Artificially layered oxides by pulsed laser deposition

Cover: Compilation of a high resolution transmission electron micrograph of an artificially layered (Ba,Sr)CuO₂ structure (top) and a drawing of the façade of the laboratory for materials research and thin film technology at the University of Twente, which has been in the view of the author looking outside while sitting behind his PC writing this thesis (bottom).

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ARTIFICIALLY LAYERED OXIDES BY PULSED LASER DEPOSITION

PROEFSCHRIFT

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Introduction

1.1 Motivation

With the advancement of electronics, miniaturization of circuits etc., the requirements for the materials to use become more stringent. Usually, the combination of properties that are needed for a certain design cannot be found in one existing material. Therefore, there is a strong demand for new materials. The more people start to understand the relation between the microstructure of materials and the macroscopic properties, e.g., electronic, magnetic, optical, mechanical, etc. properties, the more there is a desire for atomic engineering, i.e., intervention on the atomic level in a structure to obtain new materials with pre-designed properties¹. Furthermore, manipulating the microscopic structure in a systematic way can lead to a better understanding of the relation mentioned above.

For inorganic crystalline materials, so-called bulk methods have always been very successful to find new compounds, e.g., high temperature superconductors (the T_c record holder material, $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ with a T_c of $133K^2$, has been prepared in bulk). Depending on the stochiometry, temperature and pressure, a certain crystal structure will be thermodynamically stable, and if one controls the kinetics, i.e., choosing the right conditions to stabilize the structure at room temperature, it is possible to synthesize new materials. However, the samples that are prepared this way contain often a lot of phases from which the interesting one is hard to isolate. Also, the analysis of the properties is hampered by this.

An alternative way of preparing new materials became an option when thin film deposition techniques reached the level of atomic precision. Especially

after the development of molecular beam epitaxy (MBE), where growth of thin films proceeds in an atomic layer-by-layer growth mode and in particular Atomic Layer-by-Layer MBE (ALL-MBE) with the possibility to monitor growth with reflection high energy electron diffraction (RHEED). For metals and (III,V)-compounds the many efforts therein have lead to interesting structures with new properties. For example, giant magnetoresistance has been observed in Fe/Cr superlattices³. An example of an ALL-MBE deposited oxide is (La,Ca)MnO₃⁴, which displays colossal magneto resistance.

Examples of other thin film techniques, which have been used to fabricate superlattice structures are sputter deposition (e.g., Bi-2223^{i,5}) and Pulsed Laser Deposition (PLD, e.g., infinite layer structure⁶). These techniques are very suitable to be used at relatively high gas pressure, necessary to fabricate, for instance oxide materials where oxygen is needed to form a stable crystalline film. In addition, many oxide materials have a layered structure, e.g., the perovskite structure, and there are many examples of artificially layered oxide films. The disadvantage of the high oxygen pressure is that in situ RHEED growth monitoring is hampered. To overcome this problem, laser-MBE has been used as an alternative to PLD, where a stronger oxidizing gas (e.g., O₃ or NO₂) is used, allowing for deposition at lower pressures (e.g., $(BaAuO_x)(BaCuO_y)(CaCuO_2)_2^7$, $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}^8$, $(Sr,Ba)TiO_3^9).$

An advantage of the use of thin film techniques to fabricate new materials is the stabilizing effect of the substrate crystal. If properly chosen to fit the expected thin film crystal structure and, in addition, well prepared with respect to the surface quality, many crystal structures are shown to be stable. These only exist in thin film form or normally require extreme synthesis conditions. Furthermore, the structures that are formed, are highly kinetically stabilized because constituents are supplied successively. This allows one to synthesize extremely rare structures which are metastable (e.g., Bi-1278¹⁰). The accompanying macroscopic properties are expected to be correspondingly rare. Furthermore, a systematic study of the effect of structural deviations on these properties become available.

In order to be able to create artificially layered structures, a layer-by-layer growth mode is necessary. First, because the desired crystal structure will result from successive deposition of atomic layers or molecular blocks of different materials. Second, the rate control during deposition takes place through recording of RHEED intensity oscillations, present in case of two dimensional nucleation. These only provide the actual deposition rate in the case of true layer-by-layer growth, a growth mode which cannot taken for granted. Usually, damped intensity oscillations are observed, indicating roughening of the surface during deposition. Since the deposition conditions optimal for layer-by-layer growth are usually not free to choose, i.e., regarding

ⁱ Stands for Bi₂Ba₂Ca₂Cu₃O_y.

the phase stability of most complex oxide materials, other means have to be applied.

1.2 Outline

Here, we demonstrate the possibility to fabricate artificially layered structures using the standard PLD in combination with in situ RHEED, under conditions typically used for deposition of oxide thin films. The thesis is subdivided in four chapters, in which the most important hurdles to be taken to arrive at this goal are treated. Each chapter finishes with a concluding section.

In chapter 2 the techniques PLD and RHEED and their basic principles are discussed. The high pressure RHEED system, which we developed in order to overcome the problem of scattering of electrons in the relatively high background gas pressure, is described in this chapter. The chapter includes also ex situ characterization of the as-deposited films with various techniques.

In chapter 3, a thorough study of the substrate material, i.e., $SrTiO_3$, and it's surface treatment is presented. Because of the stringent requirements for the substrate surface in order to achieve atomically controlled thin film growth, a special treatment is developed for $SrTiO_3$. The results obtained here are expected to be valid for ABO_3 (or perovskite) materials in general, encompassing many compounds which are used for their crystal surface properties.

Chapter 4 deals with the detailed study of homoepitaxy of $SrTiO_3$. The parameters important for layer-by-layer growth, a prerequisite for artificial layering of thin films, as well as the implications of the typical pulsed way of deposition are discussed. Based on the results of this study, a method called interval deposition is presented to impose a layer-by-layer growth mode, despite unfavorable deposition conditions for this growth mode. The validity of this method is proven both experimentally and by computer simulations.

Finally, in chapter 5 we describe how the interval deposition method is used to fabricate artificial layered structures in the $(Ba,Sr,Ca)CuO_2$ system. Unitcell layers of $BaCuO_2$, $SrCuO_2$ and $CaCuO_2$ are sequentially deposited applying various deposition schemes, using a fully automated process. Films with different compositions are compared in terms of structure using X-ray Diffraction (XRD) and High Resolution Transmission Electron Microscopy (HREM) and of their conducting properties.

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Technology and analysis

2.1 Introduction

Pulsed Laser Deposition (PLD) has become an important technique to fabricate novel materials. Starting in the mid-sixties¹, when first attempts to produce high quality thin films showed the promise of this technique, it has taken until the discovery of high-T_c superconductors that PLD became widespread. Here, one has benefited from the main advantages of PLD, the relative easy stoichiometric transfer of material from the target to the substrate and an almost free choice of (relatively high) background pressure. For instance, during the deposition of oxides usually an oxygen background pressure up to 1 mbar is used.

Reflection High-Energy Electron Diffraction (RHEED) was limited to low background pressures only until recently. High pressure RHEED, which makes it possible to in situ monitor the surface structure during deposition of oxides at higher pressures, opened new possibilities². Besides observed intensity oscillations due to layer by layer growth, enabling accurate growth rate control, it became clear that intensity relaxation observed due to the typical pulsed way of deposition leads to a wealth of information about growth parameters³.

Here, PLD in combination with high pressure RHEED is used to fabricate artificial superlattices of perovskite materials. In this chapter the PLD system equipped with RHEED will be described. Furthermore, we will discuss some of the basics of both PLD as well as RHEED. Finally, thin film analysis with Atomic Force Microscopy (AFM), X-ray Diffraction (XRD) and High Resolution Transmission Electron Microscopy (HREM) is shortly addressed.

2.2 Pulsed Laser Deposition

2.2.1 Basic principles

Pulsed Laser Deposition refers to the thin film deposition technique based on evaporation of material with a laserⁱ. Usually an excimer or Nd-YAG laser, producing an intense pulsed (repetition rate 0-100 Hz) laser beam in the UV range, is used. Typical wavelengths are 193 nm for ArF, 248 nm for KrF and 308 nm for XeCl excimer lasers and 355 nm for Nd:YAGⁱⁱ⁴.

Important parameters for the deposition process and film properties are given in Table 2.1. Although for every material there exists a set of optimal parameters, in practice it is very hard to find this optimum since they cannot be adjusted independently. Many parameters have been investigated for $YBa_2Cu_3O_7$ thin film deposition and the conclusions with respect to, among other things⁵, laser fluence^{6,7}, spot size⁸, are expected to be applicable more generally. With our system equipped with RHEED, we are so to speak at the 'receiving end' of the PLD process and it is therefore mainly the deposition conditions (see Table 2.1) and the way of deposition (see chapter 4) that we



Figure 2.1: A schematic view of the deposition chamber, including the electron source assembly

 $^{^{\}rm i}$ The term laser ablation, more generally referring to the ablation of material with an intense laser beam, is also used frequently

ⁱⁱ 3rd harmonic.

parameter:	typical values:				
	SrTiO ₃	(Ba,Ca,Sr)CuO2	SrO	TiO ₂	
deposition conditions:					
gas pressure (Pa) ⁱⁱⁱ	3-30	3-30	3	3	
gas composition	O2	O_2	O_2	O_2	
temperature (°C) ^{iv}	650-850	500-650	600-850	700-850	
spot size (mm ²)	0.5-3				
spot shape	rectangular				
target composition and type	single Xtal	sintered pellet	single Xtal	single Xtal	
laser fluency on target (J/cm ²)	1.3	1.5-4.0	2.0	1.3	

Table 2.1: Typical parameters used in the experiments described here

have investigated more extensively. The other parameters have been chosen to expect a particle supply at the substrate surface which is homogeneous, stoichiometric (the stoichiometry being determined by the target material) and constant in time (per laser pulse) and space⁵.

Finally, the expected density of the plasma plume and the energy of the particles at the substrate surface as a function of the gas pressure are given more detailed attention. In turns out that these characteristics of PLD greatly affect the growth of thin films.

2.2.2 Deposition conditions

Besides the deposition conditions, there are three important characteristics of PLD that distinguishes it from other thin film techniques: 1) the relative high energies of particles arriving at the substrate surface, 2) the relatively high deposition rates which can be achieved and 3) pulsed deposition. The expected implication on thin film growth are discussed here and in the case of homoepitaxy of $SrTiO_3$, a case study for PLD in combination with high pressure RHEED, see chapter 4.

1) The species in the plasma plume can be divided into neutral and charged species, of which the latter have the highest kinetic energies (up to 250 eV). However, a very strong interaction of the ablated species with the ambient gas molecules has been observed⁹. Most of the energy is dispersed in a background gas through collisions with the cold gas molecules. For example, measurement of the positive ion flux as a function of pressure and distance¹⁰ revealed an exponential attenuation (for pressures between 7 and 40 Pa). To evaluate the average energy supplied by the particle flux as a function of the forward velocity of the incoming particles in a gas relative to vacuum one can use the following expression¹¹:

ⁱⁱⁱ measured with a baratron capacitive pressure gauge

^{iv} measured inside the heater block with a K-type thermocouple

$$\frac{j_{E,g}}{j_{E,v}} = \frac{n_g}{n_v} \left(\frac{v_g}{v_v}\right)^3 \tag{2.1}$$

where j_E , n, are the rate of energy supply and the particle flux, respectively, and v_g and v_ν are the forward velocities of particles in the gas (g) and in vacuum (v). From (2.1) it is expected that growth behavior is strongly dependent on the velocity of incoming particles, determined by the gas pressure and the substrate-to-target distance. The theoretical description of the velocity distribution is complicated due to the fact that the plume is usually composed of many species, from single atoms and ions to clusters and nanoparticles¹². Experimentally, different probes detect different species. Several models can be used to predict the velocity of an expanding high pressure vapor as a function of the distance and/or pressure. First, Geohegan et al. found that for the lower background pressures initially the propagation of the leading edge of the plasma can be described by the 'drag force' model, whereas for higher background pressures and longer distances the 'shock wave model' is better applicable¹³. Another approach proposed by Strikovsky et al. is based on the assumption that initially the dense particle plume act as a piston moving through the background gas and thereby losing kinetic energy¹⁴. From these models it is clear that the velocity of particles arriving at the substrate is a function of the gas pressure and, therefore, we expect a strong influence of the pressure on the growth behavior. For $YBa_2Cu_3O_7$ the optimal thin film growth parameter settings have been associated with the optimal particle velocity¹⁵, however this was based solely on the superconducting properties of the films. Subsequently, films with high critical temperatures have been obtained far from these 'optimal' settings¹⁶. In chapter 4, we investigate the relation between the pressure and the kinetics of the deposited material during homoepitaxy on SrTiO₃.

The expected influence of the particle energy on the growth of thin films is mainly through the absorption/desorption¹¹ and diffusivity of the particles on the surface^{17,18}. Moreover, high-energy particles have been shown to cause stress¹⁹ in the film and in the case of relatively high pressures, the ambient gas acts as a high-velocity particle filter.

2) We have to distinguish between the deposition rate during a laser pulse and the average rate. Typical values we observe for the average deposition rate are 0.1-0.01 unit-cell layers (uc) per laser pulse, or in case of a repetition rate of 1 Hz and ~0.16 nm² per unit-cell (the perovskite materials we have used have an in-plane lattice constant of about 0.4 nm), ~10¹³-10¹⁴ uc/cm²s. Since the actual deposition takes place when the plume is "on", of the order of 1 ms^{20,21}, the rates during one laser pulse is of the order of $10^{16}-10^{17}$ uc/cm²s. The latter is orders of magnitude higher compared with, for example, off-axis rf sputtering deposition, where typical rates are 100 nm per hour (in case of YBa₂Cu₃O₇) or 10^{-2} unit-cell layers per second, i.e., 10^{13} uc/cm²s. On average, the number of

species arriving during one laser pulse per unit area and unit time is a factor of 5-10 higher than the estimates given above.

Given the rate per pulse, one can easily vary the average rate by using different laser repetition rates (typically 0-100 Hz).

3) The high deposition rate during a laser pulse is followed by a much longer period when no deposition takes place at all. This causes the supersaturation, which is given by²²:

$$\sigma = \frac{\Delta\mu}{kT} = \ln\frac{P}{P_0} = \ln\frac{R}{R_0}$$
(2.2)

where $\Delta\mu$ is the difference in chemical potential for different aggregations, ranging from very high values during the laser pulse to zero in-between the pulses, P and P₀ are the vapor pressure during deposition and at the equilibrium, respectively, and R and R₀ are the corresponding deposition rates. Given the deposit and its interaction with the substrate material (i.e., the interface surface free energy and the stress induced by misfit), the supersaturation determines the mode of nucleation of the arriving particles²². At a very high super saturation attained during a laser pulse, the critical nucleus size is expected to be extremely small, i.e., of the order of one unit-cell. For circularly shaped two-dimensional islands the critical radius r^{*} is given by:

$$r^* = \frac{\kappa s_c}{\Delta u} \tag{2.3}$$

where κ is the edge energy and s_c the occupied surface area of a single unit^v. In contrast, these critical nuclei become unstable during the non deposition period and through recrystallization, which might be viewed as a form of Ostwald ripening²³, larger islands are formed. The theoretical description of nucleation and island formation through diffusion, which is a highly non-stationary process in the case of PLD, is very complicated. However, as we will see below, experimentally one can determine the characteristic times involved using a surface-probing technique like RHEED, during deposition. With this knowledge, it is possible to exploit the typical pulsed way of deposition and the high deposition rates (see chapter 4 of this thesis).

Besides the three characteristics mentioned above, another effect in the case of an oxygen environment is the dependence of the total amount of oxidized species arriving at the substrate surface on the oxygen pressure. Especially for copper, which has a relatively high oxidation threshold, one might expect a significant part which is not fully oxidized. This can have implications for, e.g., the phase which will be formed²⁴. However, under the conditions used here we expect a high fraction of the ablated species²⁵ to be oxidized.

v in general one atom; here it represents one unit-cell

In addition, the combination of temperature and oxygen pressure, and the stabilizing effect of the substrate material, eventually determine the phase of the film material. However, since these parameters also determine the kinetics of the ablated material on the substrate surface, often a compromise between phase stability and optimal morphology has to be made. Sometimes the formation of a phase is kinetically determined, e.g., in the case of a-axis $YBa_2Cu_3O_7^{26}$. In chapter 4 we discuss the possibility to separate kinetically favorable conditions from the phase stability conditions.

2.3 Reflection High Energy Electron Diffraction

2.3.1 Basic principles of RHEED

In a typical RHEED system, a high energy electron beam (10-50 keV) arrives at a surface under a grazing incident angle (0.1-5°), see also Fig. 2.2: a). At these energies the electrons can penetrate any material for several hundreds of nano metres. However, due to a grazing angle of incidence, the electrons only interact with the topmost layer of atoms (1-2 nm) at the surface, which makes the technique very surface sensitive^{vi}. The scattered electrons collected on a phosphorus screen form a diffraction pattern characteristic for the crystal structure of the surface and also contain information concerning the morphology of the surface.

Examples of other surface sensitive techniques, which are used to probe the crystal structure and morphology, are X-ray diffraction (see, for example, for a discussion of disadvantages and advantages of different diffraction techniques Yang²⁷) and Scanning Probe Microscopy (SPM, which includes AFM, see also section 2.5.2 of this chapter and Scanning Tunnelling Microscopy (STM)). The choice for RHEED is based on, both, the accessibility of the sample during a PLD experiment (particle plume perpendicular to the surface and electron beam from the side) and the possibility to use it in a relatively high pressure environment, see paragraph 2.4.

The main reason why RHEED is popular in combination with high vacuum deposition techniques, is the observation of intensity oscillations of the specular intensity during deposition²⁸. Intuitively, intensity oscillations can be understood by considering a layer-by-layer growth front. Material deposited on an initially flat surface leads to roughening and a decrease in intensity, whereas upon completion of a crystal layer the surface becomes smoother again accompanied with a rise in intensity, i.e., periodic island nucleation, growth and coalescence. Accordingly, RHEED can be used as a thickness monitor, since ideally the oscillation period corresponds to the deposition of one crystal layer.

 v^i In contrast, Low Energy Electron Diffraction (LEED), is surface sensitive due to the low penetration depth of low energy electrons (100-500 eV).

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Figure 2.2: Typical set up for a RHEED experiment in a) real space and b) reciprocal space.

2.3.2 Scattering of electrons by a solid

Electrons interact with the electrostatic potential $V(\bar{r})$ of a solid. To describe the scattering processes, in particular the scattering of a grazing incidence electron beam as in RHEED, one has to distinguish between electrons that lose energy after scattering (inelastic scattering) and electrons that retain their energy (elastic scattering). Examples of features in a RHEED pattern which are caused by inelastically scattered electrons are Kikuchi patterns originating from electrons that have lost some energy while channeling through the crystal; examples are indicated with arrows in Fig. 2.3 a), b). The main part of elastic electrons scatters at the outermost atomic layer²⁹, i.e., it is the most surface sensitive and the most interesting for a surface scientist. However, inelastic electrons are often indistinguishable from the elastic ones and contribute significantly to the total detected intensity. Many calculations are based on only elastically scattered electrons. If one then assumes weak scattering, i.e., that the scattering cross section of individual scatterers (atoms) is low (the higher the energy of the incoming electrons, the lower the cross section³⁰), kinematic theory or the first Born approximation is applicable. The incident and scattered electrons are treated as plane waves,

$$I_0 \exp(i\vec{k}_0 \cdot \vec{r}) \tag{2.4}$$

with $\vec{k}_0 = (\vec{k}_{//}, \vec{k}_z)$ the wave vector. The amplitude of the scattered wave for a certain direction \vec{k}_s ($|\vec{k}_0| = |\vec{k}_s| = 2\pi\lambda$, λ is the wavelength of the electrons) is then given by integrating the Fourier components of V(\vec{r}) over the volume of the sample,

$$F(\bar{k}) = \int_{-\infty}^{\infty} V(\bar{r}) e^{i(\bar{k}\cdot\bar{r})} dr$$
(2.5)

the intensity is proportional to

$$F^*(\vec{k})F(\vec{k}) \tag{2.6}$$

where $\bar{k} = \bar{k}_s - \bar{k}_0$ is the scattering vector or momentum transfer vector. In the first Born approximation it is possible to replace the potential by the electron density²⁹. The problem to be solved is then analogous to X-ray diffraction, the electron density can be thought of as being concentrated in points located at the atomic positions in a solid which act a point scatterers. The scattering power of each atom is given by the atomic scattering factor or form factor, see for example^{29,30}, and is independent of momentum transfer in case of a point scatterer.

Summation over all the atoms in the sample multiplied by the form factor gives the amplitude of the scattered wave and turns out to be non-zero at distinct values of \bar{k} , i.e., the reciprocal lattice, when the sample is an infinitely large crystal build from regularly spaced atoms. Usually the Ewald sphere construction, a sphere with radius $2\pi/\lambda$ (elastic scattering) centered on the tip of the wave vector in the reciprocal space of the incoming beam, is used to identify the diffraction angles for a specific geometry and reciprocal lattice. In Fig. 2.2: b) an example of this construction is shown for a singular (i.e., perfect two-dimensional lattice of point scatterers) surface in case of RHEED. The reciprocal lattice of such a surface is a set of parallel, regularly spaced, infinitely thin rods perpendicular to the surface which intersect the Ewald sphere at points lying on concentric circles, called the Laue circles. In Fig. 2.3 b) the 0th-order Laue circle, i.e., intersections of the (0k) rods with the Ewald sphere, is visible for a SrTiO₃ substrate surface, which is an example of a perfect surface.

Following the kinematical approach, surface disorder can be treated as a deviation from a singular surface in either lateral or vertical direction resulting in deviations from the reciprocal lattice rods of a perfect surface. For a complete overview I would like to refer to Yang²⁷ and Lagally et al.³¹.

It turns out that the above is sufficient for a qualitative description of the observed phenomena, e.g., roughening during thin film growth. For a quantitative treatment, e.g., necessary for crystallographic structure determination, one has to revert to a dynamic theory. First of all, because kinematic theory is in contradiction with the fact that elastically scattered electrons mainly interact with the outermost atoms, whereas weak interaction

is assumed. Secondly, due to the grazing incidence many atoms are involved in the scattering process, suggesting a high probability for multiple-scattering effects³².

Many dynamic calculations aim for the solution of the Schrödinger equation in the one-electron approximation and the right choice of scattering potential $V(\bar{r})$. An imaginary part of $V(\bar{r})$ is added to account for some of the inelastic scattering effects. Since a quantitative treatment is beyond the scope of this thesis I would like to refer to literature for further discussion³⁰.

