**In-situ growth monitoring with Scanning
Force Microscopy during Pulsed Laser Deposition**

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**IN-SITU GROWTH MONITORING WITH
SCANNING FORCE MICROSCOPY
DURING PULSED LASER DEPOSITION**

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Chapter 1

General introduction and motivation

1.1 Introduction

The will to explore the unknown has changed our daily lives and knowledge about the world throughout the history of mankind. Looking at or thinking about objects, species, organisms and processes has led to many discoveries. Exploring requires the courage to look and investigate the boundaries of our knowledge. Imaging and mapping “new” land, species, organisms and processes created possibilities to manipulate and control them.

Currently, microscopes make it possible to image and map objects and processes that go beyond the human senses as vision, sense and hearing.

In the Netherlands, Anton van Leeuwenhoek (1632-1723) is often considered as the inventor and “father” of microscopy for distant (telescope) and small (microscope) objects. With such equipment, based on optical lenses, it is possible to explore and map a new world. Other persons worthwhile to mention with regards to the development of the optical microscope are the Dutch spectacle makers, Zaccharias and Hans Janssen (1590) as well as the Italian inventor and scientist Galileo. The latter probably developed the first multi lens systems around 1609. At present the optical microscope is indispensable in a scientific laboratory and the most frequently used tool to amplify objects, processes and organisms. The first step in controlling and manipulating is imaging and without the microscope our daily live would have been completely different.

Another development throughout the history of mankind is the use of materials. Manipulating, shaping and controlling materials started in the Stone Age and has been important since then. During this era in human evolution, mankind spread from Africa to the rest of the world and technology was for the first time widely used. The current period is often referred to as the Silicon Age. In this era, nanotechnology, thin films and coatings are widely used to protect

and add more functionality to tools. In many applications for the consumer and industrial market, thin film technology enabled the development of devices such as mobile phones and computers. These instruments have already changed our daily activities tremendously and by the miniaturization and integration of smart sensors and actuators in the environment around us this will further evolve. Most of these applications make use of thin films and nanotechnology. Depending on the application, costs and required properties different deposition techniques are used to synthesize thin films.

In the work described in this thesis, a Physical Vapor Deposition (PVD) method called Pulsed Laser Deposition (PLD) was used. This is a widely used deposition technique in the academic world. With this technique almost any material can be deposited such as metals, metal oxides, nitrides, organics and silicides. In this work mainly oxides were studied. The choice for oxides was based on the fact that PLD is especially suitable to deposit oxide* thin films, which have a wide variety of properties. Therefore oxides are often used in thin film devices.

In 1987 it was discovered that the complex oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) [1] was superconducting above 77K, the boiling point of liquid nitrogen. The same year it was found that PLD was a suitable method to fabricate high quality YBCO films [2]. Soon it turned out that also other oxides and materials could be deposited with PLD which became more and more popular. In 1986 the Atomic Force Microscope (AFM) [3] or Scanning Force Microscope (SFM) was presented. This instrument was able to image (non)conducting surfaces with high spatial resolution. From then on, surfaces of (non)conducting oxides with substrate steps (0.1-2nm high) could be imaged. Nowadays a SFM is indispensable in a laboratory and widely used to map the surface morphology of for example thin films. This data is often used to further improve and control the fabrication of these thin films.

Finding the optimal deposition parameters for material systems is typically done by trial and error. This is a tedious and time-consuming process in which several analyzing and diagnostic tools are typically used. By the development of high pressure Reflection High Energy Electron Diffraction (RHEED) (1997) the growth could be monitored during PLD for oxide material systems such as SrRuO_3 and SrTiO_3 deposited on treated SrTiO_3 substrates. This diagnostic instrument improved the possibilities to monitor, manipulate and control the growth during deposition. Unfortunately, this diffraction based technique can not be used to control the deposition of amorphous or polycrystalline model systems.

* During deposition a relatively high oxygen pressure can be used and therefore it is relatively easy to incorporate oxygen. Oxides are interesting from an application point of view since their wide variety of properties could be used in existing or novel thin film devices.

Furthermore, it is often difficult to interpret the data and control the growth with atomic precision. The latter is for example important to study interfaces. To fabricate atomically sharp interfaces it would be helpful to image the surface morphology during deposition. SFM is the most suitable technique to capture the surface morphology in an image with high spatial resolution. For example from SFM images it can be checked if a surface is completely smooth. This information will further help clarifying the RHEED data and improve our understanding of the deposition process. By monitoring the surface morphology, especially during deposition, the thin film optimization process can be further improved and accelerated.

In this thesis a setup is described in which SFM imaging can be performed at PLD conditions. This enables in-situ growth monitoring. In the build configuration the sample was transferred towards the PLD-position during deposition. By separating the SFM-position in space from the PLD-position the standard geometry for both SFM and PLD can be maintained and unwanted material deposition on tip and cantilever, as well as other parts of the SFM-head, is prevented. Even though the sample has to be transferred towards the SFM-head, the surface morphology can be imaged shortly after the last deposition pulse. This instrument was developed to study the nucleation and growth “quasi” real-time during PLD. “Quasi” real-time is defined as imaging between consecutive depositions pulses at synthesis conditions. The availability of equipment to characterize at process conditions enables real-time process monitoring with high spatial resolution. If this can be accomplished, again a new world can be explored, mapped, manipulated and controlled.

