechanism especially when (1) AFM and PLD are laterally in position separated and (2) the back and forth sample transfer is used.

Previously, a side approach time of ≈ 4 s is measured having a stage reposition repeatability error of ± 2 μm , where a belt drive was used as stage drive mechanism [33]. However, here the (side) approach is in the order of seconds, where the typical timescale of growth kinetic processes of oxides during PLD are in the order of (sub)seconds [17, 18]. Another drawback, the reported reposition repeatability error is in the order of the typical size of the area of interest. This makes it nearly impossible to monitor local nucleation and growth phenomena at the same surface location.

The aim of this chapter is to demonstrate and test the performance of the side approach using a faster sample transfer and a better reposition repeatability as the side approach is one of the crucial steps in enabling real-time monitoring of the growth kinetics. First, the specifications and requirements of a tip-sample approach are described. Thereafter, the concept of the side approach is explained. A design to validate the performance is presented in the following section. After the design section, the performance of the side approach using a faster sample transfer is shown. The chapter ends by presenting the conclusions.

4.2 Specifications needed for AFM monitoring of PLD growth

Many oxide growth kinetic processes during PLD occur at timescales of (sub)seconds, confirmed by reflection high-energy electron diffraction (RHEED) measurements [17, 18]. The RHEED specular intensity is a measure of the surface step density, which can vary with coverage, nucleation density/radius and supersaturation. Besides that, the relaxation behavior of the RHEED intensity depends on the adatom density as well⁴. Therefore, the single pulse relaxation is characteristic for both the step density evolution and the adatom density decay after a deposition pulse shown in Fig. 4.1 [140]. The adatom density decays after a deposition pulse as adatoms diffuse and become attached to island edges. At coverages close to unity (coverage $\approx 0.7 - 1.0$), relaxation times are measured assuming most of the deposited material is deposited on top of the islands. The evolution of the step density is here neglected and only the timeconstant of diffusing adatoms is considered [18]. Relaxation times of $\tau = 0.2 - 6.2$ s are measured for homoepitaxial SrTiO_3 growth,

⁴ Diffusive adatoms act as diffusive scatterers for electrons.

Fig. 4.1 RHEED growth monitoring during homoepitaxial SrTiO₃ PLD growth. A complete SrTiO₃ monolayer is grown every single RHEED oscillation (here ≈ 40 s). The relaxation behavior of the RHEED intensity varies with both the evolution of the step density and the decay of the adatom density. The relaxation time τ can be extracted from a single deposition pulse, where τ is the timescale of e.g. the adatom density decay during oxide PLD [17, 18]. The adatom density decays as adatoms diffuse and become attached to island edges resulting in lateral growth of islands. The growth front needs to be monitored in timescale τ using AFM in order to measure to (lateral) island growth. Figs. included with permission from Koster and Broekmaat [17, 33].

where τ varies with e.g. oxygen background pressure, growth mode and surface coverage [18].

To monitor/measure the growth of islands, many datapoints of the island radius are needed in a timescale similar to the relaxation time τ . Therefore, monitoring the growth kinetics during PLD in real-time, such as growth of islands, has to start immediately after a deposition pulse. It implies that the tip-sample approach and sample transfer time from PLD to AFM should be at least within fractions of the relaxation time scale τ in order to extract growth parameters.

Small nuclei sizes are characteristic in PLD due to a high temporal supersaturation requiring high spatial resolution in AFM. Depending on the growth conditions and oxide film material, different average island areas have been measured *ex situ* after deposition stopped at the minimum RHEED intensity. *Ex situ* AFM images

4.2 Specifications needed for AFM monitoring of PLD growth

after deposition reveal that SrRuO₃ 2D islands are relative large as compared to 2D islands of SrTiO₃ [17, 18, 33]. Island sizes of around 150 nm² are found for SrTiO₃⁵ and 500 nm² for SrRuO₃⁶. Nuclei sizes are expected to be significantly smaller [193]. In addition, pulsed laser interval deposition has been applied to manipulate the island density and island radius in order to control the growth of SrTiO₃ and superlattices of (Ba,Sr,Ca)CuO₂ [44].

Other thin film growth related parameters, for example the critical nucleation density, can be measured by monitoring the nucleation density. The nucleation density increases after every deposition pulse up to a certain critical nucleation density, mainly determined by the supersaturation of the vapor, whereafter islands start to grow. As the nucleation density is assumed to be constant in between subsequent deposition pulses, it can be measured once in between deposition pulses requiring less ambitious specifications as compared to measuring the growth of islands.

AFM images of several micrometers in size are preferred regarding statistics, but small nuclei/islands can hardly be observed or less precise due to an increase in tip speed. On the other hand, submicron AFM image sizes reduce statistics, but enable the measurement of small nuclei/islands. Determination of an island size using AFM is limited e.g. by (1) the lateral AFM resolution and (2) the tip apex. AFM images of $\leq 2 \times 2 \mu\text{m}^2$ in size with 256×256 pixels enable the measurement of ≥ 16 nm island sizes. However, the average tip apex of the cantilevers used in this thesis are around 10 nm. Therefore, the limitation in lateral resolution ≈ 10 nm and therefore island sizes can be measured down to ≈ 10 nm.

Studying local nucleation and growth phenomena requires monitoring of these events at the same surface location. This requires the reposition repeatability error of the sample transfer stage to be sufficient low to follow single nuclei/islands. The required reposition repeatability error depends on the size of the monitored area. Preferably, the error is as small as possible, but should at least not exceed $\approx 10\%$ of size of the monitored area⁷, which is $\leq \pm 200$ nm of a required $\leq 2 \times 2 \mu\text{m}^2$ AFM image.

⁵ Deposition temperature of 850 °C used for SrTiO₃ deposition. Island area rapidly decreases using lower deposition temperatures.

⁶ This value is found for ≈ 0.5 monolayer. An island area of 100 nm² was measured for ≈ 1.5 monolayer. A deposition temperature of 700 °C was used for deposition of SrRuO₃.

⁷ Assumption is made that without exceeding this value growth of specific islands can be followed over time.

Below, a summary of the side approach specifications for AFM monitoring of PLD growth kinetic processes are summarized:

- $t_{\text{approach}} < \tau \approx (\text{sub})\text{seconds}$.
- Sample transfer stage reposition repeatability error $\leq \pm 200 \text{ nm}$.

The total side approach time is defined as t_{approach} , which is the time between sample transfer from PLD to AFM position and continue AFM imaging of the surface topography. In the following section, the concept of the side approach is described.

4.3 Side approach concept

Figs. 4.2 (a-c) schematically illustrate the side approach concept [206]. By definition, the z-axis is perpendicular to the sample transfer plane in the x-axis. Furthermore, the sample position at the AFM is defined as position A and the sample position at the PLD as position B. In Fig. 4.2 a), the sample is located at position A. The AFM tip and sample surface are brought once into contact by a scanner coarse approach⁸ in the z-direction to start imaging in one of the feedback-modes. The constant force feedback can be based on cantilever deflection, amplitude, phase or frequency modulation to maintain the force setpoint by adjusting the z-piezo deformation.

The AFM is raster-scanning the tip over the sample surface to reconstruct a topography image. Raster-scanning of the AFM tip is continued during and after sample transfer from position A to position B without retracting the AFM tip in the z-direction by the coarse approach mechanism, see Fig. 4.2 b) and the constant force feedback maintains the force setpoint. This results in an AFM-tip transfer in the z-direction due to the z-piezo extension. Since there is no sample below the AFM tip, the z-piezo gets a maximum extension Z^* as there is no tip-sample interaction possible.

After sample transfer from A to B and an additional wait time at position B for a deposition pulse, the sample is transferred back to position A' and approaches the AFM tip from the side (A' is defined as the new sample position after a side approach). Close to position A', the tip-sample distance decreases during sample transfer due to the small sample angle $\alpha = 1^\circ$ with respect to the x-direction. The interaction force is maintained when the AFM tip is again "in contact" with

⁸ Commonly used tip-sample approach.

Fig. 4.2 The sample is placed under a small angle α (top face sample holder shaved off $\alpha = 1^\circ$) in order to approach from the side and reposition the AFM tip at nearly the same surface location. (a) At the initial position A, AFM surface imaging is started after using the standard tip-sample coarse approach. (b) Subsequently, the sample is transferred from position A to position B. The force feedback adjusts the z-piezo deformation to maintain the interaction force set by the force setpoint. In the case the sample is not located at position A or A', the z-piezo has a maximum extension defined as Z^* . (c) After a wait time at position B, the sample is transferred from position B to position A'. At position A', the sample approaches the AFM tip from the side. Once the sample has approached the tip, the AFM displays the surface topography due to the restored tip-sample interaction.

the sample surface, because the feedback mechanism maintains the same force setpoint. During the side approach, the z-piezo turns out to follow the small angle of the sample surface until the stage is decelerated. The change in z-piezo deformation ΔZ induced by the repositioning repeatability error ΔX (because of $\alpha = 1^\circ$) is small compared to the z-range (typically, 1 - 15 μm) of the z-piezo. For instance, a repositioning repeatability error $\Delta X = \pm 1 \mu\text{m}$ induces a z-piezo deformation of only $\Delta Z = \pm 17 \text{ nm}$. This relation is described by:

$$\Delta Z = \Delta X \tan(\alpha) = \Delta X \times \frac{H}{L}. \quad (4.1)$$

where ΔZ is z-piezo deformation, ΔX is the repositioning error, α is the angle of the sample holder, H is the height of the sample holder, L is the length of the sample holder, see Fig. 4.2 a).

4.4 Design

In the experimental setup, a home-built transfer stage was attached by an aluminum mounting bracket to the sample stage of a commercial available Bruker Dimension Fastscan AFM, see Fig 4.3⁹. AFM imaging was performed in tapping mode (TM) using a Bruker FastScan-A silicon nitride cantilever/force sensor¹⁰. The transfer stage was driven by a Nanomotion HR4 ultrasonic piezomotor (length $\times$ width $\times$ height; $42\times46.6\times15 \text{ mm}^3$, weight 73 g) having a maximum sample transfer speed of 244 mm/s (maximum acceleration/deceleration of 4.8 m/s^2 , stroke 43 mm)¹¹. For stage position readout, a Renishaw RGH25F UHV optical encoder with a resolution of 5 nm was integrated. A FlexDC nanomotion controller (RS232 - software SC Shell 9.01) was used in order to control the HR4 nanomotion motor.

Two samples were prepared in order to test and demonstrate the side approach performance. Sample (I) was a silicon substrate with a titanium nanocross on top (wire dimensions: length $\times$ width $\times$ height; $10000\times100\times10 \text{ nm}^3$) fabricated by e-beam lithography. Sample (II) was a TiO_2 -terminated $\text{SrTiO}_3(001)$ substrate with 0.4 nm height substrate steps [19].

⁹ A HS-AFM is used to show the applicability of combining the side approach method with real-time surface monitoring.

¹⁰ Resonance frequency $\approx 1.4 \text{ MHz}$, 27 μm long triangular shaped, force constant 17 N/m and tip radius 5 nm.

¹¹ An UHV $\geq 10^{-9}$ mbar compatible HR4 nanomotion version was selected to meet the typical oxide PLD pressures ranging from 10^{-6} - 10^{-1} mbar O_2 .

Fig. 4.3 Experimental setup with key components labeled. (1) Home-built transfer stage, (2) AFM scanner, (3) sample stage Bruker Dimension Fastscan, (4) 1° angle sample plate suited for a $5 \times 5 \text{ mm}^2$ sample on top, (5) aluminum mounting bracket to connect the home-built transfer stage to the Fastscan sample stage.

Sample (I) was used to demonstrate the ability to monitor the same surface location after subsequent side approaches. The center of the nanocross was followed during repetitive side approaches to measure the repositioning repeatability error of the transfer stage. Sample (II) was used to test any additional tip wear after subsequent side approaches. AFM imaging was performed using a line rate f of respectively 25.3 Hz and 27.9 Hz during imaging of a surface area of $2 \times 2 \text{ }\mu\text{m}^2$ with 256×256 pixels. During the measurements, the AFM scan direction was always from top to bottom. The wait time between the subsequent sample transfers from position B to position A and vice versa was set to 10 s as a typical time used in between deposition pulses.

4.5 Performance

In this section, the performance of the side approach is demonstrated using the designed sample transfer stage. First, the AFM images before, during and after the side approach are shown. Thereafter, the AFM scanlines before, during and after the side approach are presented. Furthermore, the reposition repeatability error of the designed transfer stage is determined. This section ends by showing the results on possible tip wear caused by the side approach.

4.5.1 Continuous AFM imaging during the side approach

In Fig. 4.4 a), a single $2 \times 2 \text{ }\mu\text{m}^2$ AFM image is depicted of continuous AFM imaging of the sample surface before sample transfer from position A to position B. Continuous AFM imaging was started after bringing the AFM tip into contact with the sample surface using the coarse approach. The nanocross center was placed nearly in the center of the $2 \times 2 \text{ }\mu\text{m}^2$ AFM image in order to follow the repositioning repeatability error of the transfer stage.

After continuous AFM imaging of the nanocross sample surface at position A, the raster-scanning of the AFM tip was continued during and after retracting the sample from the AFM tip by the sample transfer from position A to position B, visible in Fig. 4.4 b). The sample positions A, A' and B in time are represented by A, A' and B in Figs. 4.4 (b-c). The sample surface topography is displayed by the AFM at position A, while during the time the sample is not located at position A or A' the tip-sample interaction force is lost and no surface topography is obtained (the latter is visible in the bottom part of the AFM image in Fig. 4.4 b)). Retracting the sample from the AFM tip is fast as there are no or only a few scanlines representing the z-piezo extension, by following the sample surface, during sample transfer from position A to B (Fig. 4.4 b)). In between sample retracting from and approaching the sample to the AFM tip from the side, the AFM displays images containing noise, since there is no tip-sample interaction force.

After the wait time at position B, the sample was transferred to position A' and the sample approaches the AFM tip from the side. Fig. 4.4 c) shows an AFM image during the sample transfer from position B to position A' and the side approach of the sample to the AFM tip at position A' (red rectangle marker surrounds AFM scanlines during the side approach, see Figs. 4.4 c)). At the top part of the AFM image in Fig. 4.4 c), the sample is located at position B and therefore the AFM displays no sample surface topography. Between B and A' in Fig. 4.4 c), the sample is transferred back to the AFM position and approaches the AFM tip

Fig. 4.4 *Ex situ* TM-AFM $2 \times 2 \mu\text{m}^2$, 256×256 pixels images of the nanocross (line rate $f = 25.3$ Hz) and $\text{SrTiO}_3(001)$ sample (line rate $f = 27.9$ Hz) using the side approach method (a) before sample transfer from position A to position B (the center of the nanocross was positioned in the center of the white rectangle marker, circle had a fixed location on the sample surface), (b) during retraction of the AFM tip at position A by sample transfer from position A to position B, (c) during sample transfer from position B to position A', the sample is approaching the AFM tip from the side and (d) continuous AFM imaging after 25 repetitive side approaches (center nanocross moved away from the center of the marker, circle marker moved closer to the rectangle marker).

from the side.

During approach, the sample surface comes close to the AFM tip and the z-piezo contracts such that the AFM tip follows the angle of the sample surface during sample transfer. At that moment, the tip-sample interaction is restored and the force setpoint is maintained by the force feedback adjusting the z-piezo deformation. However, before the sample surface topography is displayed at position A', artificial scanlines¹² are observed in the AFM image of Fig. 4.4 c).