2.3.3 Analysis of typical RHEED patterns; the influence of surface disorder

2.3.3.1 Geometrical information of a RHEED pattern

From a RHEED pattern of a perfect low index plane with the beam directed along a low index direction one can determine the in-plane lattice constants as follows: with θ_i and θ_f the angles with respect to the surface, ϕ_i (=0) and ϕ_f the azimuths (with an in-plane principal crystal direction as reference), of the incoming and scattered beam, respectively (see Fig. 2.2: a)),

$$\mathbf{k}_{//\text{beam}} = \frac{2\pi}{\lambda} \left(\cos \theta_{f} \cos \phi_{f} - \cos \theta_{i} \cos \phi_{i} \right)$$
(2.7a)

$$k_{\perp beam} = \frac{2\pi}{\lambda} \left(\cos \theta_{f} \sin \phi_{f} - \cos \theta_{i} \sin \phi_{i} \right)$$
(2.7b)

$$k_{z} = \frac{2\pi}{\lambda} \left(\sin \theta_{f} + \sin \theta_{i} \right) \approx \frac{2\pi}{\lambda} \left(\theta_{f} + \theta_{i} \right) \text{ (for small angles)}$$
(2.8)

For reflections fulfilling the Bragg condition the lattice constants can be derived using (2.7), for small angles:

$$\frac{n}{d_{x}} = \frac{1}{\lambda} \left(\cos \theta_{f} - \cos \theta_{i} \right)$$
(2.9)

$$\frac{\mathbf{n}}{\mathbf{d}_{\mathbf{y}}} = \frac{1}{\lambda} \left(\cos \theta_{\mathbf{f}} \sin \phi_{\mathbf{f}} \right)$$
(2.10)

where d_x and d_y are the lattice constants seen parallel and perpendicular to the beam, respectively, and n the order of the reflection. The angles can be determined directly by dividing the relative on-screen distances by the sample-to-screen distance R_{s} , assuming only small angles. The wavelength λ of the electrons with an energy E (eV), used in eq.'s (2.7) to (2.10) is approximately given by:

$$\lambda(\text{\AA}) = \sqrt{\frac{150}{E}} \tag{2.11}$$

For the reasons given in the next paragraph, the sample-to-screen distance $R_{\rm s}$ is kept as low as possible. This has the disadvantage that determination of

reflection angles is rather inaccurate (relative error ~10%, 5% uncertainty in the sample-to-screen distance and 5% uncertainty for on-screen distances). To eliminate the error in the sample-to-screen distance, one can calibrate the measurements to a known in-plane lattice parameter, for example, bare SrTiO₃ (~3.905 Å, ~3.93 Å at 800 °C).

To understand the influence of surface disorder on the RHEED intensity, the problem of scattering from a 2-level system, i.e., a certain distribution of islands of height d on a flat surface, will be discussed first. The diffracted intensity is given by:

$$I\left(\bar{k}\right) = \int C(\bar{r}) e^{i\bar{k}\cdot\bar{r}} d^{3}r$$
(2.12)

where $C(\bar{r})$ is the pair correlation function, i.e., the probability to find two scatterers at a distance r. More explicitly for a 2-level system with coverage θ :

$$I(\bar{k}) = [\theta^{2} + (1 - \theta)^{2} + 2\theta(1 - \theta)\cos(k_{z}d)]2\pi\delta(k_{x}) + 2C'_{ii}(k_{z})[1 - \cos(k_{z}d)]$$
(2.13)

where k_x is given by (2.7) and k_z by (2.8). The intensity consists of a delta peak, corresponding to the Bragg condition superimposed on a broadened diffuse peak, corresponding to disorder (C_{ii} is the Fourier transform of the reduced correlation function between atoms on the same level³³ and depends on the step distribution function). In practice, the delta peak in eq. (2.13) has to be convoluted by the instrument's response function (multiplication with the transfer function³⁴ in real space) to take instrumental broadening into account. In association with the transfer function a transfer width can be defined, analogous to the coherence length discussed below.

According to this model, intensity is most sensitive for disorder on the surface for the out-of-phase condition,

$$\mathbf{k}_{\mathbf{z}}\mathbf{d} = (2\mathbf{n}+1)\boldsymbol{\pi} \tag{2.14}$$

the central spike becomes zero at half coverage.

2.3.3.2 Examples

In Fig. 2.3, several RHEED patterns are shown of typical surfaces we encountered in our experiments. Here, we will discuss the different features.

Prior to any diffraction experiment, the sample is heated to 700 °C in vacuum (~10⁻⁷ mbar) to remove any contamination from the surface. If this procedure is not applied, usually charging effects due to the insulating character of the SrTiO₃ substrate destroy the diffraction pattern. In Fig. 2.3 a) a pattern is shown before any heat treatment in vacuum. Although a clear diffraction pattern is visible, the background intensity is rather high and especially the (0,±1) spots are much weaker compared to Fig 2.3 b) due to surface contamination.

In Fig. 2.3 c) a RHEED pattern is shown of a vicinal $SrTiO_3$ (001) surface, a special case of a 'disordered' surface, where the terraces lie almost parallel to one of the principal axis of the crystal. The incoming beam is directed

perpendicular to the terraces and the incidence angle is 1.6° . For 20 keV electrons used here, this is the out-of-phase condition (2.14) for SrTiO₃ (001) with only steps of one unit-cell. For a vicinal surface, with the beam perpendicular to the terraces directed down the staircase, the miscut angle is given by³⁵:

$$1/\theta_{c} = \frac{\lambda}{d\Delta\theta_{f} \langle \theta_{f} \rangle} - \frac{1}{\langle \theta_{f} \rangle}$$
(2.15)

where $\Delta \theta_f$ is the splitting of the Bragg peak due to the additional periodicity introduced by the existence of terraces, indicated with arrows for the (01) peak in Fig. 2.3. Here we determined a miscut of ~0.25°. Actually, Fig 2.3 b) is of the same surface, only with the beam directed parallel to the terraces. Here, no splitting is observed for reasons given below. When eq. (2.14) is not satisfied, e.g., by changing the incidence angle, no splitting is observed. Figures 2.3 d) and e) are patterns of a vicinal SrTiO₃ surface at an in-phase and out-of-phase condition, respectively.



Figure 2.3: Typical RHEED patterns for different surface morphologies: a) as received, b) treated (with the beam parallel to the terraces), c) treated (with the beam perpendicular to the terrace), treated (beam perpendicular to the terraces with d) in-phase e) out-of-phase incoming beam, $SrTiO_3$ (001). RHEED patterns of a $SrTiO_3$ surface after deposition of f) ~one unit-cell layer SrO, g) several unit- cell layers $SrCuO_2$ and h) >2 unit-cell layers $CaCuO_2$.

For a certain miscut the terraces become 'invisible' for the diffractometer due to instrumental broadening. More generally a surface with disorder over a surface area larger than the coherence area³⁶ appears to be flat. The critical terrace length parallel to the incoming electron beam for our diffractometer is estimated to be 3000 Å (miscut angle <0.07°); the coherence length along the beam is an integer multiple of this length (since there have to be more than one terrace to get interference). In contrast, the coherence length perpendicular to the electron beam is much smaller, i.e., substrates with terraces of <800 Å (miscut angle >0.3°) still appear to be flat in the parallel beam configuration (no splitting $\Delta \phi_f$ has been observed on our substrates). The difference in coherence length parallel and perpendicular to the beam can be explained by the grazing incidence angle geometry typical for RHEED, see for example^{31,35,36}.

In RHEED, any disorder will cause broadening of spots, which will be stronger in the direction of the beam, for similar reasons just mentioned. These so-called streaky patterns are often mistaken to be a RHEED pattern of a perfect surface³¹.

Figures 2.3 f), g) and h) show surfaces with increasing roughness, after deposition of a unit-cell layer of SrO (see also chapter 3), after deposition of several layers of $SrCuO_2$ and after deposition of several layers of $CaCuO_2$ (see chapter 4), respectively. Although the SrO surface is still very smooth, some streaking has occurred due to some inevitable disorder, whereas the $SrCuO_2$ surface is disordered and gives a more streaky pattern. Again, due to the grazing-incidence geometry, every detail on the surface responsible for broadening of the reciprocal lattice rods appears to be inflated along the beam direction.

The roughness of the CaCuO₂ surface is such that transmission takes place through small asperities on the surface. The pattern has changed from a spotty pattern, where spots lie on circles, to a spotty pattern where the spots form a rectangular pattern. From the positions we conclude that these asperities still have the expected tetragonal CaCuO₂ phase.

In conclusion, although information on the atomic structure is very difficult to extract from a RHEED pattern because the intensities can not simply be deduced using kinematic considerations, the state of the surface can be qualitatively inferred. Especially during the deposition, RHEED is a powerful tool to monitor the state of the surface and, for example, allows one to interrupt growth when undesired phases of outgrowth are being formed. In addition, monitoring the specular intensity variations, e.g., the intensity oscillations, during a deposition gives the possibility to judge the growth mode of the material, which will be discussed next.

2.3.4 Variations of the specular intensity during deposition

Here we will consider the variations of specular intensity as a function of the variation of the surface roughness during thin film growth.

2.3.4.1 Two-dimensional growth modes

For homoepitaxy of SrTiO₃ the recorded intensity oscillations are depicted in Fig. 2.4 a) together with the calculated intensities using two different models. Similar oscillations have been observed during deposition of GaAs³⁷ and Si³⁸. From the shape and amplitude we conclude that at the conditions used here, SrTiO₃ deposition proceeds in a true layer-by-layer growth mode, see also Fig. 2.4 d).

For a qualitative understanding one can first turn to the kinematic model (2.13) for a 2-level system, exemplified in Fig. 2.4 e) where interference of beams scattered from different levels is the cause of intensity variations. When a crystal layer is filled according to a geometrical distribution of steps, the calculated intensity shows cusp-like oscillations given in Fig. 2.4 b)³¹. The integral intensity depends only on the coverage θ . For θ =0.5 and at an out-of-phase condition (2.14), a minimum intensity is expected. When only the central delta peak is measured and the diffuse background is subtracted, this minimum should be zero. When more than 2 levels are participating in the



Figure 2.4: a) Intensity oscillations during homoepitaxial growth of $SrTiO_3$ at 850 °C and 3 Pa, indicative of true layer-by-layer growth, d). Calculated intensity oscillations using b) the diffraction model of which a schematic representation is given in e), and c) step-density model, of which a schematic representation is given in f). The number of pulses needed to complete one unit-cell layer is estimated to be 27.

diffraction process, the calculations become more complicated. However, the basic outcome is that the amplitude of the intensity oscillations decreases with the number of levels involved³², see also chapter 4.

Another widely used model is the step density model, where the specular intensity depends negatively on the number of up and down steps on the surface. Every step can act as a diffuse scatterer and the entailed intensity is "lost" for specular reflection, see Fig. 2.4 f). Although this model is highly empirical and there exists no diffraction model as a physical explanation, it turns out to qualitatively describe some of our results well. Following Stoyanov et al.³⁹ and assuming that nucleation of islands takes only place on t=T (the period for one unit-cell layer coverage), the step density evolution as a function of the coverage is given by:

$$\mathbf{L}(\mathbf{t}) = 2\sqrt{\pi} \mathbf{N}_0 \left(1 - \theta\right) \sqrt{-\ln(1 - \theta)}$$
(2.16)

where N_0 is the initial number of nuclei on t=T. When growth takes place at only one level and with a constant supply of particles, $\theta \! \propto \! t$, and the step density oscillations have again a cusp-like shape, see Fig. 2.4 c). A maximum of the step density L is expected at $\theta \! \sim \! 0.4$ (minimum intensity). For a multi-level system, θ_m are coupled through a series of m rate equations, where m represents the m^{th} unit-cell level. The total step density is given by a summation over all participating levels. The basic outcome is again a decrease of the amplitude of step density oscillations, as the number of involved levels m is increased.

The shape and the occurrence of a minimum for the measured intensity oscillation suggest that here the step-density model is applicable, as indicated in Fig's 2.4 a), b) and c). The fact that we used an incident angle corresponding to the in-phase condition and still observe strong intensity oscillations, also favors the step-density model.

The observation of oscillations depends primarily on the deposition conditions, i.e., the growth mode of the material under investigation^{40,41,42,43}. Also the phase can be determined by the growth conditions⁴⁴. For a complete overview, see Lagally et al.³¹. Any model describing the intensity oscillations quantitatively should ideally account for diffraction effects and fully describe the microscopic growth mechanisms. In computer simulations using a Monte Carlo algorithm (see chapter 4) the step-density model is often used to calculate the intensity from a surface model that has been generated by applying microscopic growth models^{45,46,47,48}.

Qualitatively, these simulations seem to describe the growth front for different growth conditions rather well, although the prediction for a damping coefficient by Stoyanov et al. is not applicable for strongly damped oscillations. For example, the observations for $SrTiO_3$ deposited at higher pressures (see chapter 4) or for $YBa_2Cu_3O_7^{64}$, resemble more the kinematically calculated intensity of a surface as the outcome of dynamic scaling models for

conservative growth conditions (Wolf-Villain model⁴⁹); an exponential decay of the oscillation amplitude is predicted⁵⁰.

In principle, starting with a perfect surface any damping of oscillations can be ascribed to a transition from a 2-level growth front to a multilevel growth front^{33,39}. The moment of island nucleation and the moment of coalescence do not coincide anymore and islands are formed on top of lower level islands which have not yet coalesced.

Studying intensity oscillations, the main challenge is still the discrimination of diffraction effects from growth-governed effects⁵¹⁻⁵⁶. To minimise dynamical effects, Van der Wagt³⁶ suggested to monitor the specular intensity in a slightly mis-aligned condition.

Another important application of RHEED intensity monitoring is the observation of other growth modes, apart from layer-by-layer modes, and the study of diffusion of material during deposition.

2.3.4.2 Other growth induced variations of the specular intensity

In Fig. 2.5, the observed variations of the specular intensity during deposition of $SrCuO_2$ and $CaCuO_2$ on $SrTiO_3$ are depicted.

In the case of SrCuO₂, see Fig. 2.5 a), after an initial dip, the intensity



Figure 2.5: a) Intensity of the specular beam in case of step-flow growth (in this case $SrCuO_2$ on $SrTiO_3$), schematic drawing for step flow of b) vicinal steps, c) step originating from two-dimensional islands. Intensity of the specular beam in case of d) Stransky-Krastanov growth (in this $CaCuO_2$ on $SrTiO_3$) and e) schematic drawing.

hardly changes, apart from a modulation due to the laser pulse. The amplitude of this modulation is an indication for a relatively flat surface, see also below. From this we conclude that growth proceeds in a step flow mode. Here one can distinguish two cases: First, a 'true' step flow mode, see Fig. 2.5 c), where the deposited material continuously attaches to vicinal terraces of the substrate and the surface morphology essentially stays constant. Secondly, a similar mode, see Fig. 2.5 d), however the terraces are now formed by pyramidally shaped islands^{vii}, which are constantly growing without any change of morphology. The latter seems to be more compatible with Fig. 2.5 a), which was also confirmed by Atomic Force Microscopy (many small islands are observed)⁵⁷ and is often observed for layered oxide materials⁵⁸.

For CaCuO₂, Fig. 2.5 b), there are two oscillation periods visible after which the intensity exponentially drops to below the detector limit. This is an example of a layer-by-layer growth mode, followed by three dimensional island growth, i.e., Stransky-Krastanov growth, also schematically drawn in Fig. 2.5 e).

Not shown here would be an exponential decay from the very start of deposition, indicative for three-dimensional island growth or Frank-Van der Merwe growth. Usually, this growth mode is accompanied by a transmission diffraction pattern, see also section 2.3.3.2.

Finally, in Fig. 2.6, intensity changes typical for pulsed deposition are depicted. Next to the already discussed features, such as an oscillating behavior, here I would like to focus on the extra modulation apparent in all previous presented data. As can be seen from this figure, the oscillations are modulated by the laser pulse. The intensity decreases significantly directly after the laser pulse followed by an exponential rise caused by recrystallization of initially disordered material as reported by, e.g., Karl et al.⁶⁰ and Achutharaman et al.⁴⁶. The characteristic times involved contain information about the diffusion and growth on the surface under study. One could suspect that the intensity modulation is just caused by scattering of the electrons by the dense laser plume. However, there are several arguments that rule this out. A large relaxation response is only observed when the surface is relatively smooth, for obvious reasons, e.g., in a 3D pattern as in Fig. 2.3 h), the intensity is not affected by the laser pulse. Occasionally, under specific diffraction conditions, the intensity rises after each pulse and finally, the plume 'life time' is probably too short to have any effect on the measured intensityviii.

Also from the above, it becomes immediately clear that there is an integer number of pulses available for each unit-cell layer (in the event of layer-bylayer growth), which is not necessarily the exact number of pulses needed to

 $^{^{\}mbox{vii}}$ Here, continuous two-dimensional nucleation takes place, whereas for true step flow only growth of steps occurs.

viii The sample rate of the CCD camera frame grabber combination is maximally 15 Hz.



Figure 2.6: a) Modulation of the specular RHEED intensity due to pulsed deposition, insets give enlarged intensity after one laser pulse plus fit with exponential function to give characteristic relaxation times (see also chapter 4), b) The number of laser pulses per crystal layer never being an integer sometimes results in an aliasing effect, the inset gives the calculated intensity according to a 2-level model, from the aliasing period one can deduce ~8.9 pulses per crystal layer.

complete one unit-cell layer. Sometimes one can observe an aliasing effect caused by the aforementioned discrepancy. Superimposed on the intensity oscillations due to layer-by-layer growth and the modulation of the laser pulse, a third periodical variation is seen, as indicated with in Fig. 2.6 b). The inset shows the calculated intensity according to (2.13), where the aliasing effect is simulated by choosing a certain sampling frequency.

2.4 Realization of PLD system with high pressure RHEED

2.4.1 High pressure RHEED

RHEED is often used for the analysis and monitoring of thin film growth in Ultra-High Vacuum deposition systems⁵⁹. For PLD of oxide materials the diagnostics of the growing film surfaces by in situ RHEED is hampered by the relatively high oxygen pressure. Nevertheless, several groups monitored the growth of complex oxides with RHEED and showed intensity oscillations, by depositing under pressures compatible with their RHEED set up. To incorporate oxygen in the as-grown films, different alternatives were used, e.g., low pressures $(10^{-4}-1 \text{ Pa})$ of molecular oxygen^{60.61}, NO₂^{62.63} or O₃⁶⁴, and alternatively pulsed oxygen sources⁶⁵. A low deposition pressure during PLD, however, can lead to stress, usually compressive, in the film¹⁹. As mentioned earlier, this is caused by the bombardment of the film during the deposition by high energetic particles, originating from the plasma. Furthermore, some complex oxides, like high-Tc superconductors, are not stable in low oxygen pressures of up to 30 Pa to avoid decomposition of the film⁶⁶. Finally, the

temperature and oxygen pressure determine in the case of tetragonal $ACuO_2$ whether the right phase will be formed^{24,67,68}.

In this work, we developed a RHEED system designed for growth monitoring under high deposition pressures (up to 100 Pa). The main problem to be solved is the scattering loss at high pressure. In order to minimize the losses, the travelling path of the electrons in the high pressure region has to be kept as short as possible. Furthermore, most of the commercially available electron sources use heated tungsten filaments to emit electrons. The oxygen pressure in the source should be very low ($<5 \times 10^{-4}$ Pa) to avoid short lifetime of the filaments. Our system satisfies these requirements, i.e., a low pressure in the electron gun and a high pressure in the deposition chamber, and is described in the next paragraph.

We have demonstrated the applicability of the system for the first time by observing clear oscillations of the diffracted intensity during deposition of $SrTiO_3$ and $YBa_2Cu_3O_7$ (using PLD at 15 Pa of oxygen), an evidence for two-dimensional growth. In addition we show that in situ annealing steps between deposition steps improve the smoothness of the surface as indicated by the RHEED patterns, also recorded at high pressures. The layer-by-layer growth is enhanced by the intermediate annealing steps. These results initiated the use of the system for control of thin film growth on an atomic level even at high background pressures².

2.4.2 Description of the system

2.4.2.1 PLD

A schematic view of the deposition chamber, including the electron source assembly, is given in Fig. 2.1. Here a 248 nm laser beam is focussed under 45° incidence onto a high density (>95%) target using a lens (focal length ~500 mm). Both, substrate holder including heater and multi-target holder (which can hold up to 5 different targets) are mounted on a computer controlled XYZ-rotation stage and can be inserted via a load-lock system without breaking the vacuum. Selection of the targets, laser repetition rate and the number of laser pulses per target material is fully automated and can be repeated in the desired order.

The targets are either stoichiometric sintered pellets (e.g., $YBa_2Cu_3O_7$, $SrCuO_2$, $Sr_{0.7}Ca_{0.3}CuO_2$, $BaCuO_2$ and $CaCuO_2$) or single crystals (e.g., $SrTiO_3$, SrO, BaO, CaO, TiO_2). In order to ablate from a 'fresh' part of the target with every pulse, the target is scanned horizontally and/or vertically in the laser beam.

A substrate is mounted on a thermo-coax heater using silver paint allowing for good thermal contact, and placed ~50 mm from the target. The temperature is measured inside the heater block with a K-type thermocouple and temperatures up to 850 °C can be attained. The pressure is controlled by means of two mass flow controllers (Brooks Instruments, 0-40 ml/min) in combination with a pump restriction. The aperture of the restriction and the gas flow settings determine the final pressure. Higher pressure (>10³ Pa), e.g., for

annealing purposes is obtained by closing all the valves to the pumps and flooding of the chamber with either oxygen or nitrogen. Oxygen gas (purity 4.5 or 6.0) can be used as well as inert gasses (N₂, He, Ar, Ne).

2.4.2.2 RHEED

We use an electron source (EK-2035-R, STAIB Instrumente) able to produce a beam with a minimum size of 100 μ m, which in turn gives a 0.1×3-0.1×7 mm spot on the surface (at an angle of incidence roughly 0.8-3°). For most of the experiments described in this thesis, the acceleration voltage was set at 35 keV (some experiments were performed using 20 keV).

The substrate holder can be rotated in order to adjust the angle of incidence of the electron beam onto the substrate. An additional rotation is used to change the azimuth.

The diffraction pattern on a fluorescent phosphor screen is recorded by a computer controlled CCD camera (Peltier cooled, K-space associates). A K-space software (ksa400 v.3.0) controlled frame grabber collects images at a maximum rate of ~15 Hz. Several modes of the software enable one to analyze the diffraction data, i.e., the full pattern as well as intensity variations of selected areas in the pattern. The on-chip integration option allows one to intensify reflections of weakly scattered beams, without changing the beam configuration.

2.4.2.3 High Pressure RHEED

Figure 2.1 shows the complete high pressure RHEED set up. A differential pumping unit is used to maintain a vacuum of better than $5 \cdot 10^{-4}$ Pa in the electron source. The source is mounted on a flange connected to a stainless steel extension tube with an inner diameter of 8 mm. An aperture (diameter 250-500 µm) separates the tube from the deposition chamber. The pressure inside the tube, which depends on the pump speed and the size of the aperture, is kept below 10^{-1} Pa. Using this two-stage pumping system, the pressure in the deposition chamber can be increased up to 100 Pa while maintaining low pressure in the electron source. The electron beam, which passes through the apertures inside the differential pumping unit and the tube, enters the deposition chamber near the substrate at a distance of about 50 mm. The XY deflection facility of the electron source is used to direct the electron beam through the aperture at the end of the tube. Many electron sources are also equipped with a beam rocking option, which in this case cannot be used. For this a mechanical solution has to be employed by rocking the complete gun.

Small magnetic fields, like the earth magnetic field, can influence the electron beam and complicate the alignment of the beam through a small aperture. Therefore, special care has been taken to shield the electron beam from magnetic fields using μ -metal.

The fluorescent phosphor screen (diameter 50 mm) is mounted on a flange located near the substrate. The distance between the screen and the substrate is 50 mm. The phosphor is screened from the plasma plume in order to

minimize contamination. The electron source, including the extension tube, is mounted on a XYZ-stage allowing one to adjust the distance between the substrate and the end of the tube.

Although scattering of electrons in high oxygen pressure decreases the intensity of the electron beam, we have shown that growth monitoring of complex oxides at high oxygen pressures is feasible using RHEED². By two-stage pumping and enclosing the electron beam as long as possible in a vacuum tube, intensity losses due to scattering are minimized.

2.5 Structural analysis

Analysis of the surface morphology before and after thin film growth has been mainly performed by Atomic Force Microscopy, whereas the crystal structure was analysed by XRD and HREM. Here, I will shortly address some of the experimental details.

2.5.1 Atomic Force Microscopy

Scanning probe microscopy experiments were performed on a Nanoscope III (DI, Santa Barbara, CA), capable of contact and tapping mode imaging. For the contact mode, standard DI Si₃N₄ cantilevers were used with nominal force constants of k = 0.18, 0.38, 0.58 Nm⁻¹, whereas for tapping mode Si cantilevers with resonance frequency ranging from 310 to 400 kHz were utilized. Contact forces were kept as low as possible and are estimated to be <10 nN.

Lateral or frictional forces are measured simultaneously by the fourquadrant detector. No attempts have been made to quantify the friction force, since the exact lateral force constants of the cantilevers are unknown, the alignment of the laser on the cantilever changes and the humidity in the laboratory is not constant. In friction force micrographs high frictional forces are displayed as bright white colors and lower forces as dark colors (range of 0.1 V). The topographical features in the contact mode micrographs are confirmed by tapping mode imaging.

All thermal treatments have been performed in a modified tube-oven, using flowing O_2 (at a rate of 100-300 l h⁻¹). The substrates were placed on an aluminum-oxide boat inside a quartz tube. The substrates are flashed to 650 °C for several (1-10 minutes) minutes prior to imaging or imaging took place immediately after the sample was taken out of the processing chamber in order to avoid contamination that would affect the quality of the images.

2.5.2 Bragg-Brentano configuration, θ-2θ scan

In this work the main goal was to epitaxially stabilize superstructures which are formed through successively deposition of unit-cell layers of different kinds of material, see chapter 5. Since all of these structures are expected to have in-plane cell parameters similar to those of SrTiO₃, and the modulation

should be perpendicular to the substrate surface, a θ -2 θ scan around the (001) direction of the substrate is the most suitable for analysis of the modulation period.

This type of scan is performed both on a single-crystal diffractometer (CAD4, Enraf Nonius Delft, the Netherlands) as well as on a thin film diffractometer (X'pert, Philips, the Netherlands) using a Cu-K α source.

The instrumental broadening is estimated (from the substrate peaks) to be 0.2° for the CAD4 system. Furthermore, the θ -2 θ scans performed on this system usually show additional peaks corresponding to spectral $\lambda/2$ and $\lambda/3$ lines transmitted by the strong (001) reflections of SrTiO₃. The orientation matrix of the substrate crystal was determined and scans were performed along the direction perpendicular to the substrate surface. Here, one has also the possibility to collect a full data set which can be refined, or to record a reciprocal space map around specific reflections. With the aid of a diode laser aimed at the surface acting as a small mirror and φ rotation around the (001) axis, the miscut angle of the substrate can be accurately determined⁶⁹.

On the Philips system, a sample holder with precise positioning in vertical direction allowed alignment of the sample surface to the beam placing it half way the beam profile (this diffractometer formally satisfies the definitions of a Bragg-Brentano set up^{70}). Low-angle reflectivity measurements were performed as well, allowing for thickness determination⁷⁰.

For both set ups a Ni filter was used, whereas for the Philips system on the secondary side a monochromator and a parallel plate collimator were available^{ix}; here the θ -2 θ scans did not contain any spectral contributions.

2.5.3 High Resolution Transmission Electron Microscopy (HREM)

The HREM analysis was performed in Antwerp on a JEOL 4000EX operating at 400 kV and 376 kV. The point resolution of this instrument is 1.7 Å. In this case, the samples were cut into slices, glued together and mechanically polished on diamond lapping foils using water as lubricant down to a thickness of 30 microns. Subsequently they were ion-milled until electron transparency was achieved. Previously, this method was compared to samples polished with lubricant, and no negative effects were detected. In the electron microscope we could observe irradiation damage during the measurements. All samples suffered considerably from amorphisation.

 $^{^{\}rm ix}$ The $\theta-2\theta$ scans on the CAD4 diffractometer usually revealed some spectral lines of the Cu source transmitted by strong reflecting substrate planes, which were absent on scans performed on the X'pert system.

2.6 Conclusions

For PLD, the high deposition rate and the energy of the particles at the substrate surface, both depend on the gas pressure, and the pulsed way of deposition, are expected to affect the growth of thin films.

In situ RHEED intensity monitoring of the specular reflection gives information about the nucleation of the deposited material. Moreover, analyzing the RHEED pattern, one can judge the surface quality and detect for example the origination of precipitates.

During deposition of oxide materials, an oxide ambient is used and, although scattering of electrons in high oxygen pressure reduces the intensity of the electron beam, we have shown that growth monitoring at high oxygen pressures is feasible using RHEED. By two-stage pumping and enclosing the electron beam as much as possible in a vacuum tube, intensity losses due to scattering can be minimized. Introducing this technique enabled further development of the PLD technique: The combination of the pulsed way of deposition with intensity monitoring results in the possibility of time resolved RHEED.

Besides the observed intensity oscillations in the case of layer-by-layer growth, which enables accurate growth rate control, it became clear that intensity relaxation observed due to the typical pulsed way of deposition leads to a wealth of information about growth parameters.

For the applicability of RHEED for growth rate monitoring at an atomic level, it is necessary to have a two-dimensional or layer-by-layer growth mode. If possible, one can adjust the deposition parameters to obtain a layer-by-layer growth mode, see also chapter 4. Yet, in view of phase stability, many oxide materials are not stable over a large enough temperature and pressure range. In chapter 4 we focus on the growth modes of layered oxide materials and the use of growth manipulation to impose a layer-by-layer growth mode.

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The Surface Composition of Perovskites

3.1 Introduction

In this chapter, it becomes clear that the terminating layer of a perovskite (001) ABO₃ crystal (i.e., for SrTiO₃ (001) this is TiO₂ or SrO) influences many characteristics of the surface. The morphology during a thermal treatment of the surface, epitaxial growth, microstructure (i.e., reconstructions, defects), the electronic structure and chemical properties are all determined by the composition of the surface, i.e., whether it is a BO₂, AO, or a mixed surface. Of course all of these characteristics are interdependent. A single terminated surface will turn out to be optimal with respect to mainly morphology and epitaxy.

It is demonstrated that one can take advantage of the difference in properties of the elements in the different layers, e.g., solubility in acids, in order to achieve a nearly perfect and single terminated surface^{1,11}. In this chapter we study the SrTiO₃ surface as a model system and the effects of the composition of the terminating layer on homo-epitaxial and hetero-epitaxial growth.

3.2 The ABO₃ (001) surface

Named after a Russian statesman², $CaTiO_3$ or perovskite represents a class of materials with the general crystal structure of ABO₃. Many materials with



Figure 3.1: ABO $_3$ crystal structure and possible terminating planes of a (001) surface.

an enormous variety in properties can be described in terms of this structure. High- T_c superconducting cuprates and materials with high dielectric constants like (Ba,Sr,Ca)TiO₃ belong to this class. Closely related to this structure are the K₂NiF₄ structures and the Ruddleson-Popper phases³.

In the perovskite unit-cell, the corner position is occupied by a transition metal B, 6-fold co-ordinated by corner-sharing oxygen octahedra. The large A cations occupy the body centre. Along one of the principal axes, the structure can be viewed as a stack of alternating AO and BO_2 planes, see Fig. 3.1. For different A and B cations a tolerance factor t is defined as:

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}$$
(3.1)

where R_X are the ionic radii. For the perfect perovskite structure t=1, however, for 0.75<t≤1 stable perovskite structures exist⁴, while the octahedra may be tilted.

SrTiO₃ (001), with t~0.86^{i,5}, is often chosen as the substrate material for HTS thin films. Their lattice constants and thermal expansion coefficients are rather compatibleⁱⁱ. In addition, SrTiO₃ is chemically and compositionally very stable (e.g., its melting point is 2080 °C) and thus fit to be used at relatively high deposition temperature typically used for HTS materials. In chapter 5 we discuss the structure of the HTS materials in more detail. Important here is the typical layered structure and the implication that the perovskite (001)

¹ Calculated using Pauling ionic radii

ⁱⁱ lattice constant of cubic SrTiO₃ is 3.905 Å, $\alpha_{STO}=9\times10^{-6}K^{-1}$

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Figure 3.2: AFM image of an as received substrate.

surface either terminates by an AO plane, a BO_2 plane or a mixture, depending on their surface energy. In turn, this will affect the stacking sequence of hetero-epitaxial perovskite thin films.

Of all perovskite materials, the $SrTiO_3$ (001) surface is studied in most detail, initially because of its photo-catalytic properties and, subsequently, as a substrate for thin films of other perovskite materials. In the latter case, the the primary motivation is to obtain high quality surfaces, in order to impose epitaxial growth. Depending on the requirements of the properties of these thin films, several criteria need to be fulfilled here.

First of all, a clean surface is necessary, free of contaminants like CO_2 or H_2O . Several methods have been successfully applied among which the Bi adsorption/desorption method⁶ and in situ thermal treatments^{7,8}.

Secondly, the substrate surface roughness has to be at least of the same order as the finally required thin film surface roughness^{iii,9}. It determines whether it can be applied in complex multilayer structures, e.g., the roughness of separating layers must not exceed their thickness. In addition, for many thin film materials the surface undergoes a roughening transition during deposition which implicate that the starting surface has to be of higher quality. In some cases, like ours, only roughness on an atomic scale is allowed. Fortunately, polished SrTiO₃ (001) substrates already fulfil this requirement.

However, polishing and etching usually lead to several kinds of defects on the surface and, therefore, to not-well-defined surfaces on an atomic scale (in the following these substrates will be called 'as-received'). Although unit-cell steps can be identified with AFM on as-received substrates after proper cleaning^{10,11}, the step ledges are very rough and further treatment is necessary to improve the crystallinity, i.e., the lateral order of the surface.

ⁱⁱⁱ Roughness of a surface can be described in many ways. Usually an rms value is not sufficient to capture all the characteristics of the surface. For multilayer structures a peak-to-peak value is more appropriate. An thorough description of different roughness parameters can be found in , e.g., ref. 9.

In case of HTS thin films and the infinite layer materials, the substrate also acts as a stabilising template for the desired crystalline structure which makes high crystallinity of the substrate surface a very important criterion. To obtain this, most of the time an anneal treatment is used, either in an oxidising^{10,12,13,14,15} or reducing^{16,17,18,19,20,21} ambient. The latter is also used to induce conductivity at the surface for the otherwise insulating material which is necessary for Scanning Tunneling Microscopy measurements^{22,23}.

Finally, for perovskite film materials, the stacking sequence is determined by the terminating plane of the substrate material. Empirically, the perovskite stacking sequence is, either continued over the interface (i.e., -AO-BO₂-A'O-B'O₂-), or shifted (1/2, 1/2, 0) because a rocksalt layer is formed by two AO layers (i.e., -BO₂-AO-A'O-B'O₂-). The other possibility, -AO-BO₂-B'O₂-A'O-, is hardly observed. For instance, this can be understood by looking at the compatibility of bulk SrO (rocksalt structure, compatible) and bulk TiO₂ (rutile structure, not compatible^{4.24}) with the SrTiO₃ structure. Preferably, the substrate surface has to be single terminated to impose one possible stacking sequence. Apart from this, differently terminated domains on the surface will result in different growth kinetics. None of the already mentioned treatments are sufficient to fulfil this last requirement.

One has to look for an optimal treatment which will fulfil all of the requirements combined, including single termination. Here, $SrTiO_3$ has been studied as a model system for ABO₃ in general. It turns out that once the termination is controlled, by which we mean that the composition of 0% or 100% TiO₂ for the surface termination is realized by some chemical or physical treatment, all of the other requirements are easily met.

3.3 Termination control for thin film growth

3.3.1 What is the terminating plane of SrTiO₃ (001) surface?

By considering the co-ordination number in $SrTiO_3$ of Sr (bulk 12, surface 8) and Ti (bulk 6, surface 5) one could conclude that the TiO_2 surface is more stable, since relatively fewer bonds have to be broken at the surface. However, the 'other half' will then be SrO terminated. Also shell model calculations predict a negligible surface energy difference for both bulk terminated surfaces. Therefore, a surface obtained by cleaving or cutting is expected to result in an equal amount of AO- and BO₂-terminated domains separated by half unit-cell steps²⁵.

On the other hand for relaxed surfaces (e.g., after annealing), shell model calculations predict a different surface energy for the two possible terminations, which depends on the size of the A-site cation. Accordingly, one expects a preferential termination. Unfortunately, Chen found values for rumpling of the topmost atoms that are in disagreement with experimental findings (LEED^{26,27}, RHEED^{28,29}, surface XRD³⁰ and MEIS³¹) and theoretical calculations by others, both using shell model^{32,33} as well as ab initio density

functional theory 34, . Still more convincing physical proof has to be found if a preferred termination exists $^{\rm iv}.$

Several groups performed measurements to determine the surface composition of $SrTiO_3$ after different kinds of surface treatments and/or after homoepitaxy. Ion Scattering techniques (LEIS and CAICISS) ^{7,35,36,37,38}, surface diffraction techniques^{26,30} and Scanning Probe Techniques³⁹ all indicated that so far only the chemical treatment⁴⁰ results in a single terminated surface, although Nishimura et al. recently observed only 88% TiO₂ termination after such treatment³¹.

3.3.2 Termination control

Much effort has been put in thermal treatments in different kinds of ambients, in attempts to obtain a single terminated surface. While the crystallinity is greatly improved, as can be judged from surface diffraction^{29,30} and scanning probe studies³⁹, these results still pointed to a mixed termination and it remains a question whether single termination can be achieved. Kawasaki et al.⁴⁰ suggested a chemical route to achieve single termination. The combination of a chemical treatment and a thermal treatment can then lead to perfectly crystalline, TiO₂ terminated SrTiO₃ surfaces. Based on their results we always observed etch pits⁴¹, in our opinion due to a too low pH (~4,5) value of the solution, resulting in strong etching of the surface. Obviously, the formation of etch pits negatively affects the thin film growth.

Our final optimal treatment was found after AFM experiments performed in a liquid cell filled with H₂O. A subtle change in morphology of the low friction domains (see section 3.4.2) under the influence of water was observed. It is known that SrO reacts with CO₂ and H₂O at room temperature to form stable compounds like SrCO₃ and Sr(OH)₂, respectively. It is unlikely that water will react with the chemically very stable TiO₂-terminated layers⁴². Hence, we expect that, in the presence of water, the topmost layer of SrO-terminated domains forms a Sr-hydroxide complex, which is known to dissolve in acidic solutions. To utilize this behavior in water, an as-received substrate was ultrasonically soaked in analytical-grade, and demineralized water for 10 min., followed by a short (ca. 30 s.) dip in a standard, commercially available BHF solution. To remove the remnants of the previous treatments and facilitate

 $^{^{\}rm iv}$ The shell model calculations performed by Chen et al. indicate that for a relaxed SrO termination plane the Sr ion is pulled out of the top most plane, whereas experimentally the opposite has been observed. However, these measurements were performed on surfaces where the SrO termination was realized by deposition of one unit-cell layer SrO (monitored with a Quartz Crystal) and some additional roughness must be taken into account when interpreting the diffraction intensity data.

recrystallization, a final annealing step is performed at 950 °C for one hour typically^{v,1,11}.

XPS measurements have been performed on SrTiO₃ substrates at different stages during the preparation. The O 1s envelope consists of two contributions: a peak located at ~530.0 eV from the titanate oxygen, and a peak located at ~531.6 eV due to surface hydroxyl groups. The highest concentration of surface hydroxyls is present on the water-soaked and as-received substrates as indicated by angular measurements. These hydroxyls are associated with the Sr, since the surface Sr 3p peaks are shifted slightly towards lower binding energies⁴³. The C 1s peak (located at 284.8 eV, used as the reference peak) is present on all samples and is also located on the surface. No evidence of carbonates has been found. On the etched and subsequently annealed substrate, the C-1s intensity is very low compared to the Sr 3p, Sr 3d and Ti 2p peaks, which is a further indication of the quality of this surface¹.

In conclusion, we have reproducibly obtained quasi-ideal $SrTiO_3$ surfaces for thin film deposition and fundamental growth studies. Due to the enhancement of the selectivity in solubility by the formation of a Sr-hydroxide complex, confined to the topmost SrO-layer, the pH-value of the BHF-solution and the etching-time become much less critical. Because of the possibility to reduce the etching-time, formation of etch-pits and holes due to prolonged etching is prevented.

A similar approach to obtaining single termination can be followed in a variety of multi-component oxide single crystals^{vi}. In the remainder of this thesis, substrates that are treated according to the method described above, are referred to as 'properly' or 'fully' treated substrates.

3.4 The (001) surface after different treatments

3.4.1 Morphology

The surface morphology of a typical as-received single crystal substrate⁴⁴ was imaged by AFM. As shown in Fig. 3.2, the surface consists of terraces, with disordered step ledges and islands on terraces with typical height differences of half (~2 Å) and single (~4 Å) unit-cell steps. This indicates the coexistence of the two possible surface terminations.

Annealing the as-received substrate results in re-growth of the surface, as shown in Fig. 3.3 a). Seemingly, regularly spaced steps of one unit-cell height (see also Fig. 3.3 b) are visible separated by terraces, the width of which is

 $^{^{\}rm v}$ The demineralized water was produced by Millipore Elix equipment (R = 10–15 MΩcm and pH = 6–7), whereas the BHF-solution was obtained from Merck (NH₄F: HF = 87.5:12.5 with pH = 5.5).

 $^{^{\}rm vi}$ Recently we performed a treatment based on the same approach (enhanced selective etching) of LaAlO₃, which resulted in perfect, single terminated surfaces. Other substrate materials are currently under investigation.

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Figure 3.3: AFM a) contact mode, b) cross-section c) friction contrast of a surface annealed at 950 $^{\circ}$ C for four hours and d) AFM contact mode of a surface annealed a 1100 $^{\circ}$ C for ten hours.

determined by the miscut angle of the crystal. The combination of the miscut angle, the duration and the temperature of annealing, determine the eventual morphology of the surface, i.e., whether step bunching will occur (higher miscut angles, longer times and higher temperatures) or meandering of step ledges (lower miscuts, short times and lower temperatures^{11,41}). More generally, this has been observed for other materials^{vii,45}.

Another example is given in Fig. 3.3 d), where AFM clearly shows domains with different termination at the surface. The difference in these domains is expressed by the shape of the ledges: straight and sharp-edged step ledges exist, but in addition rounded domains can be identified⁷, as indicated in the figure: This is common for all similarly treated substrates that we have studied. These differences become more pronounced at higher temperatures (or

^{vii} All thermal treatments have been performed in a modified tube-oven, using flowing O₂ (at a rate of 150 l h⁻¹). The substrates were placed on an aluminum oxide boat inside a quartz tube. The substrates were heated to 650 °C for several (1-10 min.) minutes prior to imaging. This temperature is well below the observed threshold of 800 °C for re-growth or recrystallization of the step ledges. Annealing was performed above this threshold at 950 °C for one hour. The temperature was then raised at a rate of about 0.5 °C s¹, and allowed to cool down to room temperature in 3 hours.



Figure 3.4: a)-c) AFM height images of TiO_2 terminated $SrTiO_3$ surfaces and d) cross section of c)

longer anneal times). Hence, we conclude that apart from re-growth of terrace ledges, domains with different surface termination have become clearly visible.

At this point we have to mention that for annealed surfaces the formation of other phases at the surface have been reported, especially in UHV ambient at high temperatures^{19,20,21,46}. This might also explain the existence of different domains.

After proper treatment, AFM analysis shows a nearly perfect single terminated surface with very straight terrace ledges, see Fig. 3.4 a) and c). The line scan in Fig. 3.4 d) only shows single unit-cell steps of $SrTiO_3$. Typical for these surfaces is their isotropic morphology. The terrace ledges have a more rounded appearance or in other words the ledge energy seems to be minimized by decreasing the length instead of alignment of the ledges along low-index directions. This is further exemplified in Fig. 3.4 b) of low miscut surfaces. Annealing at 950 °C for one hour (typical), always is accompanied with the formation of holes on the terraces. These holes are perfectly circularly shaped, one unit-cell deep, and turn out to diffuse to the terrace ledges in time. See for example the marked 'bubble' in Fig. 3.4 b), which has reached a terrace ledge and merges with it.

The effect of the miscut angle on the morphology can be shown very clearly now. Figure 3.5 is organized as a phase diagram (at 950 $^{\circ}$ C) for the surface morphology. The holes, Fig. 3.5 a), have all disappeared for longer anneal

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Figure 3.5: AFM images of annealed SrTiO₃ surfaces (950°C) with different miscut angles: 0.04° a), b), 0.2° c) and 0.5° d) after different anneal times: $\frac{1}{2}$ -1 a), c), 1-2 d) and >2 b) hours.

times, Fig. 3.5 b), whereas for higher miscut angles, Fig. 3.5 c), no holes are observed. For these substrates, step bunching is more likely to occur; in Fig. 3.5 d) bunched terraces are encircled. In Fig. 3.5 b), the strong curvature of the terrace ledges (encircled) must not be mistaken for step bunching, but is probably caused by an underlying crystal defect, which destroys locally the isotropy. These results suggest that the morphology is mainly determined by the diffusion of atoms on the surface trying to find optimal sites. From Einsteins diffusion law, $\langle x \rangle = \sqrt{D\tau} \tau$, for a given diffusivity D atoms diffused over an average distance $\langle x \rangle$ in τ seconds. Indeed, for the lowest miscut substrates, disproportionally longer annealing times are needed, although, the exact times were difficult to determine^{viii}.

viii First of all, the oven which was used, was a slow system and therefore the ramping times were significant. Second, the exact moment upon which a certain morphology was reached could not be determined.