After the artificial scanlines, the sample surface topography is displayed and is visible in the bottom part of the AFM image in Fig. 4.4 c). The AFM tip is now located at a new sample position A' due to the repositioning repeatability error of the stage ΔX . As a consequence, the center of nanocross slightly moves out of the center of the AFM image. Using the same scan direction, the AFM image in Fig. 4.4 c) is mirrored to the AFM image in Fig. 4.4 b) as the moment of tip-sample interaction is mirrored in the vertical direction of the AFM images.

Fig. 4.4 d) shows a single AFM image of continuous AFM imaging of the sample surface after 25 times of repetitive side approaches. The center of the nanocross has slightly moved out of the center of the $2 \times 2 \mu\text{m}^2$ AFM image (the nanocross center shifted with respect to the white rectangle marker in Figs. 4.4 a) and d)).

Thereafter, the measurements were repeated after replacing the nanocross sample by the $\text{SrTiO}_3(001)$ sample to test the side approach performance on an atomically flat surface (shown in the right panel of Fig. 4.4). The $\text{SrTiO}_3(001)$ sample was chosen by the fact that it is the most commonly used perovskite oxide substrate for PLD grown thin films. Conclusions based on the nanocross sample can be extrapolated on atomically flat samples typically used in PLD experiments, such as $\text{SrTiO}_3(001)$, see Figs. 4.4 (a-d).

4.5.2 Side approach scanline(s) analysis

In the AFM images of Fig. 4.4 c), artificial scanlines are present after the side approach, resulting in a time delay t_{delay} before the AFM displays the surface topography in the image¹³. AFM scanlines recorded during side approaching the sample to the AFM tip are indicated by the red rectangular box in Fig. 4.4 c), and the height profiles of the corresponding scanlines are analyzed.

Fig. 4.5 a) shows a zoom-in on the AFM image of the red rectangular marker

¹² Here, artificial scanlines refer to AFM scanlines recorded after stage deceleration at position A' having tip-sample interaction without displaying the sample surface topography.

¹³ The AFM acquisition time of the artificial scanlines is assumed to be equal to the additional time loss after the side approach and displaying the surface topography with AFM.

shown in Fig. 4.4 c) during one of the repetitive side approaches. In addition, the corresponding height profiles of the AFM scanlines 161 - 164 are shown in Fig. 4.5 b)¹⁴. Scanline 161 has a color gradient from dark brown to light brown due to the mean plane subtraction used in image representation. Subtraction of the mean plane is done in order to correct for the surface tilt displayed in the surface topography caused by the small angle $\alpha = 1^\circ$ (see Fig. 4.2) of the sample surface¹⁵. During acquisition of scanline 161, the sample has not approached the AFM tip from the side, but the sample is most probably in close vicinity to the AFM tip.

A large color modulation is observed in scanline 162 related to a large height modulation (Fig. 4.5 (a-b)). From the height profile of scanline 162, it seems that these height oscillations are periodic in time. The scanline recorded during stage deceleration has a gradient in its height profile due to the small sample tilt of 1° . In scanline 162, the transfer stage is most likely decelerating/decelerated at position A'. As the height profile represents the contraction/extension of the z-piezo, the z-piezo oscillates during scanline 162. Scanline 163 shows part of the nanocross, but there is still a small height modulation visible. The oscillation amplitude of the z-piezo is small compared to the previous scanline 162. In scanline 164, AFM imaging is continued without the observation of vibrational (z-piezo) oscillations.

Some vibrational modes are recorded by the AFM as the force feedback maintains the tip-sample distance. A Fast Fourier Transformation (FFT) is applied to find the vibration frequencies observed in scanline 162, which is compared to the scanlines 161, 163 and 164. Vibration frequencies of 660 Hz and 4.65 kHz are obtained in scanline 162 and not observed in the scan lines 161, 163 and 164. Therefore, it is assumed that these frequencies correspond to the resonance frequencies of the sample transfer stage. In addition, the vibrational frequencies do not match with the pixel clock frequency¹⁶ of 13.0 kHz used during the measurement, whereas it should appear in all scan lines if this were an issue.

A time delay t_{delay} of 0.08 ± 0.04 s and 0.11 ± 0.04 s is measured using the nanocross sample and $\text{SrTiO}_3(001)$ sample, respectively. A different t_{delay} is obtained because of discretisation and the different line rate used during the AFM measurement of the nanocross sample ($f = 25.3$ Hz) and $\text{SrTiO}_3(001)$ sample ($f = 27.9$ Hz). From the HR4 motor motion profile in the software SC Shell 9.01,

¹⁴ In this chapter, AFM images contain 256 scanlines in the vertical scan direction.

¹⁵ Mean plane subtraction tilts the height profiles of the scanlines such that the average angle of the scanline height profile becomes zero with respect to a horizontal height profile. The number of scanlines with or without tip-sample interaction are similar, but with an opposite sign of the angle.

¹⁶ Pixels per line $\times$ line rate $\times 2$ (latter for trace and retrace).

Fig. 4.5 Height profiles before, during and after the side approach (a) zoom-in AFM image (red rectangle marker Fig. 4.4 c)) during one of the side approaches (see Fig. 4.4 c) for a typical AFM image during side approach) and (b) the height profiles of the scanlines 161-164 during the side approach. Scanline 161 is recorded during sample transfer and the sample is in close vicinity to the AFM tip, scanline 162 during tip-sample interaction and scanline 163 during the time the AFM poses to image the height profile of the nanocross sample (nanocross height 10 nm). The scanlines 162 and 163 show vibrational modes. Displaying the nanocross sample surface topography is continued from scanline 164. Z^* means a fully extended z-piezo as there is no tip-sample interaction, where $Z + \Delta Z$ means that the z-piezo is contracted/extended within the limits of the z-range as there is tip-sample interaction since the sample is positioned below the AFM tip. The angle of the height profiles is indicative for when the tip-sample interaction is restored during the side approach.

a sample transfer (position B $\rightarrow$ position A) time of 0.22 s (depends on the user settings) was measured over 35 mm. Therefore, t_{approach} can be at least reduced to ≈ 0.3 s. The quality factor of the transfer stage is most likely an important parameter to decrease t_{delay} . Furthermore, the bandwidth of the AFM feedback seems to be a crucial parameter to reduce the side approach time t_{approach} ¹⁷.

4.5.3 Sample location reposition repeatability error

The nanocross center was followed to determine the repositioning repeatability error of this transfer stage. Fig. 4.6 shows results of the reposition repeatability error measurements. A repositioning repeatability error within $\Delta X = \pm 60$ nm is measured after correction for thermal drift. Several measurements have been performed to confirm a temperature increase of the transfer stage. The drift correction is performed by using a moving average filter. The drift of the Bruker Dimension Fastscan was minimal (few nm/min) and assumed to be negligible in these side approach experiments.

4.5.4 AFM tip wear

Continuously TM-AFM imaging of a sample surface affects the AFM image resolution due to an AFM tip apex increase [207]. This loss in spatial AFM resolution makes it harder to resolve small single islands and their growth. To study any additional loss in resolution caused by the side approach, no tip wear should occur caused by AFM surface imaging. AFM tip wear during the side approach can be expected based on the fact that the maximum sample transfer speed of 244 mm/s is much faster than the AFM tip speed of ≈ 100 $\mu\text{m/s}$ used in these experiments. Moreover, scanline 162 in Fig. 4.5 shows that the AFM tip oscillates, which might cause AFM tip wear.

The results to test tip wear after subsequent side approaches are shown in Fig. 4.7. In these experiments, 25 repetitive side approaches (similar to Fig. 4.4) were performed in order to study any tip wear caused by the side approach. A single 2×2 μm^2 AFM image ($f = 27.9$ Hz, 256×256 pixels) is depicted in Fig. 4.7 a) showing the unit cell terraces of the $\text{SrTiO}_3(001)$ sample. Continuous AFM imaging was started after the coarse approach.

In Fig. 4.7 b) an AFM image (same settings as Fig. 4.7 a)) is depicted of the

¹⁷ An oscillating piezo was used to test the maximum speed of the side approach using the LPM feedback controller. These experiments reveal that a five times faster sample transfer can be used in order to approach the AFM tip from the side.

Fig. 4.6 Repositioning repeatability error of the home-built transfer stage is within $\Delta X = \pm 60$ nm measured over 25 side approaches after correction for thermal drift. Measured thermal drift of the home-built transfer stage is $1.5 \mu\text{m}/^\circ\text{C}$ in air.

SrTiO₃(001) sample surface after 25 subsequent side approaches. The AFM resolves the unit cell terraces after 25 side approaches. In addition, the locations of the vacancy islands in the terrace, see Fig. 4.7 a) and Fig. 4.7 b), confirm the small repositioning repeatability error. The unit cell steps (0.4 nm) of the terraces can still be observed in the height profile of Fig. 4.7 d). The measured RMS surface roughness remained $\sigma_{\text{RMS}} = 0.18$ nm after 25 side approaches and was similar to the condition where 25 coarse approaches were applied, which demonstrates that there is no significant resolution degradation using the side approach method.

Fig. 4.7 *Ex situ* TM-AFM $2 \times 2 \mu\text{m}^2$, 256×256 pixels, $f = 27.9$ Hz images of the $\text{SrTiO}_3(001)$ sample (a) before the side approach (circle marker surrounds vacancy island to follow location during side approach) and (b) after 25 repetitive side approaches, (c) height profile of the $\text{SrTiO}_3(001)$ surface before the side approach experiments. Step resolution (0.4 nm) was still resolved in the (d) corresponding height profile (blue line Fig. 4.7 b)) of the AFM image after 25 repetitive side approaches. The $\sigma_{\text{RMS}} = 0.18$ nm remained after 25 side approaches.

4.6 Conclusions

In this chapter, it has been demonstrated that the side approach time t_{approach} can be reduced from several seconds to subseconds using a faster transfer stage. From the motor motion profile, it is deduced that a t_{approach} of ≈ 0.3 s is feasible using a PLD - AFM position separation of ≈ 35 mm as used in the design. An vibrational decay time t_{delay} , which is a part of t_{approach} , is observed most likely due to the resonating sample transfer stage after deceleration. A t_{delay} is found of 0.08 ± 0.04 s and 0.11 ± 0.04 s using (two) different samples, respectively.

A repositioning repeatability error of ± 60 nm is achievable using the designed transfer stage, which enables monitoring the same surface location after back and forth sample transfer. As the height resolution and image quality are not degraded after 25 repetitive side approaches, it is concluded that AFM tip wear is presumably negligible. In total, over hundred repetitive side approaches are performed without observation of additional tip wear using the same cantilever.

In summary, it is demonstrated that the side approach time can be reduced using a faster transfer stage. The achievable side approach time is inprinciple limited by the bandwidth of the AFM feedback. The side approach can become widely used as it enables sample modification and subsequent atomic force microscopy imaging at a specific surface location. For PLD growth studies, this opens the opportunity to real-time monitor growth kinetics using HS-AFM.

Part III

Experiments & Models

Chapter 5

Energetics of vicinal perovskite oxide surfaces

Abstract

The surface energetics plays an important role in the perovskite oxide growth front evolution during pulsed laser deposition (PLD). During growth, atoms diffuse and their hopping probability scales with i.e. the nearest neighbor interaction energy, where the latter can be determined from surface step meandering. In this chapter, the meandering of equilibrated step-edges at oxide surfaces is analyzed using *ex situ* atomic force microscopy (AFM). The kink formation energy of perovskite oxide unit cells is extracted from small scale meandering and amounts 0.10 eV per unit cell. It results in a nearest neighbor interaction energy of 0.21 ± 0.01 eV considering a simple square lattice with isotropic interactions. On a larger length scale, a triangular step undulation is observed with a wavelength of ≈ 2100 unit cells. This step undulation is caused by strain relaxation along the mean step direction and is estimated to be 24 meV per unit cell. These experiments reveal that the energetics of perovskite oxide surfaces is mainly governed by the local oxygen coordination. The comparable surface energetics of different perovskite oxides might result into analogous growth behavior and a similar behavior of the oxygen exchange and defect formation in perovskite oxide heterostructures at surfaces and interfaces.

W.A. Wessels, G. Koster, H.J.W. Zandvliet and G. Rijnders, "Energetics of vicinal perovskite oxide surfaces", under review.

5.1 Introduction

Surface steps have a large influence on both equilibrium (e.g. thermal roughening and faceting) and non-equilibrium (e.g. epitaxial growth and etching) surface processes. Knowledge on step-related parameters is of utmost importance for describing and understanding these surfaces. During crystal cutting, the creation of step-edges on a crystal surface is unavoidable as cutting the crystal exactly along the low Miller indices planes is nearly impossible. The miscut angle of the vicinal substrate determines the average distance between the crystal layer height surface steps. The formation of steps usually introduces surface stress influencing the step-edge morphology. Most of the step-related surface studies have been focused on Si as a model system, because of its technological importance [208, 209].

Perovskite oxides, with chemical formula ABO_3 , are often used as substrates and/or thin films. In the closed packed perovskite oxide unit cell, an oxygen octahedra is surrounded by four alkaline (rare) earth elements and a transition metal element in the center, where this ABO_3 unit cell is the elementary building block of the crystal. Such building blocks lead to well-defined steps at the surface, which can be resolved by microscopy techniques, such as scanning probe microscopy (SPM) [31]. Atomic force microscopy (AFM) [30] has the advantage that it can examine the lateral distribution of the building blocks perpendicular to the step of solid surfaces independent of its band gap. Most perovskite oxides have large band gaps and thus no tunneling current is flowing during scanning tunneling microscopy (STM).

Perovskite oxide crystal cutting gives rise to a surface, where long-range Coulomb repulsion plays a significant role in the type and strength of surface bonds. The long-range Coulomb interaction is more dominant in perovskite oxides compared to semiconductor as screening becomes less efficient [67]. Analyzing surface energetics of perovskite oxides seems to be rather complicated compared to semiconductor surfaces as for the latter the strength of long-range Coulomb interaction ($\approx 10\%$ of short range interaction energy for Ge) is mostly neglected [210, 211]. For semiconductor surfaces, the interaction energy between nearest neighbor atoms is typically extracted from its kink formation energy considering a square lattice with isotropic nearest neighbors [208, 212]. However, this isotropic nearest neighbor interaction assumption has been applied in the kinetic Monte Carlo (KMC) simulations in order to predict perovskite oxide thin film growth modes or to study the influence of/as function of pulsed laser deposition (PLD) growth parameters [213].

Several studies show that the isotropic nearest neighbor interaction assumption is plausible for simulating perovskite oxide thin film growth as KMC simulations

match with their observations in growth experiments [17, 18, 58, 148, 213]. Currently, perovskite oxide PLD thin film growth is simulated by iterative selection of energetic parameters, such as the nearest neighbor interaction energy E_N . Literature reports a wide spread in nearest neighbor interaction energy values between perovskite oxide unit cells of $E_N = 0.25 - 0.6$ eV applied in KMC simulations [17, 18, 58, 148, 213]. Reciprocal diagnostic tools, i.e. reflection high-energy electron diffraction (RHEED), have been used to extract the activation barrier for diffusion E_A , but are not suitable to determine E_N between perovskite oxide unit cells [18]. STM studies on semiconductors reveal that energetic parameters, such as E_N , can be determined from step meandering analysis on vicinal surfaces in thermodynamic equilibrium [208, 210].

Thermal roughening of step-edges occurs due to formation of kinks, resulting in meandering of step-edges [214]. Kinks can point towards the lower or upper terrace. The creation of these kinks costs energy since bonds have to be broken. This kink formation energy E_{kink} can be extracted from Boltzmann statistics assuming the surface is in equilibrium. A surface reaches its equilibrium structure by prolonged annealing at elevated temperatures. During annealing, atomic bonds can be broken resulting in atom diffusion to more energetically favorable positions. Eventually, the surface seeks its configuration with the lowest free energy. Therefore, the meandering of step-edges is governed by the step free energy.