3.4.2 Lateral Force Microscopy

It has been shown that the observation of friction contrast on several surfaces can be related to a difference in termination, either, chemically³⁹ or structurally⁴⁷. Here, we used this technique to determine the composition of the SrTiO₃ surfaces after different treatments.

LFM did not show any clear contrast on the as received substrate surfaces, unlike after annealing at 950°C in an oxygen flow. Figure 3.3 c)^{ix} shows the friction contrast observed for the surface in Fig. 3.3 a), where obviously segregation into distinct regions at the surface has taken place. In addition, a more detailed study revealed^{1,11} that different regions, which show a contrast in friction, are always separated by steps of $(n+1/2)*a_0$ height.

To shed more light on the apparent difference in friction, several imaging modes have been used. Phase contrast measurements in tapping mode reveal that domains having a high friction display higher phase changes, due to mechanical interaction^{1,11}. In addition, we observe that the low friction domains become rougher upon aging, probably due to a reaction with the ambient. On the other hand, the high friction regions usually remain flat for longer time periods.

From these observations we conclude that the observed friction contrast originates from distinct properties of the surface, depending on the termination^{x,48,49,50,51}. Indeed, after the full treatment, no friction contrast is observed. Therefore, this is a good method to test any preparation method, which is expected to result in single termination^{xi}. However, the question remains which termination corresponds to which sign of the friction contrast. After the full treatment, apparently leading to single-terminated surfaces, the surfaces are always extremely easy to image compared to solely annealed surfaces, indicating that interaction with ambient air is weaker. This leads us to believe that high friction domains correspond to TiO_2 termination. This conclusion contradicts the results obtained by Fompeyrine et al., although this can be caused by differences in preparation methods. Moreover, we observe that in some cases the friction contrast is reversed, which makes it even more

 $^{^{\}mbox{\tiny IX}}$ In the friction force micrograph, high frictional forces are displayed as bright white colors and lower forces as dark colors (range of 0.1 V). The observed friction contrast is comparable to that found by Fompeyrine et al. The topographical features in the contact mode micrographs are confirmed by tapping mode imaging.

 $^{^{\}rm x}$ The observed friction contrast can be attributed to two different properties of the surface. The first has a chemical nature: different chemical functionalities exert different friction forces on the Si₃N₄ tip, for more details see^{48,49,50}. A second origin of friction is more mechanical in nature, and deals with the stiffness of the cantilever and the tip-sample combination, as expressed in the respective Poisson coefficient, Young's and shear modulus (See also C.D. Frisbie et al.). Since the friction force depends linearly on the applied load, higher adhesion forces between tip and sample result in higher friction forces. In air, the difference in adhesion is usually caused by differences in water adsorption on the surface.

 $^{^{\}rm xi}$ Other substrate materials have been prepared in a similar way to SrTiO_3. Lateral Force Microscopy indicated that single terminated LaAlO_3 are also feasible.

difficult to make a firm statement $t^{39,xii}$. Direct chemical probing methods such as LEIS^{xiii,52} or indirect such as surface X-ray Diffraction^{xiv} have to be used to be conclusive about the terminating layer of SrTiO₃. However, one can use the deposition of different materials and their wetting on these surfaces to get information concerning the terminating layer, see also section 3.5.

3.4.3 RHEED pattern analysis

Apart from the differences observed with AFM, we also detected distinct RHEED patterns after various treatments, which correlated with the termination. RHEED patterns of as-received surfaces show broadened Bragg reflections or streaks due to disorder, see Fig. 3.6 a).

In contrast, analysis of the RHEED pattern after oxygen annealing revealed sharp 0th-order spots and a well-developed Kikuchi pattern, see Fig. 3.6 b), c) and d), which indicate a high crystallinity. Several additional spots are usually visible, possibly corresponding to a reconstructed surface. Unexpectedly, the spots lie either on $\geq 10 \times a_0$ (Fig. 3.6 b),c)) or on $3 \times a_0$ (Fig. 3.6 d)) positions in the RHEED pattern, as indicated by arrows. Rarely, we also observe merging of these patterns. To our knowledge, there has been no report of similar additional spots in literature. Usually, ordered oxygen vacancies are seen on UHV annealed surfaces, e.g., $(\sqrt{5} \times \sqrt{5})^{16,53}$, whereas on oxygen annealed surfaces, $(\sqrt{13} \times \sqrt{13})^{53}$ or $(6 \times 2)^{53,54}$ reconstructions are observed (of an unknown origin). The vicinal splitting (see Chapter 2) of the extra spots in Fig. 3.6 c) demonstrate that the features described here are truly resulting from an additional ordering at the surface, and do not originate from Kikuchi line crossings.

Finally, after proper treatment the substrate surfaces are perfectly crystalline, see Fig. 3.6 e); the spots are even narrower than in the preceding cases. Furthermore, no additional spots are visible and the positions of the spots correspond to a (1×1) SrTiO₃ surface.

The RHEED pattern after subsequent deposition of a unit-cell layer of SrO on a properly treated surface (see also section 3.5.2) is given in Fig. 3.6 f). Here, no additional spots are visible. Some streaking is observed and the relative intensity of the specular spot to the (0k) reflections has decreased compared to the case just after the treatment.

Although the exact origin of the additional spots remains obscure, we conclude from the above observations that they belong to a mixed-termination

 $^{^{}xii}$ Their substrates were reduced in vacuum (p = 10^{-7} Torr) at temperatures above 600 °C, before any friction contrast was observed. They concluded that high-friction domains are SrO-terminated.

 $^{^{}xiii}$ LEIS measurements were performed on annealed substrates, however, the preparation of ultra clean surfaces is still an obstruction for unambiguous results.

^{xiv} These measurements have to be performed by using synchrotron radiation, the experiments have been performed at the European Synchrotron Radiation Facility.



Figure 3.6: RHEED patterns of a) as-received, b), c), d) annealed, e) fully treated $SrTiO_3$ substrates and f) after deposition of ~1 unit-cell layer of SrO.

surface after thermal treatment. Single terminated substrates exhibit only a (1×1) pattern. Oxygen vacancies can be excluded as a possible explanation. A possibility here is that the topmost SrO layer, in the case of mixed termination, forms an ordered overlayer. This also explains the different periodicity observed, since the ordering is then determined by the coverage of SrO^{xv}, which might vary over different samples, whereas for full SrO coverage, no ordering is visible. Ordering of an overlayer, presumably SrO islands, has been reported earlier^{16,17,18}. Similarly, Andersen et al. observed Ca impurity ordering at the substrate surface after oxygen annealing⁵⁵. A more detailed study is in progress.

3.5 Epitaxy

3.5.1 Homoepitaxy

Figure 3.7 a) shows an AFM image after deposition of several unit-cell layers of $SrTiO_3$ on annealed $SrTiO_3$. Clearly, distinct regions with different morphologies are visible. The inclined view of the same surface in Fig. 3.7 b) elucidates the existence of different regions. Note that RHEED intensity oscillations where hardly observed during this experiment. The reason for this is the existence of two terminations (segregated into distinct regions) with apparently a different growth mode.

xv A systematic study by depositing an increasing amount of SrO is difficult since after surface annealing, a rather stable imprint of the terrace structure is formed.

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Figure 3.7: AFM images after deposition of $SrTiO_3$ on a) mixed terminated surface with b) inclined view of the same surface (deposition at 760° C and 10 Pa), c) fully treated surface and d) SrO terminated surface (deposition at 850° C and 3 Pa).

When a similar experiment is performed on a single terminated surface^{xvi}, see Fig. 3.7 c), only relatively large islands with a circular appearance are observed. The same island shapes have also been observed for SrTiO₃ homoepitaxy by others^{56,57}. Under the same conditions, a totally different picture arises on a SrO terminated surface^{xvii}, see Fig. 3.7 d); only very small islands exist, very hard to detect with the currently used tip and convolution effects dominate. In both cases, very pronounced RHEED intensity oscillations are observed. These results suggest that the kinetics is predominantly affected by the nature of termination. However, we have to keep in mind that the latter surface could be the result of additional nucleation induced by the underlying SrO layer. The effect of the deposition rate on the island size must also be considered. Nevertheless, this cannot explain the large difference observed in Fig. 3.7. Finally, deposition experiments by D.-W. Kim et al. on LaAlO₃ substrates also revealed a dependence of the growth mode on the termination of the substrate⁵⁸.

 $^{{}^{}xvi}$ Here, very pronounced intensity oscillations where observed and deposition was halted at one and half unit-cell layer.

 $^{^{}xvii}$ We deposited one unit-cell layer of SrO (monitored in situ with RHEED) on a $\rm TiO_2$ terminated surface in order to change the termination.

3.5.2 Deposition of TiO₂ and SrO

By depositing the constituents SrO or TiO_2 of $SrTiO_3$ one is able to change the composition of the surface. Here, we studied the effect on the morphology and the option to control the termination in an alternative way.

First, we deposited TiO_2 on an as-received surface and observed different wetting related to the two possible terminations, see Fig. 3.8 a)^{xviii}. Clearly, segregation has taken place: small areas with very small islands (height is difficult to determine) are seggregated from large areas with relatively large islands of unit-cell height (SrTiO₃!) and isomorphic to the ones observed in Fig. 3.7 c). The boundaries between these areas (some are indicated in Fig. 3.8 a), are strikingly sharp and are rounded in shape. Effectively, two mechanisms play a role leading to the observed morphology: recrystallization due to annealing of the surface and, the migration of as-deposited ad-atoms.

LFM indicated that the large flat-topped islands are formed on the low friction domains, whereas areas with very small islands correspond to high friction. In line with the discussion in section 3.4.2, this points towards a mechanical origin of the friction contrast.

When this surface is subsequently annealed, further segregation takes place. Figure 3.8 b) shows the resulting surface as seen with AFM. Regularly spaced terraces separated by unit-cell steps (SrTiO₃) with an extremely flat appearance, comparable to the optimally treated surfaces, are visible. In addition, elliptically shaped holes show up and in the cross section in Fig. 3.8 c) it is seen that they are exactly half-a-unit-cell of SrTiO₃ deep, indicative of a locally different termination.

Second, the same experiment was performed on annealed surfaces. Figures 3.8 d) and e) show morphologies comparable to Fig. 3.8 a), apart from the already existing terrace structure. Moreover, the large islands migrated towards the terrace 'up' steps, whereas the rough areas (indicated in Fig. 3.8 d)), reside near the 'down' steps. Again the difference in mobility for different termination is demonstrated here.

From the above we conclude that the deposited TiO_2 reacts with the SrO on the surface to form $SrTiO_3$ islands with TiO_2 termination. Apparently, the amount of TiO_2 deposited^{xix} did not match the initial amount of SrO, resulting in residual areas with a SrO termination. A possible scenario would be to control the termination through correcting the surface stoichiometry by deposition, and arriving at the maximum RHEED intensity monitoring when

 $^{^{\}rm xviii}$ All depositions are carried out at 850°C using single crystals as targets. The O_2 pressure was kept at 10 Pa for the deposition of TiO_2, whereas 3 Pa was used for SrTiO_3.

xix During deposition of TiO_2 , RHEED did not show any oscillatory behavior. The deposition rate of TiO_2 was therefore difficult to determine.

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Figure 3.8: AFM images a) after deposition of TiO₂ at 850 °C on as-received SrTiO₃, b) subsequently annealing of the surface (at 950 °C) with c) cross-section, d), e) after deposition of TiO₂ on an annealed substrate, f), g) after deposition of TiO₂ on a fully treated surface, with h) cross-section of g), i) after deposition of SrO and j) subsequent deposition of TiO₂ (at 850 °C).

sufficient material is deposited. For SrO, this has been shown on annealed substrates⁵⁹, also see below. In case of TiO_2 deposition, one would have to use a much higher deposition temperature.

After TiO₂ deposition on fully treated surfaces, see Fig. 3.8 f), a totally different picture arises. On the SrTiO₃ terraces dendritic-shaped islands are formed, which are ~5-6 Å high. These island are homogeneously distributed, indicating a single termination. Only near the steps of the underlying substrate, a lower island density is observed. A closer look at Fig. 3.8 g) reveals that some material has decorated the terrace ledges. Also in this figure a zone with a lower island density along the ledges can be identified. The width of this zone is a measure of the mobility of TiO₂ on such a surface, for the given deposition conditions. The same holds for the holes (indicated in Fig. 3.4 f)); for a certain radius, island appear inside the hole. Finally, in Fig. 3.8 h), a cross-section of the surface in Fig. 3.8 g), shows that, both the islands as well as the material along the step ledges have the same height.

The RHEED patterns recorded after deposition did not show any additional spots but merely an increase of the diffuse background intensity. This indicates that no lateral ordering of the TiO_2 islands with respect to the underlying substrate lattice has occurred; the interaction of the film material and the substrate is relatively weak. From literature it is known that a B-site material does not wet a B-site terminated crystal⁶⁰, which is in agreement with our results.

Both theoretically⁶¹ as well as experimentally^{59,60}, it has been shown that only one unit-cell layer of SrO with complete wetting can be deposited on a TiO₂ terminated substrate. Indeed, the RHEED pattern, which consists of two-dimensional spots only (see Fig. 3.6 f)), indicates that the surface is highly ordered at one unit-cell layer. The deposition rate could be monitored with RHEED, since the specular intensity exhibits a clear maximum after completion of one unit-cell layer. If more material is deposited, however, the specular intensity drops rapidly and no oscillatory behavior is observed.

Figure 3.8 i) shows the AFM micrograph after SrO deposition (>1 unit-cell layer) on an annealed surface (i.e., mixed termination). The light areas correspond to height differences of the order of 1 nm. It is clear that wetting is incomplete, which can be understood by considering the Sr-O distance in the SrTiO₃ crystal (2.76) compared to Sr-O in pure SrO (2.57). After deposition of one unit-cell layer, the perovskite stacking changes to a 'NaCl' stacking, that is stressed in the case of SrO and responsible for the observed wetting. For example, the lattice parameters of the rocksalt BaO structure is more compatible with SrTiO₃, and deposition of more than one unit-cell layer is feasible, which has been shown by Tsuchia et al.⁶⁰.

Finally, only SrTiO₃ unit-cell steps become visible, if, subsequently, TiO₂ is deposited, see Fig. 3.8 j). This indicates that the TiO₂ reacts with the surplus of SrO and the large height differences disappear. This supports the above observations of TiO₂ deposited on mixed terminated surfaces.

3.5.3 Deposition of SrCuO₂ and YBa₂Cu₃O₇

When depositing complex oxides with a similar stacking sequence as the substrate material (i.e., also consisting of AO and BO₂ stacking, where A and B may represent different elements, e.g., A=Y, Ba in YBa₂Cu₃O₇), nature wants to continue this sequence or allow a translation of (1/2, 1/2, 0) by stacking AO on AO. The option of BO₂ on BO₂ is hardly ever observed. Therefore, the termination of the substrate determines the terminating plane of the deposited material if one assumes that oxides grow unit-cell by unit-cell (e.g., 'half' unit-cells or other combinations may not be charge neutral). Two examples treated here are SrCuO₂ and YBa₂Cu₃O₇.

In the case of $SrCuO_2$, the effect of the termination on the stacking order is observed with RHEED, see Fig. 3.9. When deposition takes place on an optimally treated $SrTiO_3$ substrate, the diffraction pattern reveals incommensurate streaks next to the (0k) streaks, as indicated by arrows in Fig. 3.9 a). Compared to the pattern observed after deposition on a SrO buffered surface, no such streaks are present, see Fig. 3.9. b). Similar patterns were observed by others after sequential deposition of SrO and $CuO_2^{62,63,64,65}$. Therefore, we conclude that the initiation of the stacking sequence is determined by the termination of the substrate. Some groups reported a preferred termination for $SrCuO_2^{66,67}$, i.e., the Sr-plane and, therefore, a SrO terminated substrate is expected to give optimal growth. However, we did not observe any difference in the film quality for different surface termination. The reason might be that by depositing SrO, an initially mixed surface is transformed to a uniformly terminated surface.

This picture is much more complicated for $REBa_2Cu_3O_7$ (RE= Rare earth elements or Y, 123 materials). Several groups proposed a stacking sequence for the c-axis⁶⁸ 123 materials on SrTiO₃.

Based on HREM observations⁶⁹ and X-ray standing wave measurements⁷⁰, BaO is the expected interface layer with a TiO₂ terminated substrate surface, whereas the CuO_x chain layer lies next to a SrO terminated surface. On the other hand, shell model calculations⁷¹ indicate that for the fully oxidized or orthorhombic phase, the CuO_x chain layer forms the most stable surface layer, which was also observed by LEIS⁷² and by AFM for NdBa₂Cu₃O_y⁷³.

The -CuO₂-BaO plane is calculated to be the most stable plane in case of the tetragonal phase $REBa_2Cu_3O_6$. This phase is formed during deposition at high temperature⁷⁴, as confirmed by HREM⁷⁵.

On a TiO₂ terminated substrate, the stacking sequence for co-deposited and MBE grown films can be understood as follows according to J.G. Wen et al.⁶⁹ and V.C. Matjiasevic et al.⁷⁶: bulk-SrO-TiO₂-BaO-CuO₂-Y-CuO₂-BaO-CuO_x-bulk. In order to explain overgrowth of substrate terrace steps, T. Haage et al.⁷⁷ proposed a variable stacking sequence, with an additional possibility of one extra BaO-CuO₂ block at the interface. Note that all the above observations were made for films grown on annealed substrates, i.e., with a mixed termination.



Figure 3.9: RHEED pattern after deposition of SrCuO₂ at 600 °C and 3 Pa on a)TiO₂ and b)SrO terminated SrTiO₃, c)~1 unit-cell layer, d) ~4 unit-cell layers of YBa₂Cu₃O₇ at 780 °C and 20 Pa on a TiO₂ terminated substrate, e) idem on a SrO terminated substrate and f) suggested model for the stacking sequence of YBa₂Cu₃O₇ on a TiO₂ surface.

We observed immediately after starting the deposition of YBa₂Cu₃O₇ on a fully treated surface transmission spots in the RHEED pattern, indicated in Fig. 3.9 c). From the positions of these spots, we derive a lattice parameter close to the one of CuO and, therefore, we conclude that precipitates have formed. For thicker films, these precipitates seem to be overgrown by the 123 phase, as seen by RHEED in Fig. 3.9 d). In contrast, no such spots were observed for SrO terminated surfaces, see Fig. 3.9 e). Similar observations were done by others⁶⁰. We propose the following model which might explain these observations: BaO forms in the case of a TiO₂ terminated substrate surface, both, the interface as well as the terminating layer of the first unit-cell, see Fig. 3.9 f), whereby excess CuO precipitates. Note that one deposits the stoichiometric amount for 123. In other words, the first cell nucleating on the SrTiO₃ surface has a 122 stoichiometry. For the SrO terminated substrate the stacking sequence would be: $-TiO_2$ -SrO-CuO_x-BaO-CuO₂-Y-CuO₂-BaO. Both models are in agreement with the observations mentioned above.

3.6 Conclusions

The termination of perovskite (001) crystals determines many properties of the surface. These have been studied by analyzing $SrTiO_3$ substrates, a model perovskite, after different treatments, yielding various surface compositions, i.e., TiO_2 , SrO or a mixture of both.

First of all, the morphology strongly depends on the composition of the topmost layer of the crystal. The two possible terminations become visible through segregation into domains after annealing. These domains obviously have different thermodynamic properties resulting in distinct ledge shapes, i.e., the rounded ledges versus the ledges aligned along the principal axes of the crystal. The fact that the temperature and annealing time also determine the ultimate morphology depending on the surface treatment, suggest that the termination influences the kinetics on the surface. The smoothest and most reproducible surface morphology, is obtained after the optimal treatment, consisting of a two-step etching procedure followed by annealing at high temperature. By the enhanced selectivity for SrO using this method, apparently a single TiO_2 terminated surface with superior properties with respect to stability and morphology is obtained. Since the etching time is reduced, damaging of the surface due to prolonged exposure to the etchant is avoided.

RHEED analysis reveals that the highest degree of crystallinity on the surface is obtained after the full treatment. Furthermore, the existence of higher-order spots corresponding to a superstructure periodicity is shown on annealed surfaces, whereas such spots are absent after the proper treatment. This observation can possibly be explained by ordering of the SrO overlayer.

We used SrO and TiO₂ deposition experiments and different wetting behavior as a chemical probing method. Only on properly treated surfaces an isotropic morphology is observed, whereas otherwise always distinct regions become visible. Furthermore, it is suggested that the composition of the surface can be controlled, yielding single termination, provided that the deposition rate of the constituents is known. From the TiO₂ experiments we also conclude that high friction domains in Fig. 3.3 b) correspond to TiO₂ termination.

Finally, from initial growth studies we conclude that thin film growth on these substrates that results in highly ordered structures requires a single termination. For homoepitaxy, the termination mainly determines the kinetics of the deposited material. In the case of hetero-epitaxy (SrCuO₂ and YBa₂Cu₃O₇), the stacking sequence is determined by the terminating layer. For YBa₂Cu₃O₇ the best results for initial growth are obtained with SrO terminated surfaces.

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Homoepitaxy of SrTiO₃

4.1 Introduction

In order to be able to create a crystal structure by depositing consecutive unit-cell layers of different materials, a layer-by-layer growth modeⁱ is a prerequisite: nucleation of each next layer may only occur after the previous layer is completed. Occasionally, the deposition conditions such as the substrate temperature and ambient gas pressure (oxygen in the case of oxide materials) can be optimized for true two-dimensional (2D) growth, e.g., this is the case for homoepitaxy on SrTiO₃ (001).

In case of homoepitaxy, kinetic factors determine the growth mode, whereas in case of heteroepitaxy also thermodynamic factors, e.g. misfit, are also important. In fact, layer-by-layer growth is always predicted for homoepitaxy, from a thermodynamic point of view¹. However, during deposition of different kinds of materials, i.e., metals, semiconductors and insulators, independently of the deposition technique, a roughening of the surface is observed. Assuming only 2D nucleation, determined by the supersaturation², limited interlayer mass transport results in nucleation on top of 2D islands before completion of a unit-cell layer. Still, one can speak of a 2D growth mode. However, nucleation and incorporation of ad-atoms at step edges is proceeding on an increasing number of unit-cell levels, which results in damping of the RHEED intensity oscillations. In fact an exponential decay of the amplitude is predicted assuming conventional MBE deposition conditions³.

 $^{^{\}rm i}$ A 2D growth mode can either be layer-by-layer growth or step-flow growth. However, in case of step-flow growth, rate control is not possible.

To understand the implications of the characteristics of PLD on growth, which are expected to be kinetic in origin and have been discussed in chapter 2, homoepitaxy is the perfect system to study.

In situ RHEED studies of kinetics of growing systems have been used, as explained by the following examples.

First, the transition from step-flow growth to layer-by-layer growth on vicinal surfaces has been used to estimate the diffusion parameters⁴. With the beam directed parallel to the terraces, intensity oscillation disappear at a critical temperature, when all the material is incorporated at the vicinal steps. The critical diffusion length is then of the order of the terrace width. This simple picture has been extended to include, for instance, non-linear effects^{5,6} and the fact that the transition is not sharp^{7,8,9}.