Step meandering analysis has been applied to extract surface energetics of semiconductors in last two decades [208, 210, 212, 214]. Here, it is described how perovskite oxide steps behave and step-related energetic parameters can be extracted from AFM images of vicinal surfaces in thermodynamic equilibrium. It will be shown that energetic values of perovskite oxides can be extracted from surface step meandering analogue to semiconductors. Furthermore, the surface energetics of perovskite oxide surfaces is most likely governed by its local oxygen coordination. This study is unique in the field of complex oxides as it is a quantitative study to extract energetic parameters using AFM in contrast to qualitative stepped surface AFM studies reported in literature so far [215, 216, 217].

This chapter continues by describing the perovskite oxide surface, the perovskite oxide crystal structure and typical methods used to extract the energetics. In the subsequent section, the experiment in order to measure the kink energy at perovskite oxide surfaces is explained followed by an overview of the used methods. Thereafter, the obtained results for various oxide surfaces are shown and discussed. In the final section, the conclusions and recommended experiments are presented.

5.2 Perovskite oxide surface energetics

In this section, the perovskite oxide (ABO_3) surface is described and the (relevant) literature regarding studies to extract perovskite oxide surface energetic parameters using RHEED is briefly summarized. Furthermore, the determination of the perovskite oxide energetic parameters is discussed.

5.2.1 The (pseudo)cubic unit cell of $\text{ABO}_3(001)$

Most ABO_3 crystals can not be considered as an ideal cubic unit cell as they are slightly distorted. Often this is due to the deviation of the ideal ionic radii of the cations. An estimation for the degree of distortion and stability of the perovskite oxide can be calculated by the Goldschmidt's tolerance factor:

$$t_{\text{ol}} = \frac{(r_{\text{A}} + r_{\text{O}})}{2(r_{\text{B}} + r_{\text{O}})} \quad (5.1)$$

An ideal ABO_3 has an tolerance factor of $t_{\text{ol}} = 1$. Most stable ABO_3 materials exist with $0.75 < t_{\text{ol}} \leq 1$, while the oxygen octahedra might be tilted. The cubic $\text{SrTiO}_3(001)_c$ has been chosen often as substrate material and has a $t_{\text{ol}} \approx 0.86$.

The ABO_3 unit cell exhibits a stack with alternating planes of AO and BO_2 in the $[001]$ direction¹, see Fig. 5.1 a). Both layers appear at the surface in nearly equal proportion after surface cutting such that both universal step heights, half unit cell of ≈ 0.2 nm and single unit cell of ≈ 0.4 nm, can be expected at the surface (mixed termination). However, many studies show that achieving atomic growth control of perovskite oxide films requires vicinal ABO_3 surfaces with unit cell height surface steps of 0.4 nm having either single termination. Wet-etching together with prolonged annealing has been used successfully in order to achieve a single terminated surface of BO_2 resulting in a unit cell height steps [19, 20]. Besides the BO_2 termination approach, a different annealing procedure is proposed to achieve SrO (AO) termination in the case of $\text{SrTiO}_3(001)_c$ (subscript c denotes cubic) [218].

For orthorhombic ABO_{3_o} substrates (subscript o denotes orthorhombic), the cubic ABO_{3_c} unit cell is distorted to become $\text{ABO}_{3_{pc}}$ (subscript pc denotes pseudo-cubic). From an orthorhombic unit cell, the pseudo-cubic $\text{ABO}_{3_{pc}}$ unit cell existing of stacked alternating planes of AO and BO_2 can be found in a different crystal

¹ Most perovskite oxide thin film growth studies are conducted on substrates with alternating planes of AO and BO_2 in the $[001]$ direction.

Fig. 5.1 Schematic illustration of the perovskite oxide (ABO₃) unit cell with the possible terminating planes. O, A, B ions are ordered from large to small in size, a) (I) ABO₃ unit cell exist of stacked alternating planes of AO and BO₂ (II) AO termination plane at the surface (III) BO₂ termination plane at the surface, b) pseudo-cubic unit cell orientation with respect to the orthorhombic crystal orientation of slightly distorted ABO₃ unit cell.

orientation, see Fig. 5.1 b). Despite the different crystal structure/orientation of ABO₃(110)_o, the same terminating plane can exist such that the oxygen coordination at the surface is similar to ABO₃(001)_c after cutting. For example, the orthorhombic DyScO₃(110)_o has the DyScO₃(001)_{pc} pseudocubic equivalent.

5.2.2 ABO₃ surface energetics obtained by RHEED

Many studies regarding the measurement of ABO₃ surface energetic parameters used RHEED to extract the values [18, 58]. For example, the activation energy barrier for diffusion E_A can be calculated by measuring the single pulse relaxation time τ of the RHEED specular intensity after a single deposition pulse [17]. From the single pulse relaxation time τ , the activation barrier for diffusion E_A can be

ABO ₃ film/substrate	E_A [eV]	E_D [eV]	E_N [eV]	Reference
STO/STO (RHEED)	2.2 ± 0.2			[58]
STO/STO (KMC)		2.2	0.27	[58]
SRO/STO (RHEED)	1.0 ± 0.2			[18]
SRO/STO (KMC)		0.75	0.6	[18]
		1.3	0.3	[213]
SRO/DSO (KMC)		0.9 - 1.0 (E_D^A)	0.25	[148]
		1.3 (E_D^B)	0.25	

Tab. 5.1 Overview of reported ABO₃ surface energetic values regarding surface diffusion. E_A is the activation energy, E_D is the diffusion energy barrier, E_D^A is the diffusion energy barrier on AO termination, E_D^B is the diffusion energy barrier on BO₂ termination and E_N is the nearest neighbor energy. In literature, the surface energetic parameters are equal to $E_A = 1.0 - 2.2$ eV, $E_D = 0.9 - 2.2$ eV and $E_N = 0.25 - 0.6$ eV. The abbreviations STO, SRO, DSO are representing SrTiO₃, SrRuO₃ and DyScO₃, respectively. Both, the experimental measured values using RHEED and the KMC simulation values are presented.

extracted from the linear fit in an Arrhenius plot². The reported literature presents values of $E_A = 0.48 - 2.2$ eV for SrTiO₃ (homoepitaxial growth) dependent on PLD conditions³ [58] and an $E_A = 1.0 \pm 0.2$ eV is found for SrRuO₃ (grown on SrTiO₃(001)) [18].

In the KMC model, diffusion of adatoms is simulated by calculating the hopping rates k_{hopping} for all atoms, see Eq. 2.8. The hopping rate k_{hopping} of a diffusive atom is proportional to $\sim e^{\frac{-E_D + n \cdot E_N}{k_B T}}$, where E_D is the diffusion energy barrier on the surface, E_N is the nearest neighbor energy and n is the number of neighbor atomic bonds. E_D and E_N are necessary to calculate the k_{hopping} of the diffusing atoms. For perovskite oxides, k_{hopping} is calculated for diffusing ABO₃ blocks⁴ and the KMC simulations match with their growth experiments [17, 18, 148, 213]. The KMC model has been applied to predict ABO₃ thin film growth, whereas it is hard to perceive as a free atomistic model for oxides as it is still unknown if single atoms or ABO₃ units diffuse over the surface. Most likely, single atoms diffuse and form an ABO₃ unit cell at the moment atoms attach to a step or island edge, resulting in an effective energy barrier (and which is observed in experiments).

In the atomistic model, known E_A (extracted from RHEED measurements) is not

² For both step-flow and 2D growth.

³ An increase of E_A from 0.48 ± 0.05 eV to 2.2 ± 0.2 eV has been observed for SrTiO₃ increasing the PLD oxygen pressure from 3 to 20 Pa.

⁴ Diffusive ABO₃ blocks instead of single atoms are simulated for simplification.

sufficient as E_D and E_N contributions are still unknown. So far, iterative selection of E_D and E_N is done to match and elucidate growth experiments and KMC simulation. Tab. 5.1 shows the reported energetic values spread of $E_D = 0.75 - 2.2$ eV and $E_N = 0.25 - 0.6$ eV used in ABO_3 KMC simulations (in the case of the simulation of selective SrRuO_3 growth, it has been shown that the Ehrlich-Schwobel energy barrier E_{ES} has less influence on the results and is most of the time neglected [148]).

5.2.3 Real-space observation of surface energetics

In the semiconductor field, STM has been applied on Si and Ge surfaces to measure the kink energy E_{kink} such that energetic parameters, such as E_N can be calculated from real-space observations [208]. The kink formation on vicinal surfaces is related to the amount of kink energy it costs to create a kink. The advantage of SPM's is that they can be used to resolve surface disruptions, such as kinks at step-edges with nanometer scale resolution, where RHEED averages the signal over a spatial area > 250 μm . STM can not be applied on most ABO_3 substrates, because these materials are electrical insulators with large band gaps⁵. Therefore, the use of AFM is preferred to determine surface energetic parameters of $\text{ABO}_3(001)_{(p)c}$ crystal surfaces, such as E_N , by measuring the kink-formation characteristics at $\text{ABO}_3(001)$ step-edges⁶.

⁵ For example, band gap of $\text{DyScO}_3(110)_o$ is 5.7 eV.

⁶ The kinks perpendicular to $\text{ABO}_3(001)$ step-edges are thermally generated ABO_3 unit cells existing of an AO and BO_2 plane. To generate these kinks, the bond(s) have to be broken between two or more ABO_3 unit cells.

5.3 Experiment

A statistical analysis is performed to study kink formation at perovskite oxide step-edges. Fig. 5.2 a) shows an AFM image of a vicinal surface after applying the Canny method [219]. The lines in Fig. 5.2 a) represent the measured step-edges. In Fig. 5.2 b), a schematic representation of a perovskite oxide step-edge is shown. The continuous wavy line w is representing the step meandering of the step-edge (white pixel lines in Fig. 5.2 a)) and m is representing the mean line of the step-edge meandering. One way to extract the mean-square kink length is by measuring the deviation-deviation correlation function $G(r)$ of the step [208]:

$$G(r) = \langle (h(r) - h(0))^2 \rangle = \langle k^2 \rangle \frac{r}{a_0} \quad (5.2)$$

where $h(r)$ is the deviation measured in the direction perpendicular to the step-edge at position r , $h(0) = \langle h(r) \rangle = 0$ is the deviation measured in the direction perpendicular to the step-edge at position 0, r is the position along the high symmetry direction parallel to the step-edge, a_0 the unit cell length parallel to the step-edge and $\langle k^2 \rangle$ is the mean-square kink length, see Fig. 5.2 b). From the mean-square kink length, the kink energy can be calculated as described in Eq. 5.3:

$$\langle k^2 \rangle = \frac{\sum_{k=-\infty}^{\infty} k^2 e^{\frac{-E_{\text{kink}}(k)}{k_B T}}}{\sum_{k=-\infty}^{\infty} e^{\frac{-E_{\text{kink}}(k)}{k_B T}}} \quad (5.3)$$

where k is the kink length, k_B the Boltzmann constant and T the sample temperature in Kelvin. The kink energy is related to the nearest neighbor energy E_N according to:

$$E_{\text{kink}}(k) = k \cdot E_N / 2 \quad (5.4)$$

Using substitution the mean-square kink length $\langle k^2 \rangle$ and kink energy E_{kink} relation can be simplified to:

$$\langle k^2 \rangle = \frac{2y}{(1-y)^2} \quad (5.5)$$

Fig. 5.2 Statistical analysis on a 512×512 pixels² *ex situ* TM-AFM image. a) Canny method applied to an AFM image of a $\text{DyScO}_3(110)_o$ surface in thermodynamic equilibrium after annealing. The lines represent the step-edges. b) Schematic representation of a triangular step-edge undulation with amplitude A and wavelength λ_{step} . The wavy w line represents a step-edge of the surface, whereas its mean line is called m .

with,

$$y = e^{\frac{-E_{\text{kink}}}{k_{\text{B}}T}} = e^{\frac{-E_{\text{N}}}{2k_{\text{B}}T}} \quad (5.6)$$

Eqs. 5.2 - 5.6 reveal that the kink energy E_{kink} and therefore E_{N} can be extracted by measuring the slope $\langle k^2 \rangle$ of the correlation function for small r . The linear dependence in the correlation function implies a random kink formation distribution.

A triangular step undulation model has been used to fit the correlation function of the perovskite oxide step waviness. This model is derived from a square-wave model expressing the total free energy F for a square step [210]. It is used to elucidate strain relaxation behavior of $\text{ABO}_3(001)_{(p)c}$ step-edges.

5.4 Methods

Standard commercial available $5 \times 5 \text{ mm}^2$ $\text{LaAlO}_3(001)_c$, $\text{SrTiO}_3(001)_c$, $\text{DyScO}_3(110)_o$, $\text{ZrO}_2\text{:Y}(001)_c$ and $\text{Al}_2\text{O}_3(0001)_h$ (subscript h denotes the hexagonal crystal structure) substrates were ordered from Crystec GmbH. Here, $\text{LaAlO}_3(001)_c$, $\text{SrTiO}_3(001)_c$ and $\text{DyScO}_3(110)_o$ samples were taken as perovskite oxide model systems as they are the most commonly used substrates in thin film growth methods, chemically stable and are known to have a low defect density. In addition, these materials have a well-defined surface of alternating AO and BO_2 planes, which is neutral in the case of $\text{SrTiO}_3(001)_c$, polar for $\text{DyScO}_3(110)_o$ and polar for $\text{LaAlO}_3(001)_c$ (with a phase transition below 830 K) [220, 221]. Furthermore, $\text{LaAlO}_3(001)_c$, $\text{SrTiO}_3(001)_c$ and $\text{DyScO}_3(110)_o$ have a wide range of pseudo-cubic lattice constants in the perovskite oxide spectrum of $a_0 = 0.3821 \text{ nm}$, 0.3905 nm and 0.395 nm , respectively [42]. Other oxides, such as $\text{ZrO}_2\text{:Y}(001)_c$ (fluorite) and $\text{Al}_2\text{O}_3(0001)_h$ (corundum) were selected as these materials have a different crystal structure and local oxygen coordination at the surface as compared to the perovskite oxides mentioned before [67].

Prior to the annealing procedure, all samples were ultrasonically rinsed in acetone and ethanol both for 10 min. After rinsing, substrate treatments were applied to achieve single terminated substrates in order to ensure a BO_2 terminated plane at the surface [19, 20]. Then, the samples were annealed in a tube furnace using an O_2 flow of 150 l/h at a temperature of 1000 °C. The annealing time and temperature were varied in order to find at which temperature the surface equilibrates. All AFM images were taken *ex situ* in tapping mode (TM) using a Bruker ICON AFM

and a Bruker TESPA doped Si cantilever $f_0 = 320$ kHz. Step-edge analysis was performed on the AFM images by first applying a Gaussian filter in order to remove any noise. Subsequently, leveling of the height data was done by plane fitting the topography. Step-edges were detected by applying the Canny method [219]. The surface steps were aligned perpendicular to the fast scan direction to prevent tip artifacts in the AFM image.

5.5 Experimental results & discussion

The experimental results are shown and discussed in this section. First, experiments are done to confirm that the studied surfaces are in thermodynamic equilibrium. Thereafter, the terrace width distribution and the correlation functions of perovskite oxide $(001)_{(p)c}$ are shown, which are used to extract energetic parameters, such as the nearest neighbor energy. A model is proposed to describe the observed step-edge undulation. Finally, a terrace width dependence of the correlation function is presented together with the correlation function of oxides with a different local oxygen coordination at the surface.

5.5.1 Thermodynamic equilibrium

Figs. 5.3 (a-d) show four AFM images of a $\text{DyScO}_3(110)_o$ surface a) as-received and after b) 30 min, c) 4 h, and d) 12 h of annealing, respectively. The polished as-received surface exhibits disordered step-edges, without a well-defined step distribution. After 30 min annealing, the steps become visible, but are still slightly disordered. Some terraces display one layer deep vacancy islands, which are located in the vicinity of the step-edges. Prolonged annealing up to 4 h results in meandering of the surface steps and a well-defined and narrow terrace width distribution. No vacancy islands are present in the terraces after 4 h annealing. Continuing annealing to 12 h reveals no change of the surface or step-edge correlation function analysis.

Our assumption that the $\text{DyScO}_3(110)_o$ surface is in equilibrium after annealing more than 4 h at 1000 °C is based on our AFM observations. The length scale at which equilibrium is reached scales as t^α , where t is the time and α an exponent that depends on the exact mass transport mechanism [222, 223, 224]. An exponent $\alpha = \frac{1}{2}$ describes mass exchange between the step-edge and adatoms on the terrace, whereas $\alpha = \frac{1}{4}$ describes mass transport along step-edges [225]. The large wavelength along the meandering step-edge suggests that a non-equilibrium step instability is unlikely [226, 227]. Furthermore, $\text{SrTiO}_3(001)_c$ samples annealed

Fig. 5.3 *Ex situ* TM-AFM images of $\text{DyScO}_3(110)_o$ surface at room temperature of a) an as-received surface, b) surface after 30 min annealing at 1000 °C, c) surface after 4 h annealing at 1000 °C and d) surface after 12 h annealing at 1000 °C, respectively. Note that these samples were cut from the same crystal.

for 16 h at 1000 °C show a similar correlation function and surface morphology (measured with AFM) compared to $\text{SrTiO}_3(001)_c$ samples annealed for 4 h.

5.5.2 Terrace width distribution

The terrace width distribution $P(l)$ vs. the terrace width l is extracted for the 4 h annealed $\text{DyScO}_3(110)_o$ surface and shown in Fig. 5.4. Neglecting the weak shoulders and the slight asymmetry in the distribution, the data has been fitted with a Gaussian. An average terrace width $\langle L \rangle$ of $760 a_0 \equiv 300 \text{ nm}$ is found for this particular surface. The width σ of this distribution is $86 a_0 \equiv 34 \text{ nm}$, which is relatively small and indicative for step-step interactions. Typically, $\langle L \rangle$ and σ are measured in order to calculate the strength of the step-step interactions. This very narrow distribution of $\text{DyScO}_3(110)_o$ compared to Si can be explained by the coherent behavior of the $\text{DyScO}_3(110)_o$ step-edges [208]. The right shoulder in the distribution is most probably present due to step-step repulsion.

Fig. 5.4 Normalized terrace width distribution $P(l)$ vs. terrace width l of the $\text{DyScO}_3(110)_o$ surface annealed for 4 h at 1000 °C. An average terrace width $\langle L \rangle = 760 a_0$ is found for the 4 h annealed $\text{DyScO}_3(110)_o$ surface. The narrow width $\sigma = 86 a_0$ and asymmetry of the distribution are indicative for entropic and energetic step-step interactions.

5.5.3 Correlation functions perovskite oxides $(001)_{(p)c}$

In Fig. 5.5 a), the average correlation functions are shown for $\text{SrTiO}_3(001)_c$ (AFM image - Fig. 5.7 d)) and $\text{DyScO}_3(110)_o$ (AFM image - Fig. 5.3 c)) step-edges with in the inset the correlation function of a single step-edge together with a zoom-in of the correlation functions for r ranging from 0 - 200 a_0 in Fig. 5.5 b). At large length scales, see Fig. 5.5 a), the correlation functions of both systems show a clear correlation with an average periodicity of $\lambda_{\text{step}} \approx 2100 a_0 \equiv 830 \text{ nm}$, which slightly varies from step to step. Multiple minima and maxima are present demonstrating the strong correlation along the step-edges. At short length scales, see Fig. 5.5 b), the correlation function starts to deviate from the linear fit ($G(r) \sim r$, $\langle k^2 \rangle = 2.1 \pm 0.1 a_0^2$) around $r > 60 a_0$ to a quadratic relation ($G(r) \sim r^2$). The ratio between minima and maxima and amplitude A (see Fig. 5.2 b)) slightly varies from step to step, but the periodicity remains constant for both material systems. The correlation along the $\text{DyScO}_3(110)_o$ surface steps depends on the average terrace width $\langle L \rangle$. When the $\text{DyScO}_3(110)_o$ average terrace width is smaller than $\langle L \rangle < 170 \text{ nm}$, the correlation function becomes less pronounced and the mean-square kink length decreases.

Fig. 5.5 Average correlation functions a) of $\text{SrTiO}_3(001)$ (STO) and $\text{DyScO}_3(110)$ (DSO) surface step-edges with in the inset a correlation function of a single step-edge. The correlation functions show an average periodicity of $\lambda_{\text{step}} \approx 2100 a_0 \approx 830 \text{ nm}$ for both surfaces, which slightly varies from step-edge to step-edge. In b) a zoom-in $r = [0 - 200] a_0$ of the correlation functions is shown. The average terrace widths of the samples investigated are in between $\langle L \rangle = 250 - 300 \text{ nm}$.

5.5.4 Model

The triangular step undulation is indicative for a strong energy relaxation mechanism along the step. There is a competition between two energy terms in minimizing the surface free energy, the energy cost to create additional step length and the energy reduction by strain relaxation due to the triangular undulations along the step-edge.

The total free energy of a simple square-wave like step with periodicity λ_{step} can

5.5 Experimental results & discussion

be described as [210]:

$$F = \gamma + \frac{2F_{\text{step}}}{\lambda_{\text{step}}} - \frac{(1-v)(\Delta\sigma)^2}{\pi\mu\lambda_{\text{step}}} \ln\left(\frac{\lambda_{\text{step}}}{2\pi a} \cdot \sin(\pi p)\right) \quad (5.7)$$

where γ is the free energy per unit area (in perovskite oxides, the free energy per unit area for a step-up and step-down domain are equal), F_{step} is the step free energy per unit length, v is the Poisson ratio ($v = 0.24$ for single crystal SrTiO_3) [228], μ the bulk modulus (183 GPa for SrTiO_3) [229] and $\Delta\sigma$ the force monopole at the step-edge. Perovskite oxide step-edge undulations have a more triangular wave-like behavior. The total free energy per unit area of a triangular step-edge can be written as:

$$F = \frac{1}{A} \left[\int_{h=0}^A \gamma dh + \int_{h=0}^A \frac{2F_{\text{step}}}{\lambda_{\text{step}}} dh - \int_{h=0}^A \frac{2C}{\lambda_{\text{step}}} \ln\left(\frac{\lambda_{\text{step}}}{2\pi a}\right) dh - \int_{h=0}^A \frac{2C}{\lambda_{\text{step}}} \sin(\pi p) dh \right] \quad (5.8)$$

where,

$$C = \frac{(1-v)(\Delta\sigma)^2}{2\pi\mu} \quad (5.9)$$

and,

$$p = \frac{A-h}{A} \quad (5.10)$$

Eq. 5.8 can be rewritten as:

$$F = \gamma + \frac{2F_{\text{step}}}{\lambda_{\text{step}}} - \frac{2C}{\lambda_{\text{step}}} \ln\left(\frac{\lambda_{\text{step}}}{2\pi a}\right) + \frac{2C}{\lambda_{\text{step}}\pi} \int_{\pi}^0 \ln[\sin(x)] dx \quad (5.11)$$

The integral of Eq. 5.11 can be solved by using trigonometric identities and integration by substitution:

$$\begin{aligned}
 \int_{\pi}^0 \ln[\sin(x)]dx &= \int_{\pi}^0 \ln[2\sin(\frac{x}{2})\cos(\frac{x}{2})]dx \\
 &= \int_{\pi}^0 \ln(2)dx + \int_{\pi}^0 [\sin(\frac{x}{2})]dx + \int_{\pi}^0 [\cos(\frac{x}{2})]dx \\
 &= -\pi\ln(2) + 2 \int_{\frac{\pi}{2}}^0 [\sin(y)]dy + \int_{\pi}^0 [\sin(\frac{x+\pi}{2})]dx \\
 &= -\pi\ln(2) + 2 \int_{\frac{\pi}{2}}^0 [\sin(y)]dy + 2 \int_{\pi}^{\frac{\pi}{2}} [\sin(y)]dx \\
 &= -\pi\ln(2) + 2 \int_{\pi}^0 [\sin(y)]dy
 \end{aligned} \tag{5.12}$$

Since $\int_{\pi}^0 \ln[\sin(x)]dx = \pi\ln(2)$ see Eq. 5.12, the total free energy per unit area F of a triangular step-edge is equal to:

$$F = \gamma + \frac{2F_{\text{step}}}{\lambda_{\text{step}}} - \frac{2C}{\lambda_{\text{step}}} \ln\left(\frac{\lambda_{\text{step}}}{2\pi a}\right) + \frac{2C\ln(2)}{\lambda_{\text{step}}} \tag{5.13}$$

The critical periodicity $\lambda_{\text{stepminF}}$ follows from the minimum free energy per unit area by calculating $\frac{dF}{d\lambda_{\text{step}}} = 0$ as:

$$\lambda_{\text{stepminF}} = 2\pi a e^{\left(\frac{F_{\text{step}}}{C} + 1 + \ln(2)\right)} \tag{5.14}$$

Besides the $\ln(2)$ term in the exponent, Eq. 5.14 is identical to the relation derived by Alerhand *et al.* [230]. From the correlation function, the critical periodicity λ_{stepc} is found to be equal to $2100 a_0 \approx 830$ nm which results in a ratio of $\frac{F_{\text{step}}}{C} = \frac{E_{\text{kink}}}{C} = 4.13$. From Fig. 5.5, a $\langle k^2 \rangle = 2.1 \pm 0.1 a_0^2$ is extracted assuming random kink formation on short length scale, which results in $E_{\text{kink}} = 0.10$ eV/ a_0 using Eqs. 5.5 - 5.6. The nearest neighbor energy E_N can be determined using $E_N = 2 E_{\text{kink}} = 0.21 \pm 0.01$ eV for SrTiO₃(001)_c and DyScO₃(110)_o as a (pseudo-)cubic system [212]. Furthermore, the strain relaxation energy constant C is found to be equal to 24 meV/ a_0 . The nearest neighbor energy is close to $E_N = 0.25 - 0.6$ eV, a value commonly used in KMC simulations to simulate thin film growth [213]. The

proposed model explains the quasi 1D character of a perovskite oxide step-edge for terrace widths larger than 170 nm. Smaller terrace widths result in a more 2D character caused by the step-step interaction, which requires a more sophisticated model.

5.5.5 Terrace width dependence:

The small terrace width distribution of $\text{DyScO}_3(110)_o$ is indicative of step-step interactions. In the case that step-step interactions are present, a change in the step-edge morphology, correlation function and extracted energetic values should be found for smaller terrace widths. From Fig. 5.6, it can be seen that $\text{DyScO}_3(110)_o$ vicinal surfaces with a small average terrace width below $\langle L \rangle = 170$ nm results in a change in step-edge morphology, correlation function and a different extracted nearest neighbor energy E_N .

Here, a mean-square kink length is found of $\langle k^2 \rangle = 2.1 \pm 0.1 a_0^2$ for $\text{DyScO}_3(110)_o$ having average terrace widths of $\langle L \rangle = 170$ nm and 300 nm. For both, a similar correlation function behavior is found on small length scales (0 - 100 a_0), but on large length scales (1000 - 3000 a_0) the correlation has less pronounced minima and maxima for the $\text{DyScO}_3(110)_o$ surface having $\langle L \rangle = 170$ nm. A smaller mean-square kink length of $\langle k^2 \rangle = 1.6 \pm 0.1 a_0^2$ is found for the $\text{DyScO}_3(110)_o$ surface with an average terrace width of 92 nm.

The mean-square kink length decreases with larger step-step repulsion as the entropy of steps decreases for small step-step separations. Typically, the influence of step-step interaction potential on a meandering step increases with $1/L^2$ [208]. The decrease of the mean-square kink length $\langle k^2 \rangle = 2.1 \pm 0.1 a_0^2$ to $\langle k^2 \rangle = 1.6 \pm 0.1 a_0^2$ results in a change of the found nearest neighbor energy of $E_N = 0.21 \pm 0.01$ eV to 0.23 ± 0.01 eV. $\text{DyScO}_3(110)_o$ surfaces with smaller terrace widths have a more 2D character caused by the step-step interaction, which requires a more sophisticated model. Both, the entropic step-step interaction [231] and step interaction energy models [230] used to describe the interaction of Si step-edges are not valid for $\text{DyScO}_3(110)_o$ step-edges. The models assume a meandering Si step-edge caught between two straight step-edges, while the triangular undulation of step-edges on a $\text{DyScO}_3(110)_o$ surface behaves coherent.

Fig. 5.6 *Ex situ* TM-AFM images of annealed $\text{DyScO}_3(110)_0$ exhibiting different average terrace widths $\langle L \rangle$ in the left panel. In the right panel the accompanying average correlation functions. The mean-square kink length $\langle k^2 \rangle$ decreases from $2.1 \pm 0.1 a_0^2$ to $1.6 \pm 0.1 a_0^2$ below $\langle L \rangle = 170$ nm.

5.5.6 Oxides with different oxygen coordination

Different oxide materials were selected to compare the energetics of the perovskite oxide $\text{LaAlO}_3(001)_c$ with different local oxygen coordinated oxides, such as $\text{ZrO}_2\text{:Y}(001)_c$ and $\text{Al}_2\text{O}_3(0001)_h$. Note that the average terrace widths $\langle L \rangle$ in the same range (80 - 101 nm) were selected on purpose as the found mean-square kink length $\langle k^2 \rangle$ depends on the terrace width $\langle L \rangle$. Fig. 5.7 shows the AFM images of the different oxide materials used to extract the correlation functions.

From the AFM images in Fig. 5.7, it can be seen that the step-edge morphology is different for $\text{LaAlO}_3(001)_c$ ($\langle L \rangle = 89$ nm), $\text{ZrO}_2\text{:Y}(001)_c$ ($\langle L \rangle = 101$ nm) and $\text{Al}_2\text{O}_3(0001)_h$ ($\langle L \rangle = 80$ nm). The stepped morphology of the $\text{LaAlO}_3(001)_c$ surface is similar to $\text{DyScO}_3(110)_o$ with almost the same terrace width. The $\text{LaAlO}_3(001)_c$ surface contains single unit cell steps. In contrary, the step-edge height of $\text{ZrO}_2\text{:Y}(001)_c$ and $\text{Al}_2\text{O}_3(0001)_h$ consists of a single atomic layer, while for these type of oxides the unit cell exist of two and four atomic layers, respectively. $\text{ZrO}_2\text{:Y}(001)_c$ exhibits a less coherent behavior in the stepped morphology compared to $\text{LaAlO}_3(001)_c$. XPS measurements (performed in the same manner as described in Ch. 6) show no significant Yttrium segregation at the sur-

Fig. 5.7 *Ex situ* TM-AFM images of an annealed a) $\text{LaAlO}_3(001)_c$ (LAO) perovskite surface, b) $\text{ZrO}_2\text{:Y}(001)_c$ (YSZ) fluorite surface, c) $\text{Al}_2\text{O}_3(0001)_h$ (sapphire) hexagonal surface. The average terrace width of LAO, YSZ, sapphire is $\langle L \rangle = 89$ nm, $\langle L \rangle = 101$ nm and $\langle L \rangle = 80$ nm, respectively. d) TM-AFM image of the annealed $\text{SrTiO}_3(001)_c$ surface ($\langle L \rangle = 250$ nm) used for analysis.