Secondly, another approach has been given by Vvedensky et al.¹⁰, by studying the relaxation of the RHEED intensity after interruption of the MBE growth. Comparing the characteristic relaxation times observed during experiments to Monte Carlo simulations, the participating microscopic events can by identified provided that all the relevant mechanisms are included in the simulation model. Note that this approach is closely connected with PLD, since after each laser pulse, relaxation of the RHEED intensity is observed and can be viewed as a kind of interrupted growth.

Finally, the relaxation behavior of the RHEED intensity after each laser pulse has been studied in case of PLD of $YBa_2Cu_3O_7^{11}$, SrO^{12} and $SrTiO_3^{13}$ on $SrTiO_3$. By time-resolved RHEED, the relaxation times for different temperatures have been measured and an estimate of the diffusion barrier is obtained.

Here we have studied the relaxation behavior of the RHEED intensity during homoepitaxy of $SrTiO_3$ as a function of the deposition temperature and pressure. In the regime where true layer-by-layer growth or true step-flow growth is observed, a simple model for diffusion of atoms on the surface can be applied, an extension of the known steady-state theory¹⁴, which accounts for the measured characteristic relaxation times. We derive an activation energy for diffusion from these measurements.

From the point of view of phase stability for many oxide materials, temperature and oxygen pressure have to be fixed. The only way to obtain true layer-by-layer growth is to apply manipulated growth, reducing the island size during growth. We propose a method, based on the high supersaturation attained during PLD; Pulsed Laser interval Deposition. Although there is the general impression that, due to the pulsed deposition, the growth mechanism differs partially from continuous physical and chemical deposition techniques, this fact has hardly been made use of so far. Here, we introduce a growth method, based on a periodic sequence: fast deposition of the amount of material needed to complete one monolayer followed by an interval in which no deposition takes place and the film can reorganize. This makes it possible to grow in a layer-by-layer fashion in a growth regime (temperature, pressure) where otherwise island formation would dominate the growth. By using the parameters obtained from experimental relaxation and oscillation data, solidon-solid model Monte Carlo simulations are used to further investigate the characteristics of the interval deposition method.

4.2 Growth modes during homoepitaxy

4.2.1 Standard nucleation theory

An important quantity which determines whether layer-by-layer growth occurs is the rate of two-dimensional nucleation J_0 (atomistic theory^{1,2}):

$$J_0(n_s) = C^* n_s^{n^* + 1}$$
(4.1)

where n^* is the critical number of atoms in a nucleus to become stable for a given supersaturation, $C^* \equiv C(n^*)$ is a function of the critical size n^* and n_s is the ad-atom density on the surface. Important here is that the rate of nucleation increases with the ad atom density. Thus, the high deposition rate typical for PLD during a laser pulse (see also chapter 2), ensures a high nucleation rate on the surface during the pulse. For example, sputter deposition, with a much lower deposition rate, yields a surface with a lower island density. Subsequently, atoms can rearrange through different mechanisms: incorporation of material at steps, ripening and/or coalescence. Because of the pulsed way of deposition, the processes of nucleation and rearrangement are expected to be separated in time. The transport properties of the material on the surface as a function of the deposition conditions eventually determines the surface morphology.

To illustrate this, we first look to the stationary diffusion problem for a constant flux of particles arriving on a circularly shaped island, which subsequently diffuse to the island edge to be incorporated there. In polar coordinates, the diffusion equation becomes:

$$\frac{\mathrm{d}^2 \mathbf{n}_s}{\mathrm{d}r^2} + \frac{1}{\mathrm{r}}\frac{\mathrm{d}\mathbf{n}_s}{\mathrm{d}r} + \frac{\mathrm{R}}{\mathrm{D}_s} = 0 \tag{4.2}$$

Here, R is the constant arrival rate of particles and D_s the diffusivity. The boundary condition is given by:

$$\mathbf{n}_{\mathbf{s}}\left(\mathbf{r}=\mathbf{r}_{\mathbf{0}}\right)=\mathbf{n}_{\mathbf{s}\mathbf{e}}\tag{4.2}$$

with $n_{se} {\sim} 0$ the equilibrium density at an edge, i.e., the edge acts as a sink for particles, and

$$\left(\frac{\mathrm{dn}_{\mathrm{s}}}{\mathrm{dr}}\right)_{\mathrm{r}=0} = 0 \tag{4.2}$$

The nucleation frequency on the island is given by:

$$\widetilde{\mathbf{J}}_{0} = \int_{0}^{r_{0}} \mathbf{J}_{0}(\mathbf{r}) 2\pi \mathbf{r} d\mathbf{r}$$
(4.3)

From eq. (4.1) and eq. (4.3) and solving Eq. $(4.2)^{15}$, one gets a relation for the nucleation frequency as a function of the island radius¹⁶:

$$\widetilde{J}_0 \propto r_0^{2(n^*+1)} \tag{4.4}$$

Thus as the island size increases, the probability of formation of another island on top of this island increases as well. The condition for true layer-by-layer growth for a surface consisting of such islands is given by:

$$N = \int_{0}^{T} \widetilde{J}_{0}(\mathbf{r}_{0}) dt = 1$$
(4.5)

where $T=N_0/R$ is the time for completion of one unit-cell layer, i.e., the moment of nucleation of a new layer and the coalescence of the islands coincide. If the diffusivity is too low for particles to reach the island edge or if an additional barrier¹⁷ exists for particles to come off an island, the transport of material to the island edge is hindered, and the probability for nucleation on top of an island increases.

For PLD, the stationary diffusion eq. (4.2) has to be replaced by a time-dependent equation:

$$\frac{\partial^2 \mathbf{n}_s}{\partial \mathbf{r}^2} + \frac{1}{\mathbf{r}} \frac{\partial \mathbf{n}_s}{\partial \mathbf{r}} = \frac{1}{\mathbf{D}_s} \frac{\partial \mathbf{n}_s}{\partial \mathbf{t}}$$
(4.6)

with the initial condition $n_s(r,0) = n_0$, the density of particles just after one laser pulse (approximately instantaneously deposited) and with the boundary condition given by eq. (4.2), analogous to B. Matuftschiev¹⁴, but who considered only the steady state solution. The solution of eq. (4.6) is of the form¹⁸:

$$n_{s}(\mathbf{r}, \mathbf{t}) = n_{0} \sum_{m=1}^{\infty} A_{m}(\mathbf{r}; \mathbf{r}_{0}) \exp\left(-\frac{\mathbf{t}}{\tau_{m}}\right)$$

$$(4.7)$$

where $A_m(r;r_0)$ are pre-factors depending only weakly on r and $r_0,$ and τ_m are given by:

$$\tau_{\rm m} = \frac{r_0^2}{D_{\rm s} \mu^{(0)} {}_{\rm m}^2} \tag{4.8}$$

Eq. (4.7) converges rapidly and, for long enough times, only the first term needs to be considered ($\mu^{(0)}{}_m$ are the roots of Bessel functions, $\mu^{(0)2}{}_1$ =5.05). Since from experiments it is concluded that SrTiO₃ has no additional edge barrier¹⁹, factors which determine whether nucleation will occur on top of the island, are

the diffusivity and the size of the island. The diffusivity can generally be expressed as:

$$D_{s} = va^{2} \exp(-\frac{E_{A}}{k_{B}T})$$
(4.9)

where E_A is the activation energy for diffusion, ν is the attempt frequency (10¹³ Hz) and a is the 'jump distance' (3.9 Å).

From eq.'s (4.1) and (4.7) we conclude that, for a given island distribution on the surface, parameterized by r_0 , the diffusivity given by eq. (4.9) determines whether material finds the existing ledges formed by the islands on the surface, or nucleates. Eq. (4.9) subsequently tells us that for a given barrier E_A the temperature should be increased to obtain layer-by-layer growth. Finally, from both eq. (4.4) as well as eq. (4.8), it is clear that a small value of r_0 during growth favours layer-by-layer growth.

4.2.2 Experiments; time resolved RHEED

As been shown in section 2.3.4.1, Fig. 2.4 and Ref. 20, true two-dimensional RHEED intensity oscillations are observed when $SrTiO_3$ is deposited with PLD, at a temperature of 850 °C and an oxygen pressure of 3 Pa. Also at lower temperatures, see Fig. 4.1, this behavior is still visible. In this figure, another feature of PLD is exemplified- the relaxation phenomenon. In the case of PLD, a typical value for the deposition rate within one pulse is of the order of 10 μ m/s^{21,22}. Therefore, from eq. (2.3), a high supersaturation is expected when the plume is on and thus the number of 2D nuclei can be very high. Subsequently, when the plume is off, larger islands are formed through re-crystallization, manifested as the typical relaxation of the RHEED intensity of the specular spot²³. The insets in Fig. 4.1 are enlargements of the relaxation after a laser



Figure 4.1: Modulation of the specular RHEED intensity due to the pulsed way of deposition (T=750 $^{\circ}$ C, pO₂=3 Pa) the insets give enlarged intensity after one laser pulse plus the fit with eq. (4.11) to give characteristic relaxation times. Here, a deposition rate of 19 pulses per unit-cell layer was inferred.

pulse. From this it is clear that the characteristic relaxation time depends, among other things, on the coverage during deposition.

The relatively high temperature, in combination with a low oxygen pressure, enhances the mobility of the ad-atoms on the surface and, therefore, the probability of nucleation on top of a 2D island is minimized. The asdeposited ad-atoms can migrate to the step edges of 2D islands and nucleation only takes place on fully completed layers.

In chapter 2, we already argued that the oscillations correspond to the fluctuations of the step density on the surface, assuming that nucleation takes place exactly when each unit-cell layer is completed and N₀ nuclei are formed. The step density is then given by eq. (2.16). In addition, if this model is applicable, only diffusion of material towards ledges has to be considered. Therefore, we assume that, in this growth regime, the relaxation behaviour of the intensity after each laser pulse can be attributed to diffusing particles on the surface, treating each particle as a diffuse scatterer^{ii,24}. In fact, we can integrate $n_s(r,t)$, given by eq. (4.7), over the surface of the island, to describe the intensity variations of the specular reflection after each laser pulse. From eq. (4.7) we expect an exponential increase of the intensity after each laser pulse, when one assumes a direct coupling between the particle density and the RHEED intensity. The intensity during relaxation is approximately given by:

 $I \propto 1 - \overline{n}_{s}(t) \tag{4.10}$

where the ad-atom density is averaged over the surface of the circular island. Using this approach we can extract the kinetic factors important for layer-by-layer growth 25 .

When a step flow like growth mode is observed, also the relaxation is expected to be a function of the ad-atom density on the terraces, now determined by the average terrace width on the surface.

At a given coverage, r_0 now represents an average maximum distance for material to diffuse in order to find a ledge (the mean field approximation). In the first approximation, r_0 is considered to be constant for one laser pulseⁱⁱⁱ: We evaluated the relaxation times by fitting the intensity for each laser pulse for different coverage's, temperatures and pressures using eq. (4.10). Provided that the assumptions for layer-by-layer growth are still valid, we can use a function of the form:

$$I \sim I_0 (1 - \exp(-\frac{t}{\tau})) \tag{4.11}$$

ⁱⁱ In case of diffraction theory, J.P. van der Wagt derived an expression for the contribution of the ad-atom density on the surface to the intensity, which is zero for the in-phase condition. ⁱⁱⁱ For this to be true, the amount of deposited material per laser pulse has to be sufficiently small.



Figure 4.2: The logarithm of the relaxation times obtained from a fit with eq. (4.11) for different coverages and different temperatures, in the Arrhenius form, at a) 20 Pa and b) 3 Pa.

where τ given by eq. (4.8), if only the first term of eq. (4.7) is used in eq. (4.10). For some examples of fits with eq. (4.11) see the insets in Fig. 4.1.

The relaxation times found as a function of temperature are given in Fig. 4.2 for 20 Pa (a) and 3 Pa (b). The figures represent Arrhenius plots for different values of the coverage, and for a fixed coverage we observe a linear dependence. From the slope of these lines, a value for E_A , using eq.'s (4.8), (4.9), can be calculated. The fact that these lines do not coincide can be understood from the fact that different values for the coverage mean a different step density, or in terms of eq. (4.8) a different r_0 . Moreover, from the abscissa, for each θ , a value for r₀ can be calculated, and these can be shown to correlate with each other²⁶. Apart from the dependencies described above we have to take several other things into account. First, for θ =0-0.4, in Fig. 4.1, the relaxation behavior usually does not correspond to an exponential increase. For these pulses, the step density itself is a rapidly changing function, affecting the intensity strongly: the assumption in the model that r_0 is constant is not valid here. Second, relaxation is difficult to observe at coverages close to a minimum in intensity where the relaxation times are or the order of the sampling rate of the frame-grabber/CCD-detector combination (~15 Hz) and because of the relatively high noise level. This is indicated in Fig. 4.2 a) by the error bars; closer to a minimum intensity the relative error increases. Still, the slopes are constant for all the measurements at a given pressure. We derive a value for E_A of 0.48 \pm 0.05 eV for 3 Pa and 2.2 \pm 0.2 eV for 20 Pa.

This difference can be explained by examining the pressure dependence of the relaxation times. In Fig. 4.3, the typical relaxation times are plotted as a function of the deposition pressure (at a constant temperature of 850 °C). Here, it becomes clear that starting at 3 Pa, the relaxation times sharply increase with pressure. However, at a pressure of about 9 Pa, this trend stops, and a much weaker dependence is observed at higher pressures. This can be



Figure 4.3: Relaxation times as a function of the deposition pressure for θ ~0.95, the temperature was set at 850 °C.

explained by assuming that the kinetic energy of the incoming particles at a given distance from the target, see chapter 2, eq. (2.1), is a function of the gas pressure. Above a certain pressure, here 9 Pa, the arriving particles are thermalized.

This was predicted theoretically by Strikovsky et al.²⁷, noting that the critical substrate-to-target distance and pressure for thermalization are related. Subsequently, we assume that the energy of the incoming particles influences the diffusivity on the surface²⁸. Thus one expects below 9 Pa a stronger effect of the pressure on the relaxation times, whereas beyond that pressure a weaker effect is expected. From this we conclude that the actual diffusion activation energy for SrTiO₃ lies closer to the value found for 20 Pa. This also can explain the different activation energies found for YBa₂Cu₃O₇ by B. Dam et al.²⁸ compared to the values found by Karl et al.¹¹. Their experiments were performed at different pressure/distance conditions.

The value for 20 Pa will be used in simulations described in section 4.3.3, where we don't take the energy of arriving particles into account. Effectively, the energy barrier for diffusion is reduced with decreasing pressure, which is seen in the lower value for E_A for 3 Pa, compared to 20 Pa, resulting in faster relaxation. Physically, the extra energy of the particles has to result in a higher effective temperature on the surface. However, through dissipation of this energy to the crystal this temperature is not constant, which complicates a theoretical description. Obviously, when comparing simulations with experiments done at lower pressure, one has to take this correction into account, see for example the work of Taylor et al.²⁹.

Depositing SrTiO₃ at the temperature of 800 °C and the oxygen pressure of 10 Pa, with a continuous pulse frequency of 1 Hz, the surface is evolving from a single-level system to a multi-level system, as indicated by the strong damping of RHEED intensity oscillations in Fig. 4.6. A higher pressure, just beyond the critical point in Fig. 4.3, causes the mobility of the particles on the surface to

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Figure 4.4: Intensity of the specular reflection during 'continuous' deposition of $SrTiO_3$ at 800 °C and 10 Pa.

be lower. The probability of nucleation on top of a two-dimensional island has increased, resulting in the observed roughening. In Fig. 4.5 a), AFM shows the surface after deposition of a 30 nm thick $SrTiO_3$ film. Also from this image it is clear that the surface consists of multiple levels, at least four unit-cell levels can be seen.

To overcome the roughening at lower temperatures and higher pressures, several groups suggested the use of periodically interrupted growth^{30,31}, leading to smoother surfaces. Any roughness that has developed during deposition will be leveled off by annealing the surface. This option is especially useful in the case of co-evaporated thin films. However, one still needs a considerable mobility on the surface, despite the longer waiting times. Sometimes increasing the temperature to increase the activity is an option. In the next section, a much more effective method is presented, without changing the temperature and pressure that are determined by the phase stability of the film material.



Figure 4.5: AFM image of a) $SrTiO_3$ surface after continuous deposition and b) after interval deposition both of a ~30 nm thick film.

4.3 Growth manipulation; Interval deposition

4.3.1 Growth manipulation

Usually, for epitaxy of complex oxide materials, the regime of temperatures and pressures is limited by the stability of the desired phases, e.g., $YBa_2Cu_3O_7$ can only be grown in a specific temperature and pressure regime³². At low temperatures a-axis oriented films are formed, whereas at high temperatures the material decomposes. In order to get layer-by-layer growth, without changing the deposition conditions, we have to influence the last parameter at our disposal, r_0 .

Several groups have investigated the possibility to apply a form of growth manipulation to promote interlayer mass transport. G. Rosenfeld et al.^{33,34} suggest to periodically vary the temperature, vary the growth rate or apply ion bombardment to increase the number of nucleation sites in the initial stage of growth and thus decrease the average island size (r_0). This should enhance the transport of material from an island to a lower-lying level in later stages, which can be understood by eq.'s (4.4) and (4.8).

Because of the phase stability mentioned above, changing the temperature (or oxygen pressure) is not an option. Periodical ion bombardment is difficult to realize, while still maintaining the right stoichiometry in the case of oxide materials. Especially in artificial layered structures mixing of neighboring layers is undesirable.

Growth-rate manipulation to impose layer-by-layer growth could be a possibility to overcome this problem, where fast deposition at the beginning of each unit-cell layer is used to promote the formation of islands, thereby reducing their average size. However, the problem for PLD is not the formation of nuclei at the beginning of each unit-cell layer, but is more in the subsequent coalescence and ripening in between the laser pulses.

A completely different approach would be to use surfactants³⁵. However, a suitable candidate for complex oxides has, to our knowledge, not yet been found.

4.3.2 Pulsed Laser interval Deposition

Since small islands promote interlayer mass transport, one can utilise the high supersaturation achieved by PLD (see section 2.2.3) by maintaining it for a longer time interval and suppressing subsequent coarsening.

Accordingly, to circumvent premature nucleation due to the limited mobility of the ad-atoms at a given pressure and temperature, causing a multi-level 2D growth mode, we have utilized interval deposition. Exactly one unit-cell layer is deposited in a very short time interval, i.e., of the order of the characteristic relaxation times, see section 4.4.3, followed by a much longer interval during which the deposited material can rearrange. During the short deposition intervals, only small islands will be formed due to the high supersaturation typical for PLD. The probability of nucleation on the islands increases with

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Figure 4.6: Intensity variations of the specular reflection during interval deposition using the laser repetition rate of 10 Hz.

their average radius² and is, therefore, small in the case of fast deposition. The total amount of pulses needed to complete one unit-cell layer has to be as high as possible, to minimize the error introduced by the fact that only an integer number of pulses can be given. Both, a high deposition rate and sufficiently accurate deposition of one unit-cell layer can be obtained by PLD using a high laser pulse frequency.

To prove the validity of this growth method, $SrTiO_3$ was deposited using the KrF excimer laser with maximum repetition rate of 10 Hz as well as the XeCl excimer laser with a maximum repetition rate of 100 Hz. We used the same oxygen pressure and substrate temperature as in the case of continuous deposition where strong damping of the specular intensity is observed (Fig. 4.4). During deposition the growth was monitored using high pressure RHEED^{iv}. The incident angle of the 20 keV electrons was set at 1°. Wafers with the smallest miscut angles (<0.2°) were selected for this study to exclude step-flow like growth behavior.

Figure 4.6 shows the RHEED intensity during 10 cycles of deposition (at 10 Hz) followed by a period of no deposition. In this case the number of pulses needed per unit-cell layer was estimated to be about 27. In Fig. 4.8 a) the intensities at each maximum are compared for both methods. The decay of the intensity after each unit-cell layer is significantly lower compared to the situation in Fig. 4.4.

From Fig. 4.6, it can be seen that the recovery of the intensity after each deposition interval is fast at the beginning of deposition. The decrease in intensity can be ascribed to the fact that only an integer number of pulses can

 $^{^{\}rm iv}$ The deposition rate per pulse was estimated by depositing one unit-cell layer at low frequencies followed by annealing at 850 $^{\circ}{\rm C}$ to restore the initial surface.

be given to complete a unit-cell layer, besides nucleation on the next level. A slightly lower or higher coverage causes a change in recovery time. This situation deteriorates with every subsequent unit-cell layer, as follows from increasing relaxation times.

The intensity change during deposition of one unit-cell layer at 10 Hz is given in Fig. 4.8 b). The shape of the intensity curve at 10 Hz strongly resembles the calculated parabola from the intensity change of a two-level growth front with randomly distributed islands and island sizes³⁶. From the shape of the curve it can be seen that the time needed to deposit one unit-cell layer is still too long. This is because the deposition time interval of 2.7 sec. is longer than the characteristic relaxation time (~0.5 sec.). However, a significant suppression of the formation of a multilevel system has already been achieved at this point.

To avoid the above mentioned situation, a similar experiment was performed using the XeCl laser with a pulse frequency of 100 Hz. The number of pulses needed to complete one unit-cell layer was estimated to be 43 (i.e., deposition time of 0.43 sec.). Here, the increase of the RHEED intensity occurs after the deposition interval and recovers almost to the same level. The fact that the overall RHEED intensity slightly decreases is an indication that the number of 43 pulses is not exactly correct. If we continue the growth with 43 pulses per unit-cell layer, the RHEED intensity will decrease continuously. Therefore, we periodically changed this number to 42 and observed, after an initial decrease of the interval maxima, that the intensity increased again, indicating that the surface becomes smoother. We repeated this procedure several times and in Fig. 4.7 an example of this sequence is given. Only the intensity change during the final 30 intervals of a total of 90 intervals (each constituting one unit-cell layer) is depicted here. This led us to the possibility to, partly, correct for the error due to the integer number of pulses: adjusting



Figure 4.7: The intensity changes of the specular beam during interval deposition of $SrTiO_3$; the repetition rate used here is 100 Hz. The number of pulses needed to complete one unit-cell layer is estimated to be 43. Sometimes, the number of pulses was changed by one, as indicated in the graph, to fine-tune the amount of deposited material.



Figure 4.8: a) Intensity variation of the specular beam during one deposition interval (10 Hz) and subsequent relaxation. b) Intensities of the maxima during continuous deposition (reversed triangles compared with the maxima during interval deposition at 10 Hz (upright triangles).

the amount of deposited material, by changing the number of pulses by one just after a decrease in maximum intensity. This way we can maintain the level of RHEED intensity during deposition, suppressing the formation of a multi-level system. In fact by doing this we proved the validity of this approach.