Fig. 5.8 Average correlation functions of an annealed a) $\text{LaAlO}_3(001)_c$ (LAO) perovskite surface, b) $\text{ZrO}_2\text{:Y}(001)_c$ (YSZ) fluorite surface, c) $\text{Al}_2\text{O}_3(0001)_h$ (sapphire) corundum surface. The found E_N values of LAO ($\langle L \rangle = 89$ nm), YSZ ($\langle L \rangle = 101$ nm), sapphire ($\langle L \rangle = 80$ nm) are 0.26 ± 0.01 eV, 0.20 ± 0.01 eV and 0.09 ± 0.01 eV, respectively.

face [232]. The $\text{Al}_2\text{O}_3(0001)_h$ stepped surface morphology is rough compared to $\text{LaAlO}_3(001)_c$, showing no signature of a triangular undulation and the steps are less coherent. Furthermore, an AFM image is depicted of the $\text{SrTiO}_3(001)_c$ surface as comparison to $\text{DyScO}_3(110)_o$ used for extraction of the correlation function. From the stepped morphology of $\text{SrTiO}_3(001)_c$, it can be seen that this vicinal surface is similar to the 4 h annealed $\text{DyScO}_3(110)_o$ vicinal surface.

For the $\text{LaAlO}_3(001)_c$ surface having $\langle L \rangle = 89$ nm, a slightly lower $\langle k^2 \rangle = 1.3 \pm 0.1 a_0^{-2}$ was found compared to $\langle k^2 \rangle = 1.6 \pm 0.1 a_0^{-2}$ found for $\text{DyScO}_3(110)_o$ having $\langle L \rangle = 92$ nm. The correlation function of $\text{LaAlO}_3(001)_c$ is plotted in Fig. 5.8 together with other types of oxides having different local oxygen coordination, such as $\text{ZrO}_2\text{:Y}(001)_c$ and $\text{Al}_2\text{O}_3(0001)_h$. An E_N of 0.26 ± 0.01 eV, 0.20 ± 0.01 eV and 0.09 ± 0.01 eV is found for small terrace widths (80 - 100 nm) on $\text{LaAlO}_3(001)_c$, $\text{ZrO}_2\text{:Y}(001)_c$ and $\text{Al}_2\text{O}_3(0001)_h$, respectively. For $\text{Al}_2\text{O}_3(0001)_h$, a hexagonal unit cell was used in order to calculate E_N for its triangular lattice [211].

From the comparable step meandering along the step-edges of perovskite oxides and contrast to other oxide types, it is most likely that the surface energetics depends on the local oxygen coordination. According to this remark, the surface energetics should change with different alternating planes, for example in the case of $\text{SrTiO}_3(001)_c/\text{AO} - \text{BO}_2$, $\text{SrTiO}_3(110)_t/\text{ABO} - \text{O}_2$ (subscript t denotes the tetragonal crystal structure) and $\text{SrTiO}_3(111)_h/\text{AO}_3 - \text{B}$, which is supported by DFT calculations and difference in required annealing times [233]. The importance of

the oxygen coordination is also supported by the specific terminating plane at the surface, as it has been shown that nanostructures can be grown selective on mixed terminated substrates [217, 234]. Furthermore, the oxygen coordination changes with a termination switch and therefore an expected change in surface energetics might explain the difference in interface properties of oxide heterostructures [235].

5.6 Conclusions & outlook

In conclusion, perovskite oxide vicinal surfaces are analyzed after annealing LaAlO_3 -(001)_c, SrTiO_3 (001)_c and DyScO_3 (110)_o substrates. Using the deviation-deviation correlation function, triangular step-edge undulations are found with an average periodicity of $\lambda_{\text{step}} \approx 2100 a_0$. This step undulation is caused by strain relaxation along the step direction. The ratio between step formation energy and elastic interaction is calculated using the Marchenko-Alerhand model applied for a triangular perovskite oxide step with average terrace widths of 250 - 300 nm. A kink formation energy $E_{\text{kink}} = 0.10$ eV is found for the perovskite oxides SrTiO_3 (001)_c and DyScO_3 (110)_o. Assuming a square lattice with isotropic nearest neighbor interactions, a nearest neighbor energy of $E_N = 0.21 \pm 0.01$ eV is determined. This nearest neighbor interaction energy is close to $E_N = 0.25 - 0.6$ eV commonly used in KMC simulations to simulate perovskite oxide thin film growth. The experiments reveal that the surface energetics of perovskite oxide surfaces are mainly governed by the local oxygen coordination. It might result in a similar behavior of the oxygen exchange and defect formation in perovskite oxide heterostructures at surfaces and interfaces. Finally, it needs to be emphasized that a change in perovskite oxide alternating stacking or terminating plane might influence the surface energetics due to the difference in local oxygen coordination at the surface.

The following experiments are suggested to further validate the assumption that the surface energetics of perovskite oxides are governed by the oxygen coordination at the surface:

- Studying of different ABO_3 crystal orientations, such as (001)_c, (110)_t and (111)_h under the same conditions. It is expected that the stepped morphology and the correlation function will change with crystal orientation as the oxygen coordination changes.
- Annealing experiments at different oxygen pressures to create oxygen vacancies. Oxygen deficient surfaces might for example lead to a change in nearest neighbor energy.

Chapter 6

Sticking of volatile species in perovskite oxides

Abstract

Stoichiometric transfer of species from target to film during pulsed laser deposition (PLD) is often a prerequisite for optimization of perovskite oxide structural and physical properties. However, when diffusive atoms on a surface are prone to re-evaporate, off-stoichiometric films can be obtained. These volatile species have a lower probability to stick at a step-edge, before the species start to re-evaporate from the surface. One way to increase the sticking probability of volatile species is to increase the step density and therefore shortening of the average distance between adatoms and step-edges. In this chapter, the influence of temperature modulation pulsed laser deposition (TM-PLD) on the growth (step density) and sticking of volatile species is investigated. Both kinetic Monte Carlo (KMC) simulations and experiments of SrTiO_3 homoepitaxial growth show that the step density modulation during layer-by-layer growth can be increased using TM-PLD compared to PLD at constant temperature. Furthermore, this method has been applied during PbTiO_3 growth, where Pb is the volatile element. In the temperature range where Pb starts to re-evaporate, an increase in Pb:Ti ratio is observed for TM-PLD PbTiO_3 films compared to PbTiO_3 films deposited only at the higher temperature during TM-PLD.

W.A. Wessels, G. Koster and G. Rijnders, "Sticking of volatile species in perovskite oxides", in preparation.

6.1 Introduction

Pulsed laser deposition (PLD) is a relative simple and versatile technique to deposit complex thin film materials, such as perovskite oxides [3]. One key feature of PLD is the stoichiometric transfer of species from target to thin film material [7, 127]. Therefore, most thin films can be fabricated containing the stoichiometry of the target. However, for some perovskite oxide thin films stoichiometry is hard to achieve as these materials contain volatile elements, e.g. Pb, Na and Bi [127]. The volatile elements might desorb from the surface after absorption and diffusion due to effects, such as re-evaporation [127] and re-sputtering [236]. When these effects do not take place, atoms diffuse until they become attached to a step-edge, which is called "sticking" of adatoms. Here, the sticking coefficient is defined as the ratio between the number of incorporated elements in the film (elements that "stick") and the number of arriving elements.

Off-stoichiometric thin films are often unwanted as it strongly influences the structural and physical properties. For example, the transport properties have been negatively affected by cation off-stoichiometry in Pt/Nb-SrTiO₃ junctions [237]. Furthermore, high leakage currents in BiFeO₃/PbTiO₃ are ascribed to volatilization of Bi/Pb [238]. The lattice parameter and growth mode of homoepitaxial SrTiO₃ films depends strongly on the oxygen content in the film [126]. On the other hand, Zalutayev *et al.* report that cation off-stoichiometry can be beneficial for high p-type conductivity and transparency in Co₂ZnO₄ and Co₂NiO₄ thin films [239]. These studies show that control of stoichiometry leads to control of structural and physical properties.

Previously, several manners have been used in order to achieve stoichiometric films of materials containing volatile species. Frequently, non-stoichiometric targets are used to compensate for the loss of the volatile species [127]. The amount of excess of volatile species put in a target was based on how much of the volatile species re-evaporates. An other method, which was proposed to obtain stoichiometric films containing volatile elements, was the use of segmented evaporation targets [240]. Using segmented targets of KNbO₃, KTO₃ and cold-compressed KN₃ (extra potassium source), Christen *et al.* succeeded to grow stoichiometric epitaxial KNbO₃ films and KNbO₃/KTO₃ superlattices [241]. Recently, pulsed laser interval deposition (PLID) was applied in order to increase the sticking of Bi during deposition of YBiO₃ and BaBiO₃ films at a growth effective temperature, where Bi becomes volatile [242].

PLD parameters, such as the deposition flux and deposition temperature are expected to have an influence on both the nucleation density and diffusivity of

adatoms. An increase of deposition flux results in an increase of nucleation density and on its turn increases the probability for adatoms to stick at a step-edge before re-evaporation [44]. Using deposition flux modulation, first the step density is kept high, whereafter adatoms have longer time to diffuse before new material is ablated. This deposition flux modulation method has been used to impose layer-by-layer growth of superconductors, whereas the materials otherwise prefer to grow in a multilayer fashion [17, 58]. Another parameter, the PLD deposition temperature, is expected to have an effect on both the diffusivity of adatoms (therefore on the nucleation density) and the re-evaporation probability of species. Higher temperatures increase the probability for adatoms to find a step-edge due to a higher adatom diffusivity. Moreover, it increases the re-evaporation probability of adatoms and a lower sticking coefficient is obtained [243]. However, synthesizing perovskite oxides at higher temperatures (containing the stoichiometry) generally results in an increase in crystalline state and improvement of film properties.

Here, the influence of temperature modulation pulsed laser deposition (TM-PLD) on the growth and sticking of perovskite oxides was investigated. This chapter is organized as follows. In the first section, the theory and background of the sticking coefficient in perovskite oxides are described. Thereafter, the temperature modulation experiment performed to increase sticking of volatile species is explained. In the subsequent section, the experimental and simulation methods used in this chapter are described. Then, the kinetic Monte Carlo simulation and experimental growth results of TM-PLD are presented in the next two sections. The chapter ends with a discussion about the TM-PLD growth of SrTiO_3 and PbTiO_3 films, and the sticking coefficient of PbTiO_3 at constant deposition temperature and after TM-PLD.

6.2 Sticking coefficient in perovskite oxides

In this section, the general theory behind the sticking of species during perovskite oxide thin film growth is described.

6.2.1 Sticking coefficient

The sticking coefficient κ_{stick} is defined as the ratio between incorporated and deposited elements in a thin film. PLD has the key feature of stoichiometric transfer and often all deposited elements show no difference in sticking. For non-volatile species, it results in a sticking coefficient of (nearly) one. However, for volatile elements the sticking coefficient can become close to zero at elevated temperatures.

During PLD, particles arrive at the surface, they diffuse over the surface and stick at step-edges of nucleation centers or surface steps. Sometimes particles diffuse without becoming attached to a step-edge and will re-evaporate. Particles with extreme high kinetic energy can either implant or cause re-sputtering of atoms. Both re-evaporation and re-sputtering result in sticking coefficients lower than one. Re-sputtering can be circumvented during PLD by depositing perovskite oxide films in high (oxygen) background pressures and with a relatively low laser fluence [242].

6.2.2 Re-evaporation

Atoms are prone to re-evaporate from the surface after arriving from the plasma plume on the substrate. In particular, the probability of volatile species to re-evaporate is larger compared to non-volatile species¹. Lets assume atoms diffuse over a surface for a residence time τ_{res} needed to find a step-edge before they re-evaporate from the surface. Then the relation between the average diffusion length l_D and the residence time before re-evaporation τ_{res} is given by [3]:

$$l_D = \sqrt{2D_S \cdot \tau_{\text{res}}} = (2\nu\alpha^2\tau_{\text{res}}e^{-E_{\text{abs}}/k_B T})^{1/2} \quad (6.1)$$

where D_S is the diffusion coefficient, ν the attempt frequency, α the characteristic jump distance and E_{abs} the energy activation barrier for absorption. From Eq. 6.1, it is clear that the deposition temperature T is an important parameter in the sticking of volatile species. On the other hand, an increase in step density S results in a shorter diffusion length l_D of adatoms needed to find a step-edge [127]. The main reason that volatile species re-evaporate is that the average diffusion length $l_D < \rho$, where ρ is the average radius of the area in between growing islands (the perovskite oxide PLD growth kinetics is extensively discussed in Ch. 2 and Ref. [18]).

6.2.3 Sticking coefficient vs. deposition temperature

The absorption rate R_{abs} is defined as the average number of adatoms absorbed per surface area and time. This can be expressed according to Eq. 6.2:

$$R_{\text{abs}} = \frac{dn}{dt} \quad (6.2)$$

¹ The residence time τ_{res} is assumed to be shorter for volatile species.

6.3 Experiment

The desorption rate R_{des} is defined as the average number of adatoms desorbed per surface area and per time τ_{res} until re-evaporation. The residence time can be calculated according to $\tau_{\text{res}} = 1 / \nu \cdot e^{-E_{\text{des}}/k_{\text{B}}T}$ and therefore R_{des} is given by:

$$R_{\text{des}} = \frac{n(t)}{\tau_{\text{res}}} = n(t) \cdot \nu \cdot e^{-E_{\text{abs}}/k_{\text{B}}T} \quad (6.3)$$

where, $n(t)$ is the number of desorbed adatoms. The sticking coefficient is defined κ_{stick} as the difference between the absorption and desorption rate and is expressed as:

$$\kappa_{\text{stick}}(t) = \frac{R_{\text{abs}} - R_{\text{des}}}{R_{\text{abs}}} = 1 - \frac{n(t) \cdot \nu}{R_{\text{abs}}} \cdot e^{-E_{\text{abs}}/k_{\text{B}}T} \quad (6.4)$$

At temperatures T where species become volatile, the sticking coefficient κ_{stick} decreases to a value in between zero and one². Eq. 6.4 has been used as model to fit the Pb:Ti ratio (sticking coefficient) measurements.

6.2.4 Atomic ratio measurement

Sticking of species is not directly measured. This is due to the fact that it is hard to determine the number of arriving and re-evaporating species. In order to estimate the sticking coefficient, typically the atomic ratio is measured between the A and B cations of perovskite oxides in a temperature range of interest³. In this study, PbTiO₃ is used as system to explore the effect of temperature modulation sequence during PLD on the sticking coefficient. The atomic ratio between Pb:Ti is 1:1, when the sticking of Pb is similar to the sticking of Ti⁴. However, Pb starts to become volatile ≈ 600 °C [127]. Measuring the ratio between Pb:Ti in the temperature range below the Ti evaporation temperature indicates at which temperature Pb starts to re-evaporate or not.

6.3 Experiment

Temperature modulation pulsed laser deposition (TM-PLD) is proposed here as a method to extend the deposition temperature of volatile perovskite oxides. The

² Non-volatile species have a sticking coefficient $\kappa_{\text{stick}} = 1$.

³ Note that this is only valid when at least one of the A and B cations does not re-evaporate.

⁴ In the case of stoichiometric transfer of species from target to substrate.

Fig. 6.1 TM-PLD illustrated by a instantaneously and ramp-rate (dashed line) temperature interval during ML (assuming 20 pulses) deposition. The temperature is increased from T_{down} to T_{up} after pulse number n_{up} in a ML (number in between 0 - 20) and the temperature is decreased from T_{up} to T_{down} after pulse number n_{down} in a ML (number in between 0 - 20).

method differs from pulsed laser interval deposition (PLID) as the PLD growth takes place at two modulating growth temperatures instead of deposition rate modulation [44, 58]. TM-PLD is based on achieving a high nucleation density N_s in the first growth stage of a single monolayer (ML) and is aiming for a larger diffusion length l_D at the final part of a ML growth stage. This is done to promote interlayer mass transport. Eq. 6.5 gives the relation (for defect-free surfaces) between the nucleation density N_s , deposition rate F and adatom diffusion coefficient D_S [244]:

$$N_s = (F/D_S)^x \quad (6.5)$$

where the exponent x is the scaling order and depends on the smallest stable nucleation size. Starting the first growth stage of a ML at lower T results in a decrease of D_S and l_D , see Eq. 6.1. From Eq. 6.5, it becomes clear that a larger N_s is obtained having a lower D_S at lower T . The increase in nucleation density results in an increase in step density S and decreases the radius of the area between islands ρ . Therefore, the probability for volatile species to find a step-edge is increased in the first part of the monolayer and sticking should be enhanced. When the island diameter is equal to the length of the area in between

islands, island coalescence takes place and l_D is not large enough for interlayer mass transport and perfect 2D growth does not occur. By increasing T at n_{up} (pulse number in a ML, whereafter the temperature is increased from T_{down} to T_{up}), the D_S/l_D is increased and the diffusion of adatoms overcomes the average radius of islands r_{island} [18].

Fig. 6.1 represents an illustrated scheme of TM-PLD during a ML. The scheme is based on SrTiO₃ homoepitaxy, where in typical PLD parameters 20 pulses are needed to deposit one ML, see Refs. [44, 58]. In Fig. 6.1, a TM-PLD sequence is presented, where the first part of a ML is (mainly) deposited at the lower temperature T_{down} after decreasing the temperature from deposition pulse number n_{down} . After several deposition pulses, the temperature is increased up to T_{up} from deposition pulse n_{up} ⁵. This temperature sequence in a ML has been used throughout this chapter. SrTiO₃ has been used as perovskite oxide system to study the influence of TM-PLD on the step density S , where PbTiO₃ is utilized for exploring the effect of TM-PLD on the Pb:Ti ratio and sticking of Pb.

6.4 Methods

Kinetic Monte Carlo (KMC) simulations were performed to gain growth understanding and to elucidate the TM-PLD growth experiments. Note that the KMC simulations are utilized to study the effect of TM-PLD on the step density S , whereas any volatility of the adatoms is not taken into account. A detailed description of the KMC simulation algorithm is described elsewhere [148]. A lattice grid of 512×128 u.c.² was used in the KMC simulations⁶ (in this work, the algorithm was modified such that the temperature is defined per deposition pulse). Two temperatures are included, namely T_{up} the higher temperature of the temperature interval and T_{down} the lower temperature of the temperature interval. The pulse number n_{up} is the deposition pulse number, whereafter the deposition temperature is increased from T_{down} to T_{up} and this is reversed for n_{down} . The values used for the parameters in the KMC simulation have been extracted from other work: $E_D = 2.2$ eV, $E_N = 0.27$ eV, $k_0 = 10^{13}$ Hz, $\phi = 0^\circ$ and $f_{rep} = 1$ Hz [17, 18, 58]. Two types of temperature functions have been included separately in the KMC algorithm. First, a step function having an infinite ramp-rate, where the temperature increases instantaneously from the lower temperature T_{down} to the higher temperature T_{up} . Second, as the heater has a finite ramp-rate, a typical ramp-rate of 20 °C/s has been included in the KMC algorithm in order to get more realistic

⁵ Time between a constant n_{down} and n_{up} varies with PLD repetition rate f_{rep} .

⁶ Here, u.c. stands for unit cell.

results⁷.

SrTiO₃ and PbTiO₃ thin films were deposited by PLD in the COMAT system. The COMAT system is equipped with a COHERENT ArF-KrF laser (wavelength 248 nm) suitable for deposition of perovskite oxide thin films. A recently developed infrared laser system was utilized in order to apply a temperature modulation and/or fast heating/cooling sequence during growth. The infrared laser system contains a 120 W Coherent Quattro FAP laser for direct heating. The maximum temperature can be increased up to 1100 °C with a maximum ramp-rate⁸ of 20 °C/s. A typical spot of 1 cm was aligned on the backside of the sample plate. To obtain near black body absorption, the backside was roughened and oxidized. An infrared pyrometer (temperature accuracy ± 3 °C at 710 °C) was used to measure and control the temperature of the sample plate.

The SrTiO₃ substrates were prepared using a standard procedure to obtain TiO₂ terminated surfaces [19]. SrTiO₃ homoepitaxial films were deposited using a laser fluence = 1.3 J/cm², spotsize = 2.35 mm², oxygen pressure PO₂ = 0.1 mbar O₂ and repetition rate $f_{\text{rep}} = 0.5$ Hz (It is more easy to maintain n_{down} and n_{up} manually at $f_{\text{rep}} = 0.5$ Hz instead of $f_{\text{rep}} = 1$ Hz, where the latter has been used in the KMC simulations). PbTiO₃ was chosen as the material containing a volatile element, namely Pb. These heteroepitaxial films were deposited using a laser fluence = 2.0 J/cm², spotsize = 2.35 mm², $f_{\text{rep}} = 0.5$ Hz and PO₂ = 0.14 mbar O₂. SrRuO₃ has been deposited as buffer layer for inducing layer-by-layer growth of PbTiO₃ films. The deposition conditions of SrRuO₃ were similar to that of PbTiO₃.

In situ reflection high energy electron diffraction (RHEED) was used to monitor the step density S during growth as the RHEED specular intensity I_{RHEED} scales with S according to $I_{\text{RHEED}} \sim 1 - \frac{S}{S_{\text{max}}}$, see Eq. 2.5 [16]. Subsequently, *in situ* XPS was performed on an Omicron nanotechnology GmbH system using a Al $K\alpha$ x-ray source (XM1000) in a background pressure of 5×10^{-11} mbar. XPS analysis was used to study the atomic ratio. Data analysis was done using a 7 channel EA 125 electron analyzer in CAE mode. The effective peak area was determined by using a Gaussian fit after a Shirley background subtraction. *Ex situ* AFM topography images were recorded in Tapping Mode (TM) using a Bruker Dimension ICON AFM and a Bruker TESPA doped Si cantilever $f_0 = 320$ kHz. The AFM images were used in order to study the surface topography after PLD.

⁷ A temperature ramp-rate of 20 °C/s has been found for the laser heater used in the experiments.

⁸ Software infrared thermometer has been used for determination of the (maximum) laser heater ramp-rate.

6.5 Kinetic Monte Carlo simulations

Kinetic Monte Carlo (KMC) simulations⁹ have been conducted in order to study the effects of TM-PLD on the growth and step density S during PLD of perovskite oxides.

6.5.1 TM-PLD (instantaneously)

KMC simulation results after an instantaneous increase/decrease in temperature during TM-PLD are shown below.

Temperature sequence

KMC simulations are performed in order to verify whether the step density S could be strongly modulated by applying TM-PLD and which temperature sequence is required during TM-PLD. Fig. 6.2 shows the RHEED specular intensity during and surface topography images after the deposition of 10 ML's using TM-PLD. RHEED oscillations are observed for $T_{\text{down}} = 710^\circ\text{C}$, $T_{\text{up}} = 850^\circ\text{C}$, $n_{\text{down}} = 0$ and $n_{\text{up}} = 19$ (left panel). Therefore, the step density S is modulating during this TM-PLD sequence [18]. For this KMC simulation, the amplitude of the RHEED specular intensity oscillation $\approx 0.15 I/I_0$. The maximum I_{RHEED} decreases with the number of deposited ML's. The exponential decay of maximum I_{RHEED} becomes smaller and a smoother surface will be obtained when T_{down} is decreased. The terrace structure, small islands and vacancy islands are visible in the KMC surface topography after the deposition of 10 ML's. Different results are obtained when $n_{\text{down}} = 19$ and $n_{\text{up}} = 0$ (right panel). The RHEED specular intensity I_{RHEED} does not recover in the latter deposition pulses in a ML. From this observation, it becomes clear that the RHEED specular intensity I_{RHEED} keeps decreasing and S keeps increasing with almost every deposition pulse. The KMC surface topography image confirms that it results in 3D growth and the terrace structure is moreless disappeared after the deposition of 10 ML's.

RHEED specular intensity vs. n_{up}

Figs. 6.3 (a-d) show the KMC simulated RHEED specular intensities during PLD at constant temperatures of a) $T = 600^\circ\text{C}$ and $T = 850^\circ\text{C}$, and during TM-PLD deposition at $T_{\text{down}} = 600^\circ\text{C}$ and $T_{\text{up}} = 850^\circ\text{C}$ for different n_{up} , namely b) $n_{\text{up}} = 1$, c) $n_{\text{up}} = 10$ and d) $n_{\text{up}} = 19$. The RHEED specular intensity gradually decreases with every ML at both $T = 600^\circ\text{C}$ and $T = 850^\circ\text{C}$. An amplitude of $< 0.1 I/I_0$ has been found for the RHEED specular intensity oscillation of the

⁹ The basics of KMC simulations are explained in Ch. 2.

Fig. 6.2 KMC simulations of TM-PLD growth for different temperature sequences using $T_{\text{down}} = 710$ °C and $T_{\text{up}} = 850$ °C, a) $n_{\text{down}} = 0$ and $n_{\text{up}} = 19$, b) $n_{\text{down}} = 19$ and $n_{\text{up}} = 0$, c) RHEED specular intensity I/I_0 for $n_{\text{down}} = 0$ and $n_{\text{up}} = 19$, d) RHEED specular intensity I/I_0 for $n_{\text{down}} = 19$ and $n_{\text{up}} = 0$, e) KMC surface topography after the growth of 10 ML's for $n_{\text{down}} = 0$ and $n_{\text{up}} = 19$ and f) KMC surface topography after the growth of 10 ML's for $n_{\text{down}} = 19$ and $n_{\text{up}} = 0$.

KMC simulation at $T = 850$ °C, while hardly oscillations have been observed at $T = 600$ °C.

The RHEED specular intensity during TM-PLD varies with n_{up} . Varying n_{up} affects the shape of the RHEED specular intensity oscillations and its recovery of intensity after every ML. Selecting $n_{\text{up}} = 1$ still results in a similar shape of the RHEED specular intensity compared to deposition at $T = 850$ °C, see Fig. 6.2 a). Both simulations are performed for $T = 850$ °C over almost the entire ML. The amplitude of the oscillations is similar to the deposition at a constant $T = 850$ °C. A spike is observed during the first deposition pulse of the monolayer. The step density S is increased as adatoms are less mobile at a $T = 600$ °C.

Fig. 6.3 KMC simulation of RHEED specular intensity for different n_{up} at $T_{\text{down}} = 600$ °C, $T_{\text{up}} = 850$ °C, a) (I) at constant temperatures $T = 600$ °C and (II) at $T = 850$ °C, b) $n_{\text{up}} = 1$, c) $n_{\text{up}} = 10$, d) $n_{\text{up}} = 19$.

However, when $n_{\text{up}} = 10$ (see Fig. 6.3 c)) the shape and recovery of the RHEED specular intensity oscillations changes. The first half ML and the second half ML are grown at $T_{\text{down}} = 600$ °C and at $T_{\text{up}} = 850$ °C, respectively. RHEED oscillations are visible with an amplitude of $\approx 0.3 I/I_0$, which is larger than the $< 0.1 I/I_0$ found at $T = 850$ °C. The oscillations are asymmetric in shape and are furthermore indicative for a larger S at half ML compared to deposition at $T = 850$ °C. A recovery of the RHEED specular intensity is obtained starting from the moment $T = T_{\text{up}}$. After the deposition of every subsequent ML, the maximum I_{RHEED} decays as it is not completely recovered. The shape of the RHEED oscillations are similar to what has been obtained for pulsed laser interval deposition (PLID) KMC simulations [58].

Total recovery of the RHEED specular intensity has been observed when $n_{\text{up}} = 19$ and therefore no decay of the maximum I_{RHEED} is visible. From Fig. 6.3 d), it can be concluded that the RHEED specular intensity oscillations shape is different compared to $n_{\text{up}} = 10$. Between deposition pulses 11 and 19, the RHEED specular intensity decreases and therefore S is still increasing. The amplitude of the RHEED oscillations is $> 0.3 I/I_0$, a similar value which has been obtained for

Fig. 6.4 KMC simulated surface topography images during TM-PLD of pulse $n = 19$ and 20 of the tenth ML deposition with $n_{\text{up}} = 19$, $T_{\text{down}} = 600$ °C and $T_{\text{up}} = 800$ °C. Time t should be read from top to bottom followed by the number of deposition pulses n from left to right.

$n_{\text{up}} = 10$. Other simulations revealed that increasing T_{up} results in an increase of RHEED specular intensity recovery for KMC simulations, where no total recovery is obtained for a certain n_{up} .

Final growth stage ML

Fig. 6.4 shows the results of a KMC simulation using the following parameters: $f_{\text{rep}} = 0.2$ Hz, $\text{ML}(\#) = 10$, $T_{\text{down}} = 600$ °C, $T_{\text{up}} = 800$ °C and $n_{\text{up}} = 19$ (meaning $T = 800$ °C from pulse 20)¹⁰. KMC surface topography images were selected during deposition and relaxation of pulses 19 and 20, both in intervals of one second. Deposition of pulse number 20 ($n = 20$) occurs at $t = 0$ s. At this time, islands are visible on the terraces. From this moment, T_{down} is changed to $T_{\text{up}} = 800$ °C. When $t = 1$ s, the smallest islands disappeared as the diffusion

¹⁰ A repetition rate of $f_{\text{rep}} = 0.2$ Hz is chosen as there is more time between the deposition pulses in order to study relaxation.

coefficient of adatoms increases significantly. Adatoms diffuse and some become attached in vacancy islands. Others seem to become attached to other adatoms forming islands. Interlayer mass transport is visible in Fig. 6.4, when one follows the island and adatoms surrounded by the white circular marker in time t . After $t = 1$ s, a few adatoms diffuse to become attached to vacancy islands and/or islands. Most of the mass transport seems to happen from $0 < t \leq 1$.

6.5.2 TM-PLD ramp-rate

KMC simulation results after a more realistic ramp-rate temperature increase and decrease during TM-PLD are shown below.

Ramp-rate

Fig. 6.5 shows the results of a KMC simulation using the following parameters: $f_{\text{rep}} = 1$ Hz, $\text{ML}(\#) = 10$, $T_{\text{down}} = 600$ °C, $T_{\text{up}} = 710$ °C and $n_{\text{up}} = 13$. A ramp-rate of 20 °C/s was implemented and therefore it takes 5 - 6 pulses before the temperature increases from $T_{\text{down}} = 600$ °C to $T_{\text{up}} = 710$ °C. RHEED specular intensity oscillations are still clearly visible using the ramp-rate. In this specific simulation, the amplitude is $\approx 0.2 I/I_0$ of the RHEED specular intensity oscillations. The shape of the oscillations is different compared to instantaneously increase of temperature as the recovery of the RHEED specular intensity takes more time. The recovery is such that the TM-PLD RHEED specular intensity does not recover to the maximum RHEED specular intensity I_{RHEED} of the deposition at $T = 710$ °C. From the KMC surface topography image after TM-PLD, it becomes clear that islands have a high density and are smaller compared to the deposition at $T = 710$ °C. Therefore, most likely the surface contains a higher step density S .