In Fig. 4.5 the difference in surface morphology of a 90 unit-cell thick sample with continuous and interval deposition is shown. In the latter case (b), the surface consists of terraces of about 200 nm width, originating from the miscut angle of the $SrTiO_3$ substrate. On these terraces, with height differences of only one unit-cell, small islands can be seen with a height corresponding to one unit-cell of $SrTiO_3$. This is in contrast to the surface properties obtained after continuous deposition (a), where at least 4 unit-cell levels are visible.

4.3.3 Monte Carlo simulations

Since we expect that the observed relaxation behavior during interval deposition cannot be explained by the simple models given in section 4.2.1, another approach is desired. In order to describe the crystallization processes on the surface during thin film growth, an often used model is the solid-on-solid (SOS) model introduced by Weeks and Gilmer^{37,38}. Diffusion of deposited material on a simple cubic crystal surface is described in terms of single-particle lattice hopping. If we assume that the particles on the oxide surface are cubes with the size of one unit-cell, the SOS model can be applied. In reality, the diffusion process is expected to be much more complicated, consisting of (de)composition steps and the actually moving particles should be much smaller. However, effectively the process can be described by the simple cubic model. Note that the oxygen pressure will probably affect the rate of each

reaction step. In our case, the oxygen pressure is assumed to be high enough and not to be rate limiting, see also chapter 2.

The effect considered important for the kinetics on the surface here, is the additional energy of the arriving particles as a function of the oxygen pressure²⁸, see also eq. (2.1) However, from the measurements of the relaxation times as a function of pressure, given in Fig. 4.3, it has become clear that this effect is smaller above a certain pressure. This is just the regime where the interval deposition technique is applied, and we don't have to take this effect into account here. Furthermore, we assume that particles arriving at the surface have a sticking coefficient of one.

The diffusion kinetics is described by an Arrhenius hopping process on a $l \times l$ matrix, determined by the surface diffusion barrier E_s and the nearestneighbour co-ordination n (n=0,1..,4) of each particle with a lateral bond strength E_N . Note that diffusion of interacting particles (with a higher coordination) was not included in the models described in section 4.2.1. The hopping probability k is then given by:

$$\mathbf{k} = \mathbf{k}_0 \exp(\frac{-(\mathbf{E}_{\mathbf{S}} + n\mathbf{E}_{\mathbf{N}})}{\mathbf{k}_{\mathbf{B}}\mathbf{T}})$$
(4.12)

where k_0 represents an attempt frequency (~10¹³ Hz) for atomic processes. To simulate an infinitely large crystal surface, periodic boundary conditions are applied. The Monte Carlo simulation method applied here is extensively described by others^{10,39} and details can be found elsewhere⁴⁰.

The RHEED intensity, in view of the step density model, can be calculated as follows for the $l \times l$ matrix⁴¹:

$$L = \frac{1}{l^2} \sum_{i,j} |h_{i,j} - h_{i,j+1}| \cos \phi + |h_{i,j} - h_{i+1,j}| \sin \phi$$
(4.13)

and

$$I_{RHEED} \propto 1 - L \tag{4.14}$$

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

The pulsed way of deposition is simulated here by depositing a number of particles on the surface randomly and instantaneously, after which the particle can diffuse, when the next pulse arrives, is determined by the repetition rate of the laser.

Figure 4.9 shows the simulation of continuous deposition using $E_{S}=E_{A}=2.2 \text{ eV}$, $E_{N}=0.27 \text{ eV}$, $k_{0}=10^{13} \text{ Hz}$, $\phi=0^{\circ}$ and T=815 °C (curve 1). For these settings we observe damped intensity oscillations with a period of 20 seconds, indicating roughening of the surface. The relaxation behavior of the intensity after each laser pulse, as seen in the inset of Fig. 4.9 (curve 1), depends on the coverage. These observations are in agreement with the experiments. Also the


Figure 4.9: Simulated intensity variations during continuous deposition at 815 °C using a laser repetition rate of 1 Hz (curve 1) and interval deposition at the same temperature using a laser repetition rate of 10 Hz (curve 2). The deposition rate was set at 20 pulses per unit-cell layer. The inset shows the first unit-cell layer.

characteristic times obtained from the simulations agree with the measured values. Because the sampling rate (# of data points) is much higher compared to the experiments, the relaxation behavior is very pronounced even at the minimum, and the characteristic times can still be determined. Note that the amplitude is decreasing in time due to surface roughening.

Finally, for the first period the minimum intensity seems to be shifted toward θ <0.5, as indicated by the dashed line in the inset of Fig. 4.9, which is also observed in experiments.

When interval deposition is simulated, applying a laser repetition rate of 10 Hz, the typical shape of interval deposition emerges, as seen in Fig. 4.9 (curve 2). From these simulations it is clear that after each unit-cell layer, the intensity remains much higher in the case of interval deposition, which was also observed in the experiments (see Fig. 4.8).

The simulated intensity recovery after each deposition interval was fitted to an exponential function of the form of eq. $(4.11)^{v}$. In Fig. 4.10, we plotted the characteristic relaxation behaviour found for simulations for different laser

 $^{^{\}rm v}$ Usually a better fit was obtained using two exponential terms 10 , however we compared only the shortest characteristic times.



Figure 4.10: Relaxation times right after the deposition interval, distracted from simulated intensity data obtained for different laser repetition rates at temperatures of 775 °C (reversed triangle) and 815 °C (open squares). The circles are measured values for 10 and 100 Hz. The upright triangles indicate the length T of the deposition intervals for different repetition rates (20 pulses/unit-cell layer).

repetition rates. For increasing repetition rates, the relaxation times decrease. This can be explained by comparing the calculated surfaces immediately after the deposition interval; for higher values of the laser repetition rate, the number of small islands increases, causing the relative diffusion distances to be smaller⁴⁰. For comparison, the characteristic times found for the experiments (after the first deposition interval) of Fig.'s 4.6 and 4.7 are also indicated; they are in good agreement with simulations. When we compare the length of the deposition interval T_d for different repetition rates with their characteristic times, a cross-over at a repetition rate of ~80 Hz can be seen. For simulations using a lower temperature, this cross-over point shifts to a repetition rate of ~70 Hz. In our opinion, this point formation of too large islands is still significant. For the interval deposition method to achieve the best results, the laser repetition rate has to be higher than this cross-over value.

During the experiments with interval deposition we observed a clear effect of the number of pulses needed to complete one unit-cell layer on, both, the relaxation and the intensity. To simulate this, we stopped deposition after 25 pulses, where 30 pulses are needed to complete one layer, and the result is shown in Fig. 4.11 a). It can be seen clearly that the intensity after each deposition interval periodically changes to become maximal again just after five intervals. Normally, the error in the number of pulses to complete one unit-cell layer lies within one laser pulse and the effects are more subtle, e.g.,



Figure 4.11: a) Simulated intensity variations during interval deposition (using a laser repetition rate of 100 Hz). Here, the deposition was stopped after 25 pulses for each deposition interval, although 30 pulses are required to complete one unit-cell layer. b) The characteristic relaxation times after each deposition interval in a).

see Fig. 4.7, where this effect is enhanced by the periodic change from 43 to 42 pulses. More importantly, if we look at the characteristic times plotted in Fig. 4.11 b), we can see that they depend on how close is one to the completion of a unit-cell layer after each deposition interval. We expect that this predominantly explains the observation of different relaxation times during interval deposition experiments.

4.4 Conclusions

In this chapter we have investigated the kinetic parameters which are important factors for layer-by-layer growth in the case of homoepitaxy: temperature, pressure and the island size during growth.

The effect of the pressure and temperature on the diffusivity have been investigated using time resolved RHEED, by means of the relaxation behavior after each laser pulse. For different pressures we found different diffusion barriers, which could be explained by the difference in energies of arriving particles. At this point we have to mention that all the interpretations we have given to the measurements could have been put in terms of the oxidation state of the arriving particles. In addition, the diffusion of material on the surface, expected to be a complex process in the case of multi-component oxides involving chemical reactions, can be limited by an oxidation reaction on the surface, which depends on the oxygen pressure⁴². However, pressure and temperature remain important parameters, which determine the growth mode. They can be chosen in the case of homoepitaxy to achieve true layer-by-layer intensity oscillations.

Further measurements in different ambient are in progress with the aim to investigate the role of oxidation in the diffusion process. We have shown that

the combination of high pressure RHEED with PLD leads to a better understanding of both the plasma physics as well as the surface kinetics of thin film growth of oxide materials.

For co-evaporated films the initial period of RHEED intensity oscillations is expected to be a good estimate of the deposition rate for thicker films, see also chapter 5, even though the oscillations damp out and the growth front consists of multiple unit-cell levels. Of course, the estimate will be more accurate if the oscillations remain visible throughout the entire thickness of the film. Nevertheless, for $SrTiO_3$ it has been shown that, even for thick layers and when strong damping of the intensity oscillations was observed, the growth front did not exceed more than 4 unit-cell levels.

On the other hand, for successive deposition of unit-cell layers of different targets to create artificially layered structures, a true layer-by-layer mode is essential throughout the deposition of the entire film, since for every layer the starting surface has to be atomically flat again. A transition to multilevel has to be avoided as much as possible because the growth front may end up being thicker than each constituting layer.

For many oxide materials one cannot freely choose the deposition temperature and pressure, as in the case of homoepitaxy, to obtain layer-bylayer growth, in view of the phase stability. Often, the desired phase is only stable in a limited regime of the deposition conditions, depending on the substrate material.

We have shown that it is possible with PLD to impose a single-level 2D growth mode, or layer-by-layer growth mode, for $SrTiO_3$ despite unfavorable deposition conditions with respect to the mobility. Depositing every unit-cell layer at a very high deposition rate followed by a relaxation interval, we extend the typical high supersaturation for PLD keeping the average island size as small as possible. Therefore, the interlayer mass transport is strongly enhanced and the formation of a multi-level growth front does not occur. This technique, which we call Pulsed Laser interval Deposition, is unique for PLD; no other technique has the possibility to combine very high deposition rates with intervals of no deposition in a fast periodic sequence. We demonstrated the value of this method using homoepitaxy of $SrTiO_3$. From the experiments we conclude that for optimal results a high laser repetition rate and number of pulses per unit-cell layer is desirable.

The mechanisms resulting in the typical relaxation behavior of the specular intensity after each deposition interval is expected to be more complex compared to relaxation during continuous layer-by-layer growth, i.e., ot does not consist of diffusion of non-interacting particles only. Therefore, we used the solid-on-solid model and simulated interval deposition using the Monte Carlo method. Experimental parameters determined earlier have been used to characterize homoepitaxy of SrTiO₃. We clearly observed a difference in the calculated RHEED intensity variations during continuous growth and interval deposition, which resemble the experimental results, both qualitatively as well as quantitatively. By comparing the characteristic relaxation times found for

simulations using different laser repetition rates, a critical value of this repetition rate could be determined for the interval deposition method to be most effective; the deposition interval has to be shorter than this characteristic time.

Finally, an upper limit for the laser repetition rate comes from the requirement that the interaction of every succeeding pulse has to be minimal in case of high frequencies⁴³ and that the ablation process should be not affected by this.

In the next chapter we show that this method can also be used in case of heteroepitaxy. For the infinite layer structure $(Sr_x,Ca_{1-x})CuO_2/BaCuO_2$, where the choice of temperature and pressure is very critical for the conducting properties, the importance of this growth method is exemplified.

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Superlattices of (Ba,Sr,Ca)CuO₂

5.1 Introduction

Almost all high T_c superconducting oxide ceramics belong to the perovskite class of materials. As already mentioned in chapter 1, this layered structure has invited people to intervene on an atomic level. In search for new superconducting compounds, in particular the cuprates, layer-by-layer or block-by-block thin film deposition techniques have become an interesting alternative to the traditional 'bulk' methods¹. In addition, these techniques have been used to systematically investigate superconducting properties of atomically (or molecularly) engineered structures, i.e., superlattices of superconductors and insulators²⁻⁷, other combinations^{8,9,10} and 'known' structures with insertion of extra (up to eight) copper oxide planes¹¹⁻¹⁴. Finally, similar techniques have been used to fabricate very thin barrier layers for Josephson junctions with a planar layout^{11,15,16,17}.

This chapter deals with the preparation of $CuBa_2(Sr_xCa_{1-x})_nCu_{n-1}O_y$ compound by fabrication of superlattices of $(Ba,Sr,Ca)CuO_2$ with PLD using interval deposition as described in chapter 4. In this case-study, both the applicability of PLD to atomic engineering as well as the fabrication of artificial superconductors are demonstrated.

5.2 Infinite layer structure ACuO₂ (A=Ba,Sr,Ca)

5.2.1 Structure

The infinite-layer structure ACuO₂ (A=Ba,Sr,Ca) is an oxygen deficient perovskite structure, consisting of corner shared square coordinated Cu(II), copper oxide planes, and alkaline(II) earth in the body center, see Fig. 5.1. The structure of the high- T_c superconductor cuprates can be derived from the infinite layer structure, by insertion of chemically distinct metal-oxide layers parallel to the CuO2 planes. Hence, the name 'infinite': If there is no interruption of the $ACuO_2$ structure by other layers, the structure block would be infinitely large. The 'infinite-layer structure block' in all cuprate superconductors containing four, five or six-fold oxygen coordinated Cu-cations is thought to be the superconducting 'heart' of these structures. In the known compounds the Cu-planes are doped with either holes (p-type) or electrons (ntype) and, depending on the amount of doping, they exhibit different properties, see Fig. 5.2. Doping results in by a mixed-valence state of copper, i.e., the normal valence state of copper in a CuO_2 environment is 2+ and will partly change in the case of doping to +1 (n-type) or 3+ (p-type). For example, the effective valence state can range from 2.06-2.3 in La₂CuO₄. A particular compound is called optimally doped when the T_c is maximal (2.18 for La₂CuO₄ with T_c=38 K)^{18,19}.

The mechanism of doping is different for each individual compound, but in general a charge-reservoir block can be distinguished²⁰, which alternates with infinite-layer blocks. For example, in MBa₂Ca_nCu_{n+1}O_{2n+x+y+2} (M=Tl,Hg) superconductors or written in the form²¹ (BaMO_x)(BaCuO_y)(CaCuO₂)_n representing the infinite layer stacking, the M containing blocks are the charge reservoirs. In fact, many classification schemes of the known high-T_c cuprates are based on the infinite layer or 'parent' structure^{22,23}. In the search for new superconducting compounds an often chosen strategy is to assume the infinite layer compound ACuO₂ and try to periodically insert some kind of the charge reservoir.



Figure 5.1 Schematic drawing of the infinite-layer structure or 'parent' structure for high $T_{\rm c}$ cuprates.

5.2.2 Superconductivity in the infinite layer structure?

It was first thought that the 'infinite layer' compound has the simplest structure containing all the elements for high- T_c superconductivity. After the stabilization of tetragonal $Sr_{0.14}Ca_{0.86}CuO_2$ by Siegrist et al. in 1988²⁴ numerous efforts to make this structure superconducting have lead to an abundance of new compounds.

Parallel to the synthesis of bulk infinite-layer compounds at high pressures, it became clear that the tetragonal phase for different film compositions could be epitaxially stabilized on different substrate materials using PLD^{25-32} ,

RF magnetron sputtering³³⁻³⁷, laser MBE³⁸⁻⁴³ (here laser MBE refers to the technique based on PLD where for each different atomic layer a different target is used), MBE⁴⁴ or other techniques^{45,46}.

Indeed, doped structures with some Sr²⁺, Ca²⁺ replaced by Ln³⁺ (Ln=La, Nd) that were synthesized by several groups either in bulk⁴⁷⁻⁵¹ or thin film⁵²⁻⁵⁶ with T_c's up to ~40K, have the tetragonal structure. These materials are n-type or electron doped superconductors. However, in some reports the formation of foreign phases is observed depending on the doping level⁵⁷. Since the Meisner fraction for most of the n-type samples is rather small, the question still remains valid whether the observed superconductivity should be ascribed to the infinite layer structure itself.

Holes (p-type) are created in slightly alkaline earth deficient compositions with an infinite layer structure and there have been several reports of critical temperatures up to 110 K⁵⁸. However, the high critical temperatures were measured in samples containing a lot of ordered defect structures, as seen with HREM. This suggests that in fact these defects play an important role in the doping of the CuO₂-planes^{59,60,61,62}. For a detailed discussion see for example the review article of M. Laguës et al.²⁰. This observation has been explored extensively in both bulk material as well as thin films. For example, Feenstra et al.^{63,64} show that periodical insertion of extra SrO layers, acting as defects,



Figure 5.2: Schematic phase diagram for layered cuprate materials as a function of the doping level n. After ref. 18.

using thin film techniques, leads to either n-type or p-type conduction, depending on the post-anneal procedure.

Also substitution of smaller Ca^{2+} (r=1.12Å) with Sr^{2+} (r=1.26Å) or Ba^{2+} (r=1.42Å) in solid solutions of $BaCuO_2$, $SrCuO_2$ and $CaCuO_2$ led sometimes to higher T_c 's^{65,66}. Although initially incorporation of excess oxygen due to the difference in co-ordination number of Ba^{2+} compared to $(Sr,Ca)^{2+}$ was held responsible for the doping, also here different types of ordered defects were found.

Using thin film deposition, one can control the functionality of different layers by sequential deposition of distinct ACuO₂ blocks. In addition, one benefits from the stabilizing effect of the substrate on these highly unstable structures. For superlattices created by sequential deposition containing only $SrCuO_2$ and $CaCuO_2{}^{67,68,69}\!,$ no superconductivity was found. However, Norton et al. have demonstrated superconducting artificial layered structures with Ba and Sr_{1-x}, Ca_x by PLD⁷⁰, with a maximum T_c of ~70K. The idea is that by periodically substituting layers with smaller cations by larger cations, extra oxygen may be incorporated in the latter and act as charge reservoirs. They only observed superconductivity in structures with more than one BaCuO₂ block. Later, Balestrino et al. found also superconductivity (T_{c.max}~80K) using the same method, however, only in case of superlattices with Ba and Ca^{71} , i.e., Sr containing structures showed no trace of superconductivity. This was attributed to Ba/Sr interdiffusion. Both groups verified the artificial periodicity of the as-grown films with XRD⁷², after calibration of the growth rates of the individual constituents by thickness measurements: No in situ growth rate monitoring has been used and, more importantly, the growth mode has not been identified in these studies. Because these structures are very unstable, HREM analysis of these films, using high-energy electrons, is extremely difficult. The relation of superconductivity and the structure is not clear yet, e.g., whether the relation found for the number of different layers with superconductivity⁷³ has a fundamental origin or is determined by the crystalline quality.

In conclusion, as a result of the efforts to explore the origin of superconductivity in infinite-layer materials, new superconducting families were identified, e.g., $Sr_{n+1}Cu_nO_{2n+1+\delta}^{59}$, $Cu_xBa_2Ca_{n-1}Cu_nO^{74}$ and the oxy-carbonates⁷⁵⁻⁷⁹. The highest critical temperature up to now for materials without heavy metals is reported for the $Ca_{0.5}Cu_{0.5}Ba_2Ca_{n-1}Cu_nO$ system in bulk^{80,81} and is 126 K. Note that this is comparable to materials containing the highly toxic elements like thallium or mercury and, therefore, these materials are very attractive for application.

Here, the x=1 member of the $Cu_xBa_2Ca_{n-1}Cu_nO_y$ family has been fabricated in thin film by sequential deposition of (smaller) Sr_{1-x} , Ca_x containing layers and (larger) Ba containing layers, in order to obtain layers with different functionalities (e.g., charge reservoir by incorporation of excess oxygen). Superlattices are fabricated by depositing sequentially $ACuO_2$ (A= Ba, Sr or Ca) from different targets, $BaCuO_2$ (BCO), $SrCuO_2$ (SCO), $Sr_{0.7}Ca_{0.3}CuO_2$ (SCCO) and $CaCuO_2$ (CCO), using the interval deposition technique. The structures have been analysed with XRD and HREM and the morphology of the surface is monitored in situ with high pressure RHEED and ex situ with AFM.

5.3 Artificial Lattices

5.3.1 Method

There are several issues to be addressed regarding the optimal parameters for each individual layer versus the optimal growth parameters for a complete stack of layers. The former will be mainly determined by the interaction and/or mismatch with every underlying layer. This is a complicated form of heteroepitaxy where for each successive layer the starting underlayer changes every time, with implications for the sticking coefficient and growth. In contrast, the latter are determined by the properties of the film, i.e., structure, electrical properties, etc. In other words the optimal parameters are determined from both a growth as well as the materials point of view.

It is often mentioned by people who attempt to fabricate artificial layered structures without in situ monitoring of the growth rate that precisely the opposite is the only way to obtain perfect superlattices. Yet, in case of RHEED monitoring every intensity oscillation period only corresponds to the deposition of a unit-cell layer if the deposited material exhibits a true layer-by-layer or Frank-van der Merwe growth mode, see chapters 2 and 4.

As will become clear, the conditions for superconductivity in the materials under consideration are not necessarily in favor of layer-by-layer growth, i.e., high oxygen pressure and low temperature, see also chapter 4. With the interval deposition technique one ideally imposes a 2D growth mode irrespective of the temperature and pressure during deposition. These can thus be chosen to give optimal materials properties.

Apart from the choice of the deposition conditions, the choice of substrate material is of great importance. Here, it depends on the ability to stabilize a normally highly unstable structure, the in-plane lattice constant has to be compatible with the expected one of the film. For the $ACuO_2$ systems $SrTiO_3$ is a good candidate but also MgO^{82} , $LaAlO_3$ and $NdGaO_3^{83}$ have been investigated. Most important is that we have shown, that $SrTiO_3$ can be treated to give a perfect template for layer-by-layer growth, i.e., it can be single terminated. The effect of surface termination on the growth of $ACuO_2$ was discussed in section 3.5.3.

We used the interval deposition method to impose a true 2D growth mode for each succeeding layer in artificial superlattices. For this one needs to know in advance the number of laser pulses p_i to complete one unit-cell layer for each of the components i. It is possible to estimate p_i from the deposition experiments of separate thin films and use either intensity oscillations (SCO, CCO) and film thickness (SCO). Using the estimated numbers, the deposition rates can then be fine-tuned in situ by monitoring the specular intensity,



Figure 5.3: RHEED intensity changes of the specular reflection recorded during deposition of a)SCO, b)CCO on SrTiO₃ and c) BCO, d)CCO on buffered SrTiO₃

similarly to the method suggested in chapter 4. However, this is complicated by the fact that the deposition rate of more than one component has to be finetuned. We evaluate the as created superstructure ex situ using XRD. From the superlattice period

$$\Lambda = \frac{\lambda}{2|\sin\theta_{\pm 1} - \sin\theta_0|} \tag{5.1}$$

of the subsequently deposited film and the average lattice parameter

$$\bar{\mathbf{c}} = (\mathbf{n}_1 \mathbf{c}_1 + \mathbf{n}_2 \mathbf{c}_2) / (\mathbf{n}_1 + \mathbf{n}_2) \tag{5.2}$$

with λ the wavelength of the used radiation, and $\theta_{\pm 1}$ the angles of the firstorder satellite peaks and n_i the number of constituent layers with lattice parameter c_i , one can estimate p_i using that for a expected Λ , n_i have to be integers.