RHEED specular intensity vs. n_{up}

The previous KMC simulation was repeated for different n_{up} . These results are presented in Fig. 6.5 as well. From these KMC simulation results, it can be seen that n_{up} has an influence on the RHEED specular intensity. Varying n_{up} moreless changes the "offset" of the RHEED specular intensity. When $n_{\text{up}} = 13$, the maximum I_{RHEED} is not recovered to the maximum I_{RHEED} at $T = 710$ °C, while for $n_{\text{up}} = 8$ the maximum I_{RHEED} does recover. As the "offset" of the RHEED specular intensity changes with n_{up} , it seems that a higher maximum S (minimum I_{RHEED}) can be obtained while having a lower maximum I_{RHEED} .

Fig. 6.5 KMC simulation of RHEED specular intensity and surface topography for (I) $T = 600\text{ }^{\circ}\text{C}$, (II) $T = 710\text{ }^{\circ}\text{C}$, (III) $n_{\text{up}} = 13$, $T_{\text{down}} = 600\text{ }^{\circ}\text{C}$ and $T_{\text{up}} = 710\text{ }^{\circ}\text{C}$, (IV) $n_{\text{up}} = 10$, $T_{\text{down}} = 600\text{ }^{\circ}\text{C}$ and $T_{\text{up}} = 710\text{ }^{\circ}\text{C}$ and (V) $n_{\text{up}} = 8$, $T_{\text{down}} = 600\text{ }^{\circ}\text{C}$ and $T_{\text{up}} = 710\text{ }^{\circ}\text{C}$.

6.6 Experimental results

Experiments have been conducted to study the influence of TM-PLD on the growth kinetics. Furthermore, experiments have been performed to measure the atomic ratio between Pb:Ti.

6.6.1 RHEED SrTiO₃ homoepitaxial growth

Fig. 6.6 presents the RHEED specular intensities obtained during SrTiO₃ homoepitaxial PLD growth experiments. SrTiO₃ films have been grown at constant temperatures of $T = 600$ °C (see Fig. 6.6 a) and $T = 710$ °C (see Fig. 6.6 b). In both experiments, RHEED specular intensity oscillations have been observed, where the maximum I_{RHEED} mutes with (almost) every deposited ML. Dashed (red) lines are included in Fig. 6.6 to indicate the average maximum RHEED specular intensity ($0.69I_0$) and the average minimum RHEED specular intensity ($0.36I_0$) of the TM-PLD film, where I_0 is I_{RHEED} before deposition. The maximum RHEED specular intensity is below $0.69I_0$ for all ML deposited at $T = 600$ °C. At $T = 710$ °C, only 4 ML are grown where the RHEED specular intensity recovers above $0.69I_0$. Both samples show a decay of the RHEED specular intensity due to roughening of the surface (increase of S) as discussed in Ch. 2. The minimum RHEED specular intensity decreases after $t \approx 500$ s below $0.36I_0$. From $t \approx 500$ s, the average RHEED specular intensity is below $0.36I_0$ for both $T = 600$ °C and $T = 710$ °C. An amplitude of $0.33I_0$ has been found for the TM-PLD sample, where (at $t = 1000$ s) $0.06I_0$ and $0.07I_0$ have been determined for $T = 600$ °C and $T = 710$ °C, respectively.

In Fig. 6.7, a zoom-in of the RHEED specular intensity is shown for the samples grown at $T = 710$ °C and $T_{\text{down}} = 600$ °C/ $T_{\text{up}} = 710$ °C ($n_{\text{down}} = 0$ and $n_{\text{up}} = 15 - 16$). The shape of the RHEED specular intensity oscillation of SrTiO₃ deposited at $T = 710$ °C is similar to what has been observed previously (see Fig. 3.2 a) of Ref. [18]). During TM-PLD, the shape of the RHEED oscillations is different compared to the shape of the RHEED oscillations recorded at $T = 710$ °C. After pulse n_{down} , the RHEED specular intensity drops rapidly as T and l_D decrease and therefore the step density S is higher compared to the step density at a constant temperature of $T = 710$ °C. The reverse is observed after n_{up} . Here, the RHEED specular intensity increases rapidly as T and l_D increases and the step density rapidly decreases as islands grow in lateral size.

Fig. 6.6 RHEED specular intensity and diffraction pattern (I) before and (II) after experimental SrTiO₃ homoepitaxial growth at $PO_2 = 0.1$ mbar O₂, a) $T = 600^\circ\text{C}$, b) $T = 710^\circ\text{C}$ and c) $T_{\text{down}} = 600^\circ\text{C}$, $T_{\text{up}} = 710^\circ\text{C}$, $n_{\text{down}} = 0$ and $n_{\text{up}} = 15 - 16$.

Fig. 6.7 Zoom-in RHEED specular intensity during experimental SrTiO₃ homoepitaxial growth at $PO_2 = 0.1$ mbar O₂, a) $T = 710^\circ\text{C}$, b) $T_{\text{down}} = 600^\circ\text{C}$, $T_{\text{up}} = 710^\circ\text{C}$, $n_{\text{down}} = 0$ and $n_{\text{up}} = 15 - 16$.

6.6.2 AFM SrTiO₃ homoepitaxial growth

Ex situ TM-AFM images have been taken after deposition of SrTiO₃ films with a thickness of 100 MLs¹¹. Fig. 6.8 shows the surface topography of SrTiO₃ surfaces after deposition at a) $T = 600$ °C, b) $T = 710$ °C and c) $T_{\text{down}} = 600$, $T_{\text{up}} = 710$ °C. A terrace like structure is visible for all surfaces after deposition of 100 MLs. RMS roughness values σ_{RMS} have been measured of $\sigma_{\text{RMS}} = 0.37$ nm ($T = 600$ °C), $\sigma_{\text{RMS}} = 0.18$ nm ($T = 710$ °C) and $\sigma_{\text{RMS}} = 0.19$ nm ($T_{\text{down}} = 600$ °C, $T_{\text{up}} = 710$ °C). SrTiO₃ substrate surfaces after an HF treatment and annealing procedure have RMS values ranging from 0.14 - 0.18 nm. Where the RMS values are quite similar for the surfaces in Figs. 6.8 b) and 6.8 c), the step-edges of the surfaces are clearly different. The step-edges are disordered for the surface grown in Fig. 6.8 b), while this is not the case in Fig. 6.8 c).

Fig. 6.8 *Ex situ* TM-AFM images taken after 100 ML's of SrTiO₃ homoepitaxial growth, a) $T = 600$ °C, b) $T = 710$ °C and c) $T_{\text{down}} = 600$ °C, $T_{\text{up}} = 710$ °C, $n_{\text{down}} = 0$ and $n_{\text{up}} = 15 - 16$.

6.6.3 PbTiO₃ growth

PbTiO₃ films are grown on TiO₂ terminated SrTiO₃ substrates and on 10 nm thick SrRuO₃ films deposited on TiO₂ terminated SrTiO₃ substrates. A multilayer growth mode has been obtained for PbTiO₃ films grown on TiO₂ terminated

¹¹ Growth rate has been determined from the RHEED specular intensity oscillations.

Fig. 6.9 (I) RHEED specular intensity during PbTiO₃ growth and *ex situ* TM-AFM images after growth of 10 nm PbTiO₃ films a) $T = 500^\circ\text{C}$, b) $T = 600^\circ\text{C}$ and c) $T_{\text{down}} = 500^\circ\text{C}$, $T_{\text{up}} = 600^\circ\text{C}$, $n_{\text{down}} = 0$ and $n_{\text{up}} = 8$ (growth rate = 16 pulses/ML). Temperature sequence TM-PLD is started from the moment RHEED oscillations were observed.

SrTiO₃ substrates, while PbTiO₃ grows layer-by-layer on SrRuO₃ up to $T = 550 - 600^\circ\text{C}$, 3D at $T = 600 - 700^\circ\text{C}$ and layer-by-layer at $T = 700^\circ\text{C}$ ¹². Fig. 6.9 shows the (I) RHEED specular intensity of PbTiO₃ films deposited at $T = 500^\circ\text{C}$, at $T = 600^\circ\text{C}$ and at $T_{\text{down}} = 500/T_{\text{up}} = 600^\circ\text{C}$, and (II) *ex situ* TM-AFM images recorded after PbTiO₃ deposition are presented.

¹² After PbTiO₃ deposition at $T = 700^\circ\text{C}$, a Pb:Ti ratio ≈ 0 has been found.

At $T = 500\text{ }^{\circ}\text{C}$ and $T_{\text{down}} = 500\text{ }^{\circ}\text{C}/T_{\text{up}} = 600\text{ }^{\circ}\text{C}$, the first 1 - 2 PbTiO₃ ML's grow(s) in a multilayer fashion, whereafter the growth continues in a 2D growth mode (based on RHEED specular intensity). No RHEED oscillations have been observed for the PbTiO₃ film growth at $T = 600\text{ }^{\circ}\text{C}$. From the RHEED pattern after growth, it is hardly distinguishable whether the growth was 2D or 3D. During TM-PLD in Fig. 6.9 c), the maximum amplitude of the RHEED oscillation is $0.4I_0$, which decreases to a constant amplitude of $0.1I_0$. At $T = 500\text{ }^{\circ}\text{C}$, the amplitude of the RHEED specular intensity increases to a constant amplitude of $0.1I_0$ after nine ML's. RMS values of $\sigma_{\text{RMS}} = 0.5\text{ nm}$, $\sigma_{\text{RMS}} = 0.9\text{ nm}$ and $\sigma_{\text{RMS}} = 0.9\text{ nm}$ have been extracted from AFM images for $T = 500\text{ }^{\circ}\text{C}$, $T = 600\text{ }^{\circ}\text{C}$ and $T_{\text{down}} = 500\text{ }^{\circ}\text{C}$, $T_{\text{up}} = 600\text{ }^{\circ}\text{C}$, respectively. The PbTiO₃ of films grown in Figs. 6.9 a) and 6.9 c) contain surfaces where coalescence of islands did occur. This does not seem to be the case for the PbTiO₃ surface grown at $T = 600\text{ }^{\circ}\text{C}$ as it has a fingerprint structure.

6.6.4 Sticking of Pb

The atomic ratio between Pb:Ti has been measured using XPS for PbTiO₃ films grown at different temperatures. The results are shown in Fig. 6.10. Eq. 6.4 has been used as fit based on an Arrhenius plot and the fit is represented by the (I) continuous (blue) line through the datapoints. Similar Pb:Ti ratio's have been found for PbTiO₃ deposition at $T = 450\text{ }^{\circ}\text{C}$, $T = 500\text{ }^{\circ}\text{C}$ and $T = 550\text{ }^{\circ}\text{C}$. It seems that the Pb:Ti ratio starts to decrease in between deposition temperatures of $T = 550 - 600\text{ }^{\circ}\text{C}$. A significant lower Pb:Ti ratio has been measured after depositing PbTiO₃ at $T = 650\text{ }^{\circ}\text{C}$. An $E_{\text{ads}} = 0.8 \pm 0.1\text{ eV}$ is determined based on the fit for deposition at (I) constant temperature¹³.

The (II) dashed line in Fig. 6.10 is an indicative fit for the TM-PLD samples. Datapoints are included representing $T_{\text{up}} = 600\text{ }^{\circ}\text{C}$ and $T_{\text{up}} = 650\text{ }^{\circ}\text{C}$, where $T_{\text{down}} = 500\text{ }^{\circ}\text{C}$. The samples have been grown such that temperature is decreased after maximum I_{RHEED} and the temperature is increased directly after minimum I_{RHEED} . Both samples show an increase in Pb:Ti ratio when one compares these with samples grown at $T = T_{\text{up}}$. An $E_{\text{ads}} = 1.6 \pm 0.1\text{ eV}$ is used to fit the datapoints¹⁴ of the (II) TM-PLD experiments.

¹³ Assumption has been made that the sticking coefficient $\kappa_{\text{stick}} = 1$ at $T = 450 - 550\text{ }^{\circ}\text{C}$.

¹⁴ Third datapoint used for the fit is the datapoint at $T = 500\text{ }^{\circ}\text{C}$.

Fig. 6.10 The Arrhenius plot (left panel) and atomic ratio Pb:Ti (right panel) for PbTiO_3 grown at different growth temperatures, (I) line - guide-to-the-eye fit for deposition at constant temperature and (II) dashed line expected fit for TM-PLD.

6.7 Discussion

In this section the KMC simulation and experimental results are discussed.

Summary of results

The results of KMC simulations and experiments described in this chapter indicate that:

- An increase in amplitude of RHEED specular intensity oscillations can be achieved during 2D SrTiO_3 homoepitaxial growth using TM-PLD predicted by KMC simulation and experimentally observed.
- An increase in amplitude of RHEED specular intensity oscillations can be obtained by depositing the first ML growth stage at lower T and the second ML growth stage at higher T .
- An instantaneous temperature increase results in an increase in amplitude of RHEED specular intensity oscillations (compared to a more realistic ramp-rate = 20°C/s).
- Including a ramp-rate (20°C/s) instead of an instantaneous temperature increase results in a decrease of the pulse, whereafter the temperature is increased in order to achieve a maximum recovery of RHEED specular intensity.

- The Pb:Ti ratio in PbTiO_3 starts to decrease in between $T = 550 - 600$ °C. An $E_{\text{ads}} = 0.8 \pm 0.1$ eV has been found for Pb. The Pb:Ti ratio can be increased by TM-PLD.

By introducing two temperatures, a ramp-rate and the number of pulses whereafter the temperature needs to increase and decrease again, the influence of temperature cycles during PLD can be studied using an adapted solid-on-solid model. The KMC simulation results show a qualitative agreement with experimental data obtained for SrTiO_3 homoepitaxial growth using $E_{\text{D}} = 2.2$ eV and $E_{\text{N}} = 0.27$ eV. A previous study used these values and a qualitative agreement between KMC simulation and experiment has been shown [58]. Many other studies proved this qualitative agreement for PLD growth of other perovskite oxides [18, 148]. It is unknown, how TM-PLD KMC simulation results will change using an different $E_{\text{N}} = 0.21 \pm 0.01$ eV determined from AFM experiments described in Ch. 5.

From Ch. 2 (Eq. 2.5), it is known that I_{RHEED} scales with the step density S . As the amplitude of I_{RHEED} oscillations will increase using the described sequence, it seems plausible that the difference between the minimum and maximum S will become larger using TM-PLD [18]. The larger difference in S is explained by the fact that S increases at lower T and thereafter the increase in T enhances the diffusion length l_{D} /interlayer mass transport of species at the second part of a ML. An increase in interlayer mass transport at the final part of a ML results in an stronger recovery of I_{RHEED} indicating a reduced S and smoother surface topography. A similar approach and explanation has been reported using flux modulation [44]. In the reversed sequence, the amplitude of I_{RHEED} are small and at the minimum I_{RHEED} a much lower S is obtained explained by the deposition at higher T and enhanced l_{D} .

The different results between using a (more realistic) ramp-rate or instantaneous increase/decrease in temperature is explained by the time it takes to increase l_{D} . An exponential scaling between the diffusion coefficient D_{S} and T has been reported, see Ch. 2 (Eq. 2.2) [148]. Using an instantaneous increase/decrease in temperature, most of the interlayer mass transport seem to occur within a single second, while it already takes five seconds to overcome a temperature difference of 100 °C ($T_{\text{up}} - T_{\text{down}}$) using a ramp-rate of 20 °C/s. In order to achieve the same diffusion length l_{D} in the last second in a ML deposition, the ramp-rate has to start at least five seconds before. An increase in amplitude of I_{RHEED} oscillations can be achieved by using a laser heater containing a ramp-rate ≥ 20 °C/s.

The formula describing the sticking of species fits the Pb:Ti atomic ratio measurements. Previously, fitting of the atomic ratio's Bi/Y and Bi/Ba have been performed in the same manner for YBiO_3 and BaBiO_3 , where Bi is the volatile

element [242]. The experiments reveal that directly growing PbTiO_3 films on TiO_2 terminated SrTiO_3 results in multilayer growth, while on SrRuO_3 it grows in a 2D fashion. Similar PLD growth behavior have been reported for BiFeO_3 , where Bi is volatile and the A cation in ABO_3 (Pb is A cation in PbTiO_3) [191]. During the growth of the first few ML's, no RHEED specular intensity oscillations are observed, where from the third ML RHEED oscillations appear. KMC simulations need to be repeated in order to know how TM-PLD influences the PbTiO_3 growth as a different value of E_D for PbTiO_3 is expected. Other perovskite oxides containing volatile species have been considered, such as SrRuO_3 (Ru is volatile) and BiFeO_3 . However, these materials show transitions in growth mode or prefer to grow 1D or in multilevel fashion (2D growth is preferred as RHEED oscillations can be used as an indication when the temperature needs to be increased/decreased) [8, 191].

Despite the fact that TM-PLD PbTiO_3 films show a higher Pb:Ti ratio compared to PbTiO_3 films grown at $T = T_{\text{up}}$, the direct relation between an increase in S and increase in κ_{stick} was not proven yet. For example, when a PbTiO_3 film is grown alternating T_{down} during odd ML deposition (ML = 1,3,5...etc grown at T_{down}) and T_{up} during even ML deposition (ML = 2,4,6...etc grown at T_{up}), does this result in a similar Pb:Ti atomic ratio? How does TM-PLD affect the crystallization and properties of PbTiO_3 films? Follow-up investigations, both simulations and experiments, are needed to answer these research questions.

6.8 Conclusions & outlook

The influence of TM-PLD on the step density during growth is explored in order to increase sticking of volatile species in perovskite oxides. KMC simulations and SrTiO_3 homoepitaxial growth experiments reveal that the amplitude of RHEED specular intensity oscillations can be increased using TM-PLD. Therefore, an increase in the difference between the minimum and maximum step density in a ML can be achieved compared to PLD at constant temperature. Atomic ratio measurements show that the Pb:Ti ratio in PbTiO_3 starts to decrease between $T = 550 - 600$ °C. Using TM-PLD, an increase in Pb:Ti ratio has been obtained when comparing it with samples grown at $T = T_{\text{up}} \geq 600$ °C. In that case, the Pb:Ti ratio is increased. Nevertheless, a relation between an increase in maximum step density and an increase sticking coefficient was not proven yet.

The following experiments are suggested to validate whether an increase in maximum step density causes an increase in sticking coefficient:

- A different Pb:Ti should be obtained when depositing a PbTiO_3 film at the same T_{down} and T_{up} , but using a different n_{down} and n_{up} .
- Pulsed laser interval deposition (PLID) instead of TM-PLD to show increase of PbTiO_3 sticking coefficient compared to deposition at constant temperature [44].

Besides that, the experimental RHEED specular intensity scales with the step density, it has a dependence on the crystalline state as well. This dependence makes it more complicated to draw conclusions regarding to KMC simulations. Direct step density observations with (real-time) *in situ* AFM can overcome the addressed issue. So far, *in situ* AFM has not been used as the heater described in Ch. 3 is not capable of heating and cooling rates used in these experiments. Moreover, the *in situ* AFM needs to be designed such that it operates more stable when the temperature of the instrument starts to change.

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Summary

Atomic force microscopy (AFM) belongs to the selection of scanning probe microscopes (SPM). Since its invention in 1986, AFM has been applied for studying surfaces under a variety of conditions. The principle of the microscope is based on the interaction force measured between AFM tip and sample surface. While raster-scanning the AFM tip over the sample surface, the interaction force (and therefore distance) between AFM tip and sample surface is kept constant by using a feedback loop (in constant force mode). By acquiring the (X, Y and Z) piezo positions, this data can be translated into a topographical image. Conventional AFM's have low sample throughput determined by the bandwidths (which are fairly low) of the AFM scanner, cantilever, detection system and electronics. However, in order to monitor the oxide pulsed laser deposition (PLD) growth kinetics, an increase in AFM bandwidth is required. Throughout this thesis, an AFM design, containing a high resonance frequency AFM scanner together with high bandwidth SPM electronics is demonstrated, with focus on growth monitoring during PLD of oxides. Moreover, perovskite oxide growth (related) studies are explored using *ex situ* AFM and reflection high-energy electron diffraction (RHEED).

The majority of this work is focused on the developed AFM. This AFM contains a flexure scanner, typically used in the field of high speed AFM, and high bandwidth SPM electronics. The AFM is capable of operating under conditions ranging from pressures 10^{-6} - 1 mbar O_2 at temperatures ranging from RT up to 700 °C. A proof of principle is shown by imaging of the growth of $BiFeO_3$ islands on a $SrTiO_3$ substrate under PLD conditions with (sub)nanometer height resolution. Furthermore, neck formation is limiting imaging of mixed terminated $SrTiO_3$ using a Si AFM tip. Now the AFM acquisition rate under oxide PLD conditions is limited by the large response time of the cantilever. The cantilever response time can be lowered by increasing both, the damping and resonance frequency of the cantilever. Moreover, an increase in bandwidth of the detection system is needed for quasi real-time growth observations.

In order to quasi real-time monitor the oxide growth kinetics, a tip-sample (side) approach method using a faster transfer stage has been demonstrated. This tip-sample approach method, reducing the tip-sample approach time, can be applied when deposition and growth are separated in time. Both transfer stage motion time and reposition repeatability are important for monitoring PLD growth of islands using AFM. The experimental results reveal that the transfer stage motion time between the PLD and AFM position can be reduced from several seconds to (sub)seconds with a reposition repeatability error of ± 60 nm. Moreover, no signatures of loss in AFM spatial resolution are found even after more than hundred repetitive side approaches.

Diagnostic tools, such as RHEED can be utilized to extract the activation energy barrier for diffusion however, it does not allow extracting the nearest neighbor interaction energy E_N . The last is an important parameter for describing perovskite oxide thin film growth by kinetic Monte Carlo (KMC) simulations. The E_N values reported in literature however, show a wide spread. In this thesis, perovskite oxide vicinal surfaces in thermodynamic equilibrium are analyzed, analogue to earlier introduced analysis performed on STM images of semiconductor surfaces, after imaging *ex situ* AFM topography images. From perovskite oxide surfaces in thermodynamic equilibrium, the nearest neighbor interaction energy is extracted from AFM image analysis, which is impossible to extract with reciprocal diagnostic tools. The nearest neighbor interaction energy for $\text{SrTiO}_3(001)$ and $\text{DyScO}_3(110)$ is determined. This value is consistent with reported literature values. Most likely, this value is found to be constant for perovskite oxides due to the similar local oxygen coordination.

Furthermore, a study has been presented investigating growth of perovskite oxides and sticking of volatile species. Both KMC simulations and experiments of SrTiO_3 homoepitaxial growth reveal that the amplitude of RHEED specular intensity oscillations can be increased using temperature modulation pulsed laser deposition (TM-PLD). The increase of RHEED specular intensity oscillations is explained by the fact that the step density modulation during 2D growth is increased using a TM-PLD sequence, where approximately the first half of the monolayer (ML) is grown at lower T , while the second half of the ML is grown at higher T . An increased Pb:Ti ratio is found for PbTiO_3 films grown using TM-PLD compared to deposition at constant temperature. TM-PLD can be utilized most likely to enhance sticking of volatile elements during PLD growth. More research is needed in order to relate the increased Pb:Ti ratio to the increased step density during growth.

In the case of PLD, the development of an AFM suitable for monitoring growth by the use of e.g. the side approach together with (relevant) AFM growth studies, demonstrating the need for quasi real-time measurement of local perovskite oxide growth are presented. A high resonance frequency AFM scanner and high bandwidth SPM electronics are developed. Some efforts are recommended increasing the bandwidth of both the cantilever and (optical) detection system in order to increase the maximum achievable AFM acquisition rate under oxide PLD conditions. This is required for enabling AFM monitoring of growing perovskite oxide islands during PLD. Moreover, increasing both the AFM feedback bandwidth and transfer stage speed will result in a faster tip-sample approach time using the side approach method.

Samenvatting

Atomic force microscopy (AFM) behoort tot de groep van scanning probe microscopes (SPM). Sinds de uitvinding van AFM in 1986 is de microscoop techniek toegepast om oppervlakken te bestuderen onder diverse omstandigheden. Het werkingsprincipe is gebaseerd op een wisselwerkingskracht tussen de AFM naald en monsteroppervlak. Tijdens het rasterscannen van de AFM naald over het monsteroppervlak wordt de wisselwerkingskracht constant gehouden door gebruik te maken van een terugkoppelingslus. Doordat de X, Y, Z posities worden opgenomen kan een topografisch plaatje worden gereconstrueerd. Gebruikelijke AFM's hebben een lage data verwerkingscapaciteit die op zijn beurt door de bandbreedte van de AFM scankop, bladveer, detectiesysteem en elektronica wordt bepaald. Echter, een toename van AFM bandbreedte is nodig om in staat te zijn om de groei kinetische processen tijdens gepulste laser depositie (PLD) te volgen. In dit proefschrift, een AFM ontwerp, bestaande uit een hoge resonantie frequentie AFM scankop en elektronica, is gedemonstreerd met doel de groei van oxidische materialen met behulp van PLD te volgen. Daarnaast zijn perovskiet oxidische gerelateerde groei studies beschreven die zijn onderzocht door gebruik te maken van technieken zoals *ex situ* AFM en reflectie hoge energie electronendiffractie (RHEED).

Het grootste deel van het werk is gericht op de ontwikkelde AFM. Deze AFM bevat een hoge bandbreedte AFM elektronica en een flexure scankop die typisch gebruikt wordt in hoge snelheids AFM toepassingen. De microscoop is in staat om afbeeldingen te maken van oxidische oppervlakken op temperaturen van kamer temperatuur tot 700 °C in drukken variërend van 10^{-6} tot 1 mbar O_2 . Dit principe is bewezen door (sub) nanometer resolutie afbeeldingen op te nemen van $BiFeO_3$ eilanden op een $SrTiO_3(001)$ monster in PLD condities. Daarnaast is geobserveerd dat nek formatie de oorzaak is dat dubbel getermineerde oppervlakken niet kunnen worden afgebeeld wanneer gebruik wordt gemaakt van een Si AFM naald. Op dit moment is de AFM snelheid in oxidische PLD condities beperkt door de lange reactietijd van de bladveer. De bladveer reactietijd kan worden verkort door zowel de demping en resonantie frequentie te verhogen. Daarnaast

zou de detectie bandbreedte moeten worden verhoogd om quasi real-time groei observaties te bewerkstelligen.

Een laterale naald-monster naderingsmethode is gedemonstreerd door gebruik te maken van een snellere verplaatsings mechanisme om oxidische groei kinetische processen te volgen. Deze naald-monster naderingsmethode, met een veel kortere naderingstijd, kan toegepast worden wanneer depositie en groei zijn gescheiden in tijd. Zowel de monster verplaatsingstijd als repositioneringsherhaalbaarheid zijn belangrijk voor het volgen van groeiende PLD gedeponeerde eilanden met AFM. De experimentele resultaten onthullen dat de naderingstijd kan worden verkort van enkele seconden tot subseconden met een repositioneringsherhaalbaarheid van ± 60 nm. Verder zijn er geen sporen gevonden van een verlies in AFM resolutie zelfs niet na meer dan honderd herhaalbare laterale naderingen.

Diagnostische technieken zoals RHEED kunnen worden gebruikt voor het bepalen van de activatie barriere voor diffusie, maar niet voor het bepalen van de naaste nabuur energie E_N . De laatste is een belangrijke parameter voor het beschrijven van perovskiet oxidische dunne film groei met behulp van kinetische Monte Carlo (KMC) simulaties. Echter, de E_N waardes beschreven in literatuur vertonen een grote spreiding. In dit proefschrift zijn perovskiet oxidische oppervlakken in thermodynamisch evenwicht geanalyseerd vergelijkbaar met een eerder geïntroduceerde analyse toegepast op halfgeleider oppervlakken, nadat oppervlakte afbeeldingen zijn gemaakt met *ex situ* AFM. Het bepalen van E_N is onmogelijk met reciproke technieken zoals RHEED. De E_N waardes zijn bepaald voor zowel het $\text{SrTiO}_3(001)$ als $\text{DyScO}_3(110)$ oppervlak. De gevonden waardes zijn vrijwel vergelijkbaar met de waardes beschreven in literatuur. Zeer waarschijnlijk is deze waarde constant voor alle perovskiet oxidische materialen met dezelfde vergelijkbare oxidische coördinatie aan het oppervlak.

Daarnaast wordt er een studie gepresenteerd waarin de groei en sticking van (vluchtige) perovskiet oxidische materialen zijn bestudeerd. Zowel KMC simulaties als SrTiO_3 homoepitaxiale groei experimenten onthullen dat de amplitude van RHEED intensiteits oscillaties kunnen worden vergroot door gebruik te maken van temperatuur gemoduleerde gepulste laser depositie (TM-PLD). De toename in amplitude van de RHEED intensiteits oscillaties is verklaard door het feit dat de stap dichtheid modulatie is toegenomen tijdens 2D groei en een TM-PLD volgorde waarbij de eerste helft van de monolaag is gegroeid op een lagere temperatuur en de tweede helft op hogere temperatuur. Een toegenomen Pb:Ti verhouding is gevonden voor PbTiO_3 dunne lagen die gegroeid zijn met TM-PLD wanneer ze vergeleken worden met depositie op constante temperatuur. TM-PLD kan hoogstwaarschijnlijk worden gebruikt om de sticking van vluchtige elementen in

perovskiet oxidische PLD groei te verhogen. Meer onderzoek is nodig om te bewijzen dat de toegenomen Pb:Ti verhouding is gerelateerd aan de toegenomen stap dichtheid tijdens de groei.

De ontwikkeling van een AFM geschikt voor de volgen van groei met behulp van de laterale naald-monster naderingsmethode en AFM gerelateerde groei studies in het geval van PLD zijn gepresenteerd. Dit werk demonstreert de noodzaak om quasi real-time metingen te kunnen doen aan lokale perovskiet oxidische groei. Zowel een hoge resonantie frequentie scankop als hoge bandbreedte AFM elektronica zijn ontwikkeld in dit werk. Er worden werkzaamheden aangeraden om de maximale haalbare AFM acquisitie snelheid in PLD condities te verhogen door zowel de bandbreedte van de bladveer als detectiesysteem te verhogen. Dit is noodzakelijk om de lokale groei van perovskiet oxidische eilanden te kunnen volgen met AFM. Daarnaast zou de laterale naald-monster naderingsmethode snelheid kunnen worden verhoogd door de AFM terugkoppelingslus bandbreedte en monster verplaatsingssnelheid te verhogen.

Publications

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Curriculum Vitae

Werner Wessels was born in Markelo on December 4, in 1986. He started to study Applied Physics at the Saxion Hogeschool Enschede in 2005. In 2009, he received a B. Eng. degree in Applied Physics. Thereafter, he continued to study Applied Physics at the University of Twente. In 2012, he received a M.Sc. degree in Applied Physics from the University of Twente Enschede, The Netherlands. After obtaining a M.Sc. degree, Werner accepted a Ph.D. position in the Inorganic Materials Science group at the University of Twente under supervision of Prof. dr. ing. Guus Rijnders and Prof. dr. ir. Gertjan Koster. Werner has continued his career as R&D engineer at Twentsche Kabelfabriek in Lochem, The Netherlands.

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