We use the following procedure for the superlattices. First, the number of pulses needed for one unit-cell layer is estimated by counting the oscillation period during the deposition of each component at fixed deposition conditions. If possible, this estimation is verified with X-ray reflectivity thickness measurements. Sometimes, intensity oscillations were only observed in the presence of an extra buffer layer, for example in case of CCO.

Subsequently, the interval deposition technique is used to deposit stacks of layers where two unit-cell BCO layers (Balestrino et al. observed that the BCO is only stable when at least a double block is deposited^{83,88,89}) are alternated

with CCO, SCCO or SCO layers of different thickness (up to four tetragonal unit-cell layers) and combinations.

5.3.2 Results

5.3.2.1 Deposition of constituents

To be able to fabricate superlattices in the $(Ba,Sr,Ca)CuO_2$ system, we first studied the growth of the individual constituents on SrTiO₃. In Fig. 5.3 we show the RHEED intensity changes of the specular reflection recorded during deposition of CCO, SCO and BCO on SrTiO₃.

During the growth of the infinite layer $ACuO_2$ on $SrTiO_3$ (a₀=3.905 Å), the observed behavior strongly depends on the size of the alkaline earth ion A, i.e., r_{Ca} =1.12 Å, r_{Sr} =1.26 Å and r_{Ba} =1.42 Å. The bulk lattice constants for CCO and SCO are 3.855 Å, 3.926 Å and 3.18 Å in-plane, 3.43 Å for the c-axis, respectively^{30,65,84}, whereas for BCO exists no data since it for the tetragonal structure is not stable in bulk. The lattice constants for thin films on $SrTiO_3$ tend to deviate a little from these values, possibly due to the underlying crystalline template of $SrTiO_3$, see below.

Here, SCO was deposited on SrO terminated $SrTiO_3$ at a temperature of 550 °C and a pressure of 3 Pa. After an initial dip of the specular intensity (see also chapter 2), a stationary variation is observed. SCO (or SCCO) with a lattice constant comparable to the one of $SrTiO_3$ exhibits a layer-by-layer growth mode, as seen from the pronounced intensity oscillations in Fig. 5.3 a).

In contrast, for CCO a Stransky-Krastanov growth behaviour, i.e., two unitcell layers are stabilized by the substrate, as seen in Fig. 5.3 b) by the existence of two maxima, followed by an exponential decay. This can be explained by the small in-plane lattice constant, compared to $SrTiO_3$ and the relaxation of stress.

The tetragonal BCO phase is not stable in in bulk, and it only can exist through the stabilizing effect of substrate. The tetragonal phase of BCO has been reported to be stable in thin film form up to thickness' of 30nm^{85} . Due to the larger size of Ba²⁺ compared to Sr²⁺, one expects considerable compressive



Figure 5.4: XRD θ -2 θ scans of a) SrCuO₂, b) CaCuO₂ on Sr_{0.7}Ca_{0.3}CuO₂,c) BaCuO₂ on SrCuO₂, on SrTiO₃. Arrows indicate film peaks, * indicate peaks originating from the substrate. Some very small peaks were found, marked with ? in Fig. 5.4 c), corresponding to an unidentified phase or superstructure.



Figure 5.5: Typical RHEED patterns after deposition of a) a BCO block and b) a (Sr,Ca)CO block. The profile along the 'specular' streak as a function of the composition of the latter is given in c).

stress in the BCO film which will eventually be released in thicker films. During deposition of BCO on SCO buffered SrTiO₃, a transition in the period of the intensity oscillations is observed, as indicated by the arrows in Fig. 5.3 c), which might indicate that the growing unit has changed. The change during the growth of BCO, as seen in the figure, might be explained by a phase transformation for thicker films, although it was suggested by Del Vecchio et al. that growth proceeds in double BCO unit-cell blocks⁸⁹. This behavior was observed both on a bare substrate as well as on substrates buffered, e.g., with SCO.

When a buffer layer of BCO is used prior to the deposition of CCO, see Fig. 5.3 d), the intensity increases and intensity oscillations are observed. This has also been observed for growth of CCO on SCO buffered $SrTiO_3$. A better estimate can be made of the deposition rate in this case, since more periods are counted.

In Fig. 5.4, the θ -2 θ XRD data are given for the different constituents. From the (00l) reflections marked in Fig 5.4 a) to c) by arrows, we found the c-axis periods for CCO, SCCO, SCO and BCO to be 3.21 Å, 3.41 Å, 3.45 Å and 4.21 Å, respectively. These values are comparable to ones found in literature for different deposition techniques. From the RHEED patterns we estimate that the in-plane lattice constants are comparable to SrTiO₃. Note that the value found for BCO is the one expected for the tetragonal phase and not some other phase as one would expect from the RHEED dataⁱ. This supports the assumption of stable double tetragonal BCO block.

 $^{^{\}rm i}$ Some very small peaks were found, marked with ? in Fig. 5.4 c), corresponding to an unidentified phase or superstructure

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Figure 5.6: Intensity of the specular reflection during deposition of a) and b) $[2BaCuO_2/2SrCuO_2]_{30}$, c) $[2BaCuO_2/3Sr_{0.7}Ca_{0.3}CuO_2]_{30}$ and d) $[2BaCuO_2/2CaCuO_2]_{20}$

Although these results suggest that only for SCO and SCCO the RHEED intensity oscillations can be used for rate monitoring, the initial periods of both CCO and BCO have been used for a first estimation of their deposition rate.

5.3.2.2 Deposition of superlattices

In Fig. 5.5 typical RHEED patterns are shown which are observed after sequential deposition of a BCO layer (a) and a subsequent layer containing Ca and/or Sr (b). The pattern after deposition of BCO is always streaky and the intensity drops significantly. After subsequent deposition of the SCO, SCCO or CCO layer, the intensity increases again and usually a spotty pattern is observed, see Fig. 5.5 b). In Fig. 5.5 c) the profile, of the 'specular' streak after 7 blocks of BCO/SCO, BCO/SCCO, BCO/CCO and BCO/SCCO/CCO, is given, respectively. In all cases the deposition temperature was kept at 575 °C with an oxygen pressure of 30 Pa. Apparently, the specular reflection has a sharper profile, indicating a smoother surface, when the in-plane lattice constant of the composition approaches the lattice constant of SrTiO₃, see section 5.3.2.1.

Examples of the intensity of the specular reflection recorded during interval deposition of these layers are given in Fig. 5.6 b), c) and d). Figure 5.6 a) shows an enlargement of Fig. 5.6 b), RHEED intensity variations during deposition of: first, a double BCO block in one interval, as seen from a sharp drop of the



Figure 5.7: θ -2 θ scans of a)BCO?/SCO? (Λ ~38 Å, i.e., corresponds <u>not</u> to 2BCO/4SCO), b)BCO₂/CCO₂/SCCO (Λ ~18.03 Å) and c)BCO₂/CCO₂ (Λ ~15.2 Å). The (001) reflections of the films are indicated with arrows, peaks corresponding to the substrate are indicated with an asterix.

intensity. Second, a single block of SCO is deposited and this causes by an initial drop, followed by a rise of the intensity, which is repeated once. These oscillations are typical and they are induced by this deposition method, see chapter 4.

For the SCO containing films, a more-or-less constant amplitude of the intensity oscillations is observed, see Fig. 5.6 b) and c), where films have been deposited with compositions 2BCO/2SCO and 2BCO/3SCO, respectively. It indicates a constantly smooth surface. This is in contrast to the rapid decrease of the intensity after a certain thickness (~17 BCO/CCO blocks) of films with only CCO and BCO, see Fig. 5.6 d). This difference can be attributed to the larger in-plane lattice mismatch between BCO and CCO tetragonal structures, causing stress.

Ex situ AFM shows that in case of the SCO/SCCO containing films, see Fig. 5.8 a) and b), true layer-by-layer growth has occurred. The initial terrace morphology of the substrate surface is still visible with height differences of only SrTiO₃ unit-cell steps, even after deposition of a >40 nm thick film. On the terraces, the morphology consists of small islands, as expected from the interval deposition method. In Fig. 5.6 a) an interesting feature can be seen. In this case the miscut angle of the $SrTiO_3$ substrate was very low (<0.05^o) and after full treatment, of one unit-cell deep circular holes became visible on wide terraces (see chapter 3). After subsequent deposition of (2SrO/2BCO), still the imprint of the underlying substrate is visible. This is a strong evidence for layer-by-layer growth. It means that the constantly high RHEED intensity is not due to step-flow. The imprint of the substrate morphology is absent in the case of CCO containing films, see Fig. 5.8 c). However, as expected from RHEED analysis, the films are still reasonably smooth, which was also confirmed by X-ray reflectivity measurements. Note that the morphology of all these surfaces is affected by interaction with airⁱⁱ.

 $^{^{\}rm ii}$ The alkaline earth (II) elements react easily with H_2O and CO_2 from the ambient.



Figure 5.8: Surface morphology as seen with AFM of a) $(BCO_2/SCO_2)_{25}$ superlattice, b) $(BCO_2/SCCO_2)_{25}$ and c) $(BCO_2/CCO_2)_{25}$

Finally, the θ -2 θ scans in Fig. 5.7 show clear satellite peaks, indicated with arrows, originating from the artificial superstructures. The positions of these satellite peaks were used to further calibrate the deposition rate of each constituent.

When the deposition rate for BaCuO₂ was derived from the longer RHEED intensity oscillation period, see Fig. 5.3 c), the resulting films gave a superlattice period, which could not be fitted by simply adding the expected thickness of each constituent block. For example, Figure 5.7 a) shows superlattice peaks up to high order, indicative for a high-quality superstructure. These satellite peaks are centered around the average peak located near the substrate peaks (sometimes they are merged). However, the measured Λ =38.3, determined using eq. (5.1), does not correspond to the originally intended 4+2 superlattice (Λ ~22 Å). The origin of this discrepancy will become clear form HREM analysis, see below.

Reconsidering the deposition rate, thus taking the period during the initial growth, see Fig. 5.3 c), we obtained superstructures for which examples of the θ -2 θ scans are showed in Fig. 5.7 b) and c). Here, the satellite peaks correspond to superlattice periods which are closer to the expected ones. If the exact number laser shots that correspond to each constituent layer deviates from an integer, see eq. (5.2), due to small errors in the estimate for the deposition rate or intermixing, the satellite peaks will be broadened or even splitting occurs. The difference between a film with non-integer values for n_i see Fig. 5.7 b) and one with integer n_i see Fig. 5.7 c), is exemplified; the former clearly shows broadening of the peaks located in-between the average lattice peaks (which are located near the substrate peaks), whereas in the latter case, all the film peaks have the same width, indicative of a high-quality superlattice.

5.3.3 Structural analysis of the superlattices

5.3.3.1 XRD analysis

Examples of typical θ -2 θ scans are given in Fig. 5.9. The small width and the correct positions of the satellite peaks, according to eq. (5.2), indicate high



Figure 5.9: θ -2 θ scans of a) 2BCO/2SCO (Λ ~15.7 Å), b) 2BCO/3SCO (Λ ~19.1 Å) and 2BCO/2CCO (Λ ~15.2 Å) superlattices. The (001) reflections of the films are indicated with arrows, and the peaks corresponding to the substrate are indicated with an asterix.

quality of the superstructures obtained using PLD. Superlattice periods derived for different compositions are given in table 5.1. The values found are systematically larger than the ones expected (from simple summation of the thickness of the individual blocks, using the values found in Fig. 5.4). Note that the deviations are much smaller than in the case when wrong estimated deposition rates were used, see Fig. 5.7. a). By assuming a larger value than 4.2 Å (i.e., 4.4 Å) for the BCO blocks, a better fit to the measured values is obtained, similar to the observations of Balestrino et al.⁷¹. The nature of these deviations has been studied in more detail by HREM, see section 5.3.3.2.

For 2SCO\2BCO and 2CCO\2BCO films, ω -2 θ plots of the (013) peak are given in Fig. 5.10. The FWHM values for both films are of the same order, close to the value for instrumental broadening, see section 2.5.1. although the latter film displays a little more spread in orientations, which was also concluded from the RHEED measurements during deposition. These values are somewhat higher than those reported by Aruta et al.⁸⁸, however in their later reports⁸⁹

	expected values	measured values	literature
A: BaCuO ₂	-	4.21	4.2071
B: SrCuO ₂	-	3.45	3.486;3,4687
C: SrCaCuO ₂	-	3.38	3.4067
D: CaCuO ₂	-	3.21	3.16-3.2130
2A+2B	15.3(3.83)	15.7-15.8	15.772
2A+3B	18.75(3.75)	19.1 (3.84)	19.272
2A+4B	22.2 (3.70)	22.5 (3.79)	
2A+2C	15.2 (3.79)	15.5-15.7	
2A+3C	18.5 (3.71)	19.0	
2A+2D	14.8 (3.70)	15.1-15.4(3.76-3.82)	15.189
2A+3D	18.0 (3.60)		18.289
2A+C+D	15.0 (3.74)	15,3	
2A+C+D+C	18.4 (3.67)	18.5 (3.68)	

Table 5.1: Superlattice periods, using eq. (5.1) for different compositions (Å)



Figure 5.10: ω -2 θ plots of the superstructures (each contour represents a decrease of 10% of the maximum intensity starting from the peak value): a)2SCO/2BCO($(0\bar{1}3)$ d ω =d2 θ =1.978°; 2 θ (x₀)=26.48°; ω (y₀)=-2.34°; FWHM~0.3°; b)2CCO/2BCO($(0\bar{1}3)$ d ω =d2 θ =1.978°; 2 θ (x₀)=27.07°; ω (y₀)=2.31°; FWHM~0.35°

they give values which are comparable or worse than in our case. Therefore, we conclude that our films have at least a comparable crystalline quality.

Finally, the full data set of reflections collected for some of the films can be indexed by a unit-cell with the c-axis value corresponding to the superlattice period mentioned above. In addition, the in-plane lattice constants were close to the ones of the substrates, as expected. Refinement of the data set, using a model structure and treating the structure as a single crystal, did not lead to a conclusive result yet. From HREM, however, a better understanding of the microstructure can be obtained.

5.3.3.2 HREM analysis

Figure 5.11 a) shows an HREM overview of the hetero-structure as previously studied with XRD in Fig. 5.4 a). The top of the hetero-structure contains a protective $SrTiO_3$ layer. The dark layers, 20 in total, are SCO, and the lighter layers, also 20, are BCO. Figure 5.11 b) shows a HREM image recorded near the top $SrTiO_3$ buffer layer. The BCO layers clearly have a periodicity which differs from the expected 'perovskite' spacing. The zigzag contrast in the closely spaced double rows is typical for the superconductor $(La,Ba)_2CuO_4$, were Ba layers are present and are shifted by $(\frac{1}{2}, \frac{1}{2})$ in the a, b plane, with respect to each other. The periodicity in the central row is clearly shifted by $\frac{1}{2a_0}$ after crossing the double row, as indicated by arrows in Fig. 5.11 b). The lattice parameter of the Ba-block along the c-axis measured on the image is 13.2-13.6 Å.

All these features combined let us conclude that the "BaCuO₂ layers" actually consist of Ba_2CuO_x . Similar structural features have been observed in SCO films by others⁹⁰. We observed mostly 2 unit-cells thick layers of Ba_2CuO_x ,



Figure 5.11: a) Overview TEM image of a SCO/BCO superlattice based on a 'wrong' deposition rate estimate for the BaCuO₂ layers, the white contrast corresponds to BCO, b) HREM image of the same film, the white circles indicate the positions of the Ba ions in the Ba₂CuO_x model.

with a total thickness of 27.2 Å. The observed periodicity in the image, 3 unitcells of SCO and 2 unit-cells of Ba₂CuO_x, yields a total thickness of about 38 Å. Locally we observe regions with 2 or 4 unit-cells of SCO. It is interesting to note that the incorporation of Ba double layers results in a shift of the Cu sublattice, observed as a $\frac{1}{2}a_0$ shift. In the case of $\frac{1}{2}$ unit-cell of Ba₂CuO_x this would result in a shift of the Cu sublattice in consecutive SCO layers. Also steps in the Ba₂CuO_x layer with heights of $\frac{1}{2}$ unit-cell would induce this shift. However, such steps are rarely observed; all the SCO layers are aligned, as indicated with the vertical line in Fig. 5.11 b).

The contrast in the "BaCuO₂ layers" could be matched with simulated images of Ba₂CuO_x for a defocus of -200 Å and thickness of 20 Å. The ratio of a/c for SrCuO₂ is 1.03 (15.34 pixels / 15.82 pixels) and the ratio for the Ba₂CuO_x is 3.97 (a= 15.36 pixels and c= 61 pixels). Figure 5.11 b) shows the positions of Ba (white circles) according to a model for the Ba₂CuO_x.

Fig. 5.13 a) shows a selected area electron diffraction (SAED) pattern. The superlattice periodicity obtained from this diffraction is 35.4-35.6 Å. Faint spots are present near the basic perovskite spots as indicated by the upper arrow. The lower arrow indicates the perovskite structure. This faint spot is rather elongated and it represents a periodicity ranging from 3.58 to 3.62 Å.

Apart from the highly ordered regions in the films, we also observed that the BCO layer suffered from amorphization, as seen in Fig. 5.12 a). This clearly

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Figure 5.13: a)Selected area electron diffraction (SAED) pattern of the structure as in Fig. 5.11 and b) a close-up near the (400) reflection.

illustrates the instability of the BCO structure as compared to the SCO. Possibly due to local deviations of the deposition rate, planar defects were also found, see Fig. 5.12 b). It is clear that the BCO layers contain steps as can be seen from the discontinuity of the white contrast lines. Steps in the BCO layers are indicated with arrows.

These observations explain the unexpected superlattice value found with XRD in Fig. 5.7 d) (which corresponds to 2 Ba_2CuO_x blocks and 3 SCO blocks) and point to the need to re-consider the deposition rate calibration in the case of BCO. They also might explain the change in the periodicity of the RHEED intensity oscillations seen in Fig. 5.3 d).

Figure 5.14 a) shows a superlattice structure deposited after recalibration of the deposition rate of BCO, see also Fig. 5.9 c). The HREM image was taken



Figure 5.12: a) Amorphization of the BCO layers and b) steps (indicated by arrows).



Figure 5.14: a) HREM image of a 3SCCO/2BCO structure, b) enlargement, the arrows indicate the copper oxide planes.

close to the STO substrate. The superlattice in this region is nearly perfect. Fig.5.14 b) is an enlargement of Fig. 5.14 a) from which the noise due to an amorphous overlayer has been removed. The image shows only contrast typical for perovskite blocks. The lattice spacings for each layer (measured from the images with calibration on STO) is 4.08 to 4.25 Å for BCO and 3.43 to 3.63 Å for SCCO. The super period measured from computer diffractograms obtained from image of Fig. 5.14 b) is 19 to 20.4 Å.

In summary, we conclude that BCO is indeed present in the infinite layer



Figure 5.15: a)Selected area electron diffraction (SAED) pattern of the structure as in Fig. 5.14 and b) a close-up near the (400) reflection.

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Figure 5.16: HREM image near a highly defective region of the substrate surface.

structure. In the image of Fig 5.14 b), taken at defocus of -70 nm with a thickness of about 2 nm, the contrast can be interpreted as Cu represented by white dots. Here, the order of deposition has been SrO/SCCO/BCO- on SrTiO₃. If we look into detail at the layer stacking, as starting from the inside of the film towards the substrate, we count 7 layers from the CuO layer, which is the interface between the first BCO and the SCCO. This corresponds to 3 unit-cells of SCCO in the first layer growing on a SrO terminated STO, seen to exhibit a darker contrast then the superlattice structure. The ratio between the Sr and Ba unit-cell is 1.16 (measured 13.6 pixels for Ba and 11.75 pixels for Sr c-axis) as determined from the maxima of a line plot from Fig. 5.14 b). Here, image simulations are based on a model where Cu layers are taken to be fully oxidized in both the SCCO layer as well as in the BCO layers, and Ba layers were assumed to contain no oxygen. Possibly even better matching could be achieved by varying the O distribution.

Figure 5.15 a) shows a diffraction pattern with the superstructure reflections. An enlargement around the (004) reflection is given in Fig. 5.15 b). The superstructure spots are streaked along the growth direction, impeding a precise superstructure period determination. The measured values ranges between 18.5 Å to 20.4 Å. Comparing the c-axis values with the values obtained by XRD measurements, we conclude that the superlattice periods are similar, although somewhat larger than the expected value⁹¹. However, HREM did not confirm convincingly that the observed enlargement can be explained by an expansion of the BCO block solely.

In this sample, deviations from the perfect structure were found also. Figure 5.16 shows a region of the superlattice which is highly defective. Large substrate steps are present, resulting in a highly defective superlattice. This stresses the importance of a well prepared substrate surface.

5.3.4 Electrical properties

The electrical properties of the superlattices were measured with the fourprobe technique, inside a He cryostat; the following behaviour was observed.

SCO/BCO films cooled down after deposition in a low oxygen ambient (i.e. the deposition pressure), show a high room-temperature resistance, which exponentially increases with decreasing temperature, see Fig. 5.17 a) (curve 1). When similar films were cooled down in a high pressure ambient (>200mbar) to roughly 400 °C and subsequently quenched to room temperatureⁱⁱⁱ, a significantly lower resistance was observed (curve 2). Also initially 'low pressure' cooled films which were brought to the deposition temperature again in a tube oven while flushing with pure oxygen and subsequently quenched to room temperature showed a lower resistance as well (curve 3). Yet, upon cooling in liquid He they showed always a 'semiconducting' behavior.

The observations described above indicate the possibility to control the oxygen content of the films and, thereby, the conducting properties. However, more research has to be done, to obtain the optimal settings for every film composition. For example, we have assumed the aforementioned 'quench' procedure to be optimal for all other films, which need not be the case.

A series of five films deposited at 575 °C and 31 Pa but with different compositions in general showed a decrease in resistance with an increase in CCO layers, see Fig. 5.17 b) (curves 2-6)^{iv}. Here, a film, which contained no Sr at all (curve 1) displays 'semiconducting' behavior, in contrast with other observations for films with a similar composition, indicating the difficulty of controlling the conducting properties.

Metal-like behaviour and even superconducting transitions to zero resistance were only observed for films with at least one CCO, see Fig. 5.17 b) (curves 4-6), deposited at temperature around 575 °C with an oxygen pressure >20Pa. Note, that the temperature/pressure window for good quality CCO containing films, is small, as determined from the RHEED measurements. The highest $T_{c,onset}$ was ~50K and $T_{c,zero}$ ~12K, see Fig. 5.17 c). This film showed an increase in resistance before getting into the superconducting state. Furthermore, the broad transition indicates that this is a multiphase sample. To confirm superconductivity, we performed an IV characterisation at ~8K, see the inset of Fig. 5.17 c).

ⁱⁱⁱ Here, quenching to room temperature was done by removing the sample holder from the deposition chamber and subsequently detaching the sample from the heater block as fast as possible.

^{iv} The measurements presented in this figure are performed by using sputter deposited gold contact pads in order to obtain good conducting contacts, whereas the results given in the other figures were done by directly bonding Al wires onto the film. Due to the difference in contact area, the resistance values are hard to compare.

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Figure 5.17: Resistance versus temperature of: a) 2SCO/2BCO (1) after cooling down in low pressure, 2) after cooling down at high pressure ,(3) same as (1) plus annealing in tube oven in flow of oxygen, b) 2CCO/2BCO(1), 2SCO/2BCO(2), SCCO/2BCO(3), SCCO/CCO/2BCO(4),

SCCO/CCO/2BCO(5), 2SCCO/CCO/2BCO(6), all deposited at 575 °C and 31 Pa and c)2CCO/2BCO deposited at 575 °C and 20 Pa; here, the inset is the I-V curve measured at \sim 8K

5.4 Conclusions

In this chapter, we have shown that PLD in combination with an in situ analysis technique makes feasible, fabrication of superlattice structures of oxide materials down to the atomic level. RHEED proved to be an useful tool to estimate the deposition rate of constituent materials, through the intensity oscillations. However, careful analysis showed that one cannot always rely on the observation of intensity oscillations, the period of which may correspond to unexpected quantities deposited, e.g., in the case of BaCuO₂.

The choice of $SrTiO_3$ as the substrate material proved to be valid for the stabilization of the infinite layer structure. The deposition temperature and oxygen pressure are far below the normally used conditions to stabilize this structure in the bulk phase. In addition, from AFM observations it became clear that the high quality of the substrate surface ensured a perfect template for epitaxy. HREM analysis clearly shows that the lattice of the film material, here mostly compressed in-plane, is determined by the lattice parameters of

the substrate. Therefore, other substrate materials with similar surface properties might yield different conducting properties of the films and are currently being investigated.

We proved that the interval deposition method indeed imposes a layer-bylayer growth mode almost irrespective of the deposition conditions. Thereby, the interval deposition method justifies the use of an earlier estimated deposition rate. When, from the aspect of thermodynamic stability, another phase will be formed, interval deposition cannot prevent this. Even in the case of 3D nucleation (e.g., release of stress) the method can still be useful, since the formation of large islands is prevented, although one of the requirements for the use of interval deposition was assumed to be 2D nucleation. This might explain the success achieved with the CCO/BCO films, for limited thickness, where stress is expected to be considerable.

The structural analysis with XRD and HREM of the superlattices indicates first of all a high quality structure, in both the overall crystallinity as well as in the imposed periodicity along the c-axis. Furthermore, the right estimate for the deposition rate per constituent was confirmed by the period of the superlattices. A systematic deviation turned out to be caused by the compressive stress in the film. To our knowledge, the HREM images of Bacontaining infinite layer thin films are the first reported so far.

The results presented here indicate that superconductivity is related to defect structures responsible for charge-carrier doping of the copper oxide planes. The most perfect structures, e.g., $SrCuO_2/BaCuO_2$ superlattices, were never superconducting, whereas for the superconducting films, defects are expected to be present, although we did not find a systematic proof. It is clear that true layer-by-layer growth does not necessarily lead to good superconducting properties, i.e., high T_c 's.

The difference in A-cation size for successive layers in a superlattice structure is found to influence the growth behavior. First, the Sr and Ba containing structures can be deposited in a much wider temperature and pressure window (500-600 °C and >3 Pa), compared to structures with only Ca and Ba (550 °C and >20 Pa). Secondly, the Ca and Ba containing structure were found to grow in a layer-by-layer fashion up to a certain thickness, which is explained by the release of stress beyond that thickness.

The goal to achieve atomically engineered layered oxides and interfaces, enabling to systematically investigate the relation between micro structure and macroscopic properties has been made possible with this technique- interval deposition with high pressure RHEED.

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Summary

In this thesis, a systematic study of preparation of artificially layered oxide materials is presented. An advantage of thin film techniques to fabricate new materials in this way is the stabilizing effect of the substrate crystal. If properly chosen to fit the expected thin film crystal structure and, in addition, well prepared with respect to the surface quality, many crystal structures are shown to be stable. These only exist in thin film form or normally require extreme synthesis conditions. Furthermore, the structures that are formed are highly kinetically stabilized because constituents are supplied successively. This allows one to synthesize extremely rare structures which are metastable. The accompanying macroscopic properties are expected to be correspondingly unique. Furthermore, a systematically study of the effect of structural deviations on these properties become available.

The possibility has been demonstrated to fabricate artificially layered structures using the standard Pulsed Laser Deposition (PLD) in combination with in situ rate monitoring technique Reflection High Energy Electron Diffraction (RHEED), i.e., without any concessions to the deposition conditions typically used for deposition of oxide thin films. The important hurdles to be taken to arrive at this goal are treated.

PLD has become an important technique to fabricate novel materials. Here, one has benefited from the main advantages of PLD, the relatively easy stochiometric transfer of material from the target to the substrate and the almost free choice of (relatively high) background pressure. For instance, during the deposition of oxides usually an oxygen background pressure up to 100 Pa is used.

RHEED was limited to low background pressures only until recently. Therefore we have developed a high-pressure RHEED system, in order to overcome the problem of scattering of electrons in the relatively high

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background gas pressure. High-pressure RHEED, which makes it possible to in situ monitor deposition of oxides at higher pressures, also opened new perspectives. Besides observed intensity oscillations due to layer-by-layer growth, enabling accurate growth rate control, it became clear that intensity relaxation observed due to the typical pulsed way of deposition leads to a wealth of information about growth parameters. We have also used this system, PLD in combination with high pressure RHEED, to fabricate artificial superlattices of perovskite materials.

Because of the stringent requirements on the substrate surface in order to achieve atomically controlled thin film growth, a special treatment is developed for SrTiO₃. The results obtained here are expected to be valid for ABO₃ (perovskite) materials in general, encompassing many compounds which are used for their crystal surface properties. It became clear that the terminating layer of a perovskite (001) ABO₃ crystal (i.e., for SrTiO₃ (001) this is TiO₂ or SrO) influences many characteristics at the surface. The morphology during a thermal treatment of the surface, epitaxial growth, microstructure (i.e., reconstructions, defects) the electronic structure and chemical properties are all determined by the composition of the surface, i.e., whether a BO₂, AO or a mixed surface exists. Of course all of these characteristics are interdependent. A single terminated surface turns out to be optimal with respect to mainly morphology and epitaxy.

It is demonstrated that one can take advantage of the difference in properties of the elements in the different layers, e.g., solubility in acids, in order to achieve a nearly perfect and single-terminated surface. The $SrTiO_3$ surface has been studied as a model system, and the effects of the composition of the terminating layer on homo and hetero epitaxial growth have been elucidated.

In order to be able to create artificially layered structures, a layer-by-layer growth mode is necessary. First, because the desired crystal structure will result from successive deposition of atomic layers or molecular blocks of different materials. Second, the rate control during deposition takes place through recording of RHEED intensity oscillations, which are present in the case of two-dimensional nucleation. These only represent the actual deposition rate in case of true layer-by-layer growth, a growth mode which cannot taken for granted. Usually, damped intensity oscillations are observed, indicating roughening of the surface during deposition.

The deposition parameters important for layer-by-layer growth, a prerequisite for artificial layering of thin films, as well as the implications of the typical pulsed way of deposition are given more attention through a detailed study of homoepitaxy of $SrTiO_3$.

In the case of homoepitaxy, kinetic factors determine the growth mode, whereas in the case of heteroepitaxy also thermodynamic factors, e.g. misfit, are important to understand the growth mode. In fact, from a thermodynamic point of view layer-by-layer growth is always predicted for homoepitaxy. However, during deposition of different kinds of materials, i.e., metals, semiconductors or insulators, independently of the deposition technique, roughening of the surface is observed. Assuming only two-dimensional nucleation, determined by the supersaturation, limited interlayer mass transport results in nucleation on top of two-dimensional islands before completion of a unit-cell layer. Still, one can speak of a two dimensional growth mode. However, nucleation and incorporation of ad-atoms at step edges proceeds on an increasing number of unit-cell levels, which is exhibited by damping of the RHEED intensity oscillations. In fact, an exponential decay of the amplitude is predicted assuming conventional MBE deposition conditions.

To understand the implications of the characteristics of PLD on growth, which are expected to be kinetic in origin, homoepitaxy is a convenient system to study.

Here we have studied the relaxation behaviour of the RHEED intensity during homoepitaxy of SrTiO₃, as a function of the deposition temperature and pressure. In a regime where true layer-by-layer growth or true step-flow is observed, a simple model for diffusion of material on the surface can be applied, which is an extension of the known steady-state theory and which accounts for the characteristic relaxation times measured. We derive from these measurements an activation energy for diffusion of 2.2 \pm 0.3 eV. The effect of a lower deposition pressure is measured; it effectively reduces this barrier, due to the higher energy of the arriving particles.

In order to be able to create a crystal structure by depositing consecutive unit-cell layers of different materials, a true layer-by-layer growth mode is a prerequisite; nucleation of each next layer may only occur after the previous layer is completed. Occasionally, the deposition conditions such as the substrate temperature and the ambient gas pressure (oxygen in the case of oxide materials) can be optimized for true two dimensional growth, e.g., homoepitaxy on SrTiO₃ (001).

From the point of view of phase stability for many oxide materials, temperature and oxygen pressure have to be fixed. The only way to obtain true layer-by-layer growth is to apply manipulated growth, reducing the island size during growth. We propose a method, based on the high supersaturation attained during PLD: Pulsed Laser interval Deposition. Although there is the general understanding that, due to the pulsed deposition, the growth mechanism differs from that occurring during continuous physical and chemical deposition, this has hardly even been used. Here, we introduce a growth method, based on a periodic sequence: fast deposition of the amount of material needed to complete one monolayer is followed by an interval in which no deposition takes place and the film can reorganize. This makes it possible to grow in a layer-by-layer fashion in a growth regime (temperature, pressure) where otherwise island formation would dominate the growth. By using the parameters obtained from our experimental relaxation and oscillation data, solid-on-solid model Monte Carlo simulations have been used to further investigate characteristics for the interval deposition method.

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Finally, the interval deposition method has been successfully applied to prepare the CuBa₂(Sr_xCa_{1-x})_nCu_{n-1}O_y compound, by fabricating artificial layered structures in the (Ba,Sr,Ca)CuO₂ system. Unit-cell layers of BaCuO₂, SrCuO₂ and CaCuO₂ were sequentially deposited applying various deposition schemes, in a fully automated process. Films with different compositions have been compared, both, structurally with Atomic Force Microscopy, X-ray Diffraction and High Resolution Transmission Electron Microscopy as well as with respect to their conducting properties. Films with a composition resulting in the film lattice parameters closer to those of the SrTiO₃ substrate (i.e., those that contain Sr) showed the best crystalline properties. In contrast, films with a superconducting transition always contain Ca. Here, larger stress due to lattice mismatch results in slightly inferior growth and lower stability. However, a clear correlation between the crystalline quality of the overall crystal matrix as well as the superlattice, and the resistivity, has not yet been observed.

Samenvatting

Dit proefschrift beschrijft het onderzoek naar de mogelijkheid om kunstmatig gelaagde oxiden te maken met behulp van gepulte laserdepositie. Een voordeel van het gebruik van dunne-filmtechnieken is onder andere de stabiliserende werking van het substraat kristal. Wanneer het juiste drager materiaal gekozen wordt met een geschikt groeioppervlak kunnen vele kristalstructuren stabiel gemaakt worden. Deze bestaan dan alleen in dunne film vorm en zouden anders extreme preparatieomstandigheden vergen. Bovendien zijn de gevormde structuren kinetisch gestabilizeerd omdat bestandelen na elkaar toegevoegd worden. Met dunne-filmtechnieken kunnen dus extreem zeldzame, metastabiele verbindingen gemaakt worden. Van de macroscopische eigenschappen die daarmee gepaard gaan mag worden verwacht dat deze overeenkomstig uniek zijn. Voorts heeft men een wijze om systematisch structurele afwijkingen te bestuderen.

De mogelijkheid om kunstmatig gelaagde structuren te maken met behulp van standaard gepulste laserdepositie (PLD) in combinatie met een in situtechniek om de groei te kunnen volgen (dat wil zeggen zonder concessies te doen aan de gebruikelijke depositieomstandigheden voor oxiden) reflectie-hoge energie-electronendiffractie (RHEED) en de belangrijkste horden die genomen zijn om tot dit doel te komen worden behandeld.

PLD heeft zich ontwikkeld tot een belangrijke techniek ter preparatie van nieuwe materialen. Vooral de relatief eenvoudig realizeerbare stoichiometrische overdracht van basismateriaal naar substraat en de bijna vrije keuze in (relatief hoge) achtergronddrukken worden als voordelen van PLD aangemerkt. Voor oxiden wordt meestal een zuurstofdruk tot 100 Pa gebruikt.

RHEED is tot voor kort beperkt toepasbaar –alleen bij lage achtergronddrukken werkt RHEED. Hiertoe is een hogedruk RHEED systeem

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ontwikkeld teneinde het probleem van verstrooiing van electronen bij relatief hoge achtergrond drukken aan te pakken. Door hogedruk RHEED, die de mogelijkheid van het volgen van de groei van oxiden bij de hogere drukken biedt, kwamen er ook nieuwe uitzichten. Naast het gebruik van de intensiteitsoscillaties die gemeten worden bij laag-voor-laaggroei voor het meten van de groeisnelheid werd al snel duidelijk dat het relaxatiegedrag afkomstig van de typisch gepulste manier van deponeren een schat aan informatie over de groeiparameters opleverd. Het ontwikkelde hogedruk RHEED systeem wordt gebruikt om kunstmatig gelaagde perovskiten te fabriceren.

Ten behoeve van de hoge eisen die worden gesteld aan het substraat oppervlak voor dunne film groei gecontroleerd tot op atomair niveau is er een speciale oppervlakte-behandelingsmethode ontwikkeld voor $SrTiO_3$ substraten. In bredere zin wordt van de methode verwacht dat deze meer algemeen toepasbaar is voor de perovskiten, waartoe vele materialen behoren die vanwege hun specifieke kristalstructuur gebruikt worden. Het eindvlak van een ABO₃ (001) kristal, dat wil zeggen voor $SrTiO_3$ (001) is dit TiO_2 of SrO, bepalend is voor de eigenschappen van het oppervlak. De morfologie, de microstructuur (i.e. reconstructies, defecten) en de chemische eigenschappen van het oppervlak en epitaxiale groei worden allemaal bepaald door de compositie aan het oppervlak, dat wil zeggen of het ABO₃ (001) kristal met BO_2 , AO of een mix van deze twee eindigd. Natuurlijk hangen deze eigenschappen ook van elkaar af. Een enkelvoudig eindvlak blijkt optimaal te zijn voor wat de morfologie en epitaxie betreft.

We maken gebruik van het verschil in eigenschappen tussen de elementen in de verschillende vlakken, bijvoorbeeld oplosbaarheid in zuren, om een bijna perfect enkelvoudig eindvlak te verkrijgen. Het $SrTiO_3$ oppervlak staat vanaf nu model en hiervan worden ondermeer de effecten van de compositie van het eindvlak op homoepitaxie en heteroepitaxie bestudeerd.

Om tot kunstmatig gelaagde structuren te komen is laag-voor-laaggroei noodzakelijk. Ten eerste omdat de uiteindelijke kristalstructuur gevolg is van opeenvolgende depositie van atomair of moleculair dunne lagen. Ten tweede, de groeisnelheid wordt bepaald door middel van RHEED intensiteitsoscillaties die slechts aanwezig zijn in geval van tweedimensionale nucleatie. Deze oscillaties representeren alleen dan de groeisnelheid wanneer de groei exact laag-voor-laag is, wat niet vaak voorkomt. Vaak doven de oscillaties uit ten gevolge van een verruwing van het oppervlak tijdens depositie.

Zowel de depositieparameters die belangrijk zijn voor laag-voor-laag groei, essentieel voor het maken van kunstmatig gelaagde structuren, als de implicaties van de typisch gepulste manier van deponeren worden in dit proefschrift belicht aan de hand van de studie van homoepitaxie van SrTiO₃.

In het geval van homoepitaxie zullen kinetische factoren de groei bepalen in tegenstelling tot heteroepitaxie, waar ook thermodynamische factoren belangrijk zijn voor de groei. Thermodynamisch gezien zul je altijd laag-voorlaag groei verwachten voor homoepitaxie. Echter, vaak wordt toch een
verruwing geconstateerd tijdens depositie van verschillende soorten materialen, metalen, halfgeleiders en isolatoren, onafhankelijk van de dunne film techniek. Als we aannemen dat er slechts tweedimensionale nucleatie plaatsvindt afhankelijk van de superverzadiging dan zorgt een beperkt massa transport ervoor dat eilanden ontstaan vóórdat een enkellaag compleet is. Er is nog steeds sprake van een tweedimensionale groeimode. In deze situatie neemt het aantal stapranden dat atomen kan invangen toe en ze bevinden zich op meerdere enkellaag niveau's. Dit wordt zichtbaar doordat intensiteitsoscillaties uitdoven. Wanneer groeicondities van conventionele moleculairebundel epitaxie aangenomen worden verwacht je een exponentiele afname van hun amplitude.

Om de implicaties van PLD op de groei goed te kunnen begrijpen, die voornamenlijk kinetisch van aard zullen zijn, is homoepitaxiale groei een perfect studieobject.

We hebben het relaxatiegedrag van de RHEED intensiteit gedurende homoepitaxie van SrTiO₃ bestudeerd als functie van de depositietemperatuur en druk. In een regime met laag-voor-laaggroei of step-flowgroei, kan een simpel diffusiemodel worden toegepast waarmee de gemeten relaxatietijden verklaard kunnen worden. Uit deze metingen leiden we een activatieenergie voor diffusie van 2.2 \pm 0.3 eV af. Het effect van een lagere depositiedruk is gemeten en effectief zie je een verlaging van deze barriere doordat de aankomende deeltjes een hogere kinetische energie hebben.

Om een kristalstructuur te maken waarbij elke atoomlaag, bestaande uit verschillende elementen, aangebracht wordt is een laag-voor-laag groeimode noodzakelijk.: nucleatie van elke volgende laag mag pas plaatsvinden nadat de voorgaande laag zich gesloten heeft. Soms kunnen temperatuur en druk geoptimaliseerd worden voor tweedimensionale groei, bijvoorbeeld voor SrTiO₃

Vanuit het oogpunt van fasestabiliteit van de meeste oxiden liggen de temperatuur en zuurstofdruk vast. De enige manier om dan nog laag-voor-laag groei te krijgen is door gemanipuleerde depositie toe te passen waarbij de eilandgrootte tijdens de groei klein blijft. In dit proefschrift wordt een methode besproken die gebaseerd is op de hoge superverzadiging die alleen haalbaar is met PLD; gepulste-laser-intervaldepositie. Ondanks het feit dat de indruk bestaat dat de gepulste manier van deponeren zorgt voor een afwijkend groeigedrag in vergelijking met andere physische en chemische dunnefilmtechnieken is dat nog nooit gebruikt. We introduceren een methode waarbij depositie bestaat uit de opeenvolging van eerst snelle depositie van precies een enkellaag gevolgd door een interval zonder depositie en het filmmateriaal kan uitkristalliseren. Hierdoor wordt het mogelijk een film laag-voor-laag aan te brengen onder omstandigheden waar normaal gesproken formatie van eilandjes de groei zou bepalen. Door experimenteel bepaalde parameters in te voeren in een 'solid-on-solid' model Monte Carlo simulatie kunnen de eigenschappen van intervaldepositie verder worden onderzocht.

Tenslotte kan de interval-depositiemethode succesvol worden toegepast bij de preparatie van $CuBa_2(Sr_xCa_{1\text{-}x})_nCu_{n\text{-}1}O_y$ door middel van kunstmatig

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gelaagd (Ba,Sr,Ca)CuO₂. Enkellagen van BaCuO₂, SrCuO₂ en CaCuO₂ worden sequentieel aangebracht waarbij de volgorde volledig geautomatiseerd gevarieerd kan worden. De structuur van dunne lagen met verschillende composities worden vervolgens vergeleken gebruik makende van atomaire kracht microscopie, röntchendiffractie en hoge-resolutie-transmissieelectronenmicroscopie alsook hun geleidende eigenschappen. Films met de celparameters vergelijkbaar met het substraatmateriaal SrTiO₃ (bevatten veel Sr) vertonen de beste kristallijne eigenschappen. Aan de andere kant wordt supergeleiding alleen gevonden in films met Ca. Hier komen de roosters minder goed overeen wat tot uiting komt in wat mindere groei en lagere stabiliteit. Echter een duidelijke correlatie van de kristalliniteit van de matrixstructuur en het superrooster met de weerstand kan nog niet worden aangetoond.

Dankwoord

Words, that are written on paper, or that float into the air, Dead?, alive? Let me think about it...

Steeds weer sta je voor nieuwe keuzes tijdens de nu al vijfentwintig jaar durende tocht der kennisverwerving. Enkele mijlpalen markeren de weg en telkens wanneer er een opdoemd diend zich een nieuw dilemma aan. Zo ook nu, aangekomen bij voorlopig de laatste mijlpaal. Ik zeg voorlopig want mijn nieuwsgierigheid drijft mij in de richting van het zwarte gat van de kennis, de wetenschap. Graag wil ik de mensen bedanken die mij geholpen en geinspireerd hebben en mij de mogelijkheid hebben gegeven om de keuzes te mogen maken die ik nu voor me heb.

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Een zeer speciale plaats in mijn leven heeft Dave, eeuwig energiek, altijd vol ambitie, 'a role model'.

De paranimfen: Guus, de juiste man met steeds de juiste opmerkingen, we zijn in het laboratorium bijna onafscheidelijk geweest. Ik wens jou veel succes toe met je eigen promotieonderzoek. Gerben, 10 jaar Twente waarvan we er in ieder geval 8 jaar samen hebben gevuld met volleybal, studie en studiereis, biertje halen in de stad.

De vaste staf: Frank, laat ik er verder net als jij niet meer over zeggen dan nodig is. Sybolt, na eerst mijn afstudeerbegeleider te zijn geweest en nu een zeer belangrijke rol in het onderzoek van zijn nieuwe vakgroep speelt. Dick, Harry, Ans en Inke, altijd in voor een geintje. De mensen van het CMO, nu

Dankwoord

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Joost, Eelco en Per, 'de studentjes'; ik hoop dat zij net zulke goede herrinneringen aan hun afstuderen hebben als ikzelf. En natuurlijk ook de overige horde studenten en stagiairs die de vakgroep heeft bezocht.

Tot slot, mijn ouders, mijn broer en mijn eerste keuze, Mirije.