1.2 Outline

The first part of this thesis, which covers chapters two and three, a description of the deposition process, the used synthesis technique and the characterization techniques to follow the deposition process is given. Chapter two starts with a description of the different growth modes and how parameters such as the substrate temperature can be used to manipulate the growth and therefore the thin film properties. Furthermore, an overview of the diagnostic tools to monitor the nucleation and growth during PLD is given. Chapter three is titled Scanning Force Microscopy (SFM). In this chapter a description of the history, different operating modes and the forces between a tip and sample are depicted. Besides this, the options to image the surface morphology during PLD are discussed.

In the second part of this thesis, chapter four, a description is given of the developed hardware to continue imaging the surface morphology within two seconds after the last deposition pulse. It also describes the hardware to extend

the SFM operating conditions such that a surface can be imaged at (20-850°C) in a pressure range of (10^{-6} - 10^{-1} mbar).

In the third part, which covers chapters five and six, a description of several material systems is given. Several materials are first studied with ex-situ techniques, to predict the surface morphology evolution. In this thesis three model systems were imaged in-situ. These experiments are described in chapter six. This chapter also explains that SFM has several advantages compared to Scanning Tunneling Microscopy (STM) [4] if neck formation can not be neglected.

1.3 References

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Chapter 2

Thin film growth during pulsed laser deposition

2.1 Introduction

The composition and structure of thin films often correlates with its functionality. Both are influenced by the deposition parameters such as substrate temperature, background pressure and material flux. This chapter describes the influence of these parameters on the surface morphology during vapor phase deposition. Furthermore, Scanning Probe Microscopy (SPM) will be introduced as a technique for in-situ growth monitoring. It will be shown that SPM can in

Figure 2.1: Schematic representation of the atomic processes during synthesis: (a) deposition of an adatom or cluster on a terrace; (b) diffusion of an adatom or cluster on the terrace; (c) nucleation of two adatoms; (d) attachment of adatoms at an island; (e) detachment of atoms from an island; (f) deposition of an adatom or cluster on top of an island; (g) stepdown diffusion of an adatom; (h) diffusion along a steppedge; (i) attachment of an adatom or cluster at a step; (j) desorption from a terrace.

principle be integrated in a synthesis process such as Pulsed Laser Deposition (PLD). As mentioned in chapter 1, equipment with which the surface morphology can be imaged during deposition is the first step to manipulate and control the deposition process. This could help to further control and improve thin films properties used in for example electronic and optical devices.

This chapter is divided in five sections. Section 2.2 and 2.3 give an overview of the microscopic synthesis processes, surface morphology evolution models and in-situ diagnostic instruments. The latter are used to follow and map the synthesis processes. In this thesis the thin films were synthesized with PLD. This physical vapor deposition method and an overview of the current real-time analyzing techniques to follow the nucleation and growth during PLD are described in sections 2.4 and 2.5. Section 2.6 summarizes this chapter.

2.2 Surface morphology evolution during deposition

Microscopic processes of adatoms and clusters on a vicinal surface

During vapor phase deposition a source supplies single atoms or clusters with a flux F on a substrate. The microscopic processes of an adatom on a vicinal surface are illustrated in figure (2.1). In this schematic representation several atomic processes (a-j) are depicted. The deposited atoms (a) or clusters may diffuse (b) over the surface if the activation energy for diffusion is overcome. Two or multiple atoms can also form a nucleus (c) for a two-dimensional island. Such a nucleus can progress (d) in a stable two-dimensional island or decay (e) by respectively the attachment or detachment of adatoms. The critical nucleus [1] is generally referred as the nucleus with a size for which the growth or decay probability is equal. Nuclei with a smaller or a larger dimension are respectively referred as a sub-critical nucleus and a stable island. Other processes of adatoms and clusters which influence the surface morphology are the deposition on islands (f), the attachment to a pre-existing step (i), diffusion along (h) a step, stepdown (g) diffusion and desorption (j) from a terrace.

During vapor phase deposition two important processes can be distinguished; nucleation and growth. During nucleation, islands are formed of which the density increases until a critical nucleation density n_c . The lateral movement of steps and islands ledges and even the merge of two or multiple islands is considered as the growth process. PLD is such a deposition process that the deposited material is not able to rearrange itself to minimize the surface energy. Therefore besides the thermodynamic model also the kinetic model is described to understand the nucleation and growth during PLD.

Nucleation and growth from a thermodynamic point of view

The thermodynamic model to describe crystal synthesis can be applied for a system near equilibrium. In this model, local fluctuations from this thermal

Figure 2.2: Four different surface morphology evolution scenarios during synthesis: (a) three-dimensional island growth; (b) two-dimensional layer-by-layer growth; (c) Stranski-Krastanov growth: below the critical thickness a two-dimensional and above a three-dimensional growth; (d) two-dimensional step flow growth.

equilibrium lead to nucleation and initiate a phase transition such as a change from the gas to the solid phase. A prerequisite to start the initial nucleation, which probability depends on the activation energy, is that the gas is supersaturated [2]. The initial nucleation density will increase until the critical density is reached at which the nuclei will expand and crystallization progresses.

In this thermodynamic model, neglecting the interface energy between the deposited thin film and surface, the balance between the free energies of the substrate surface γ_s and the film surface γ_f , determine the film surface morphology evolution. In figure (2.2) a schematic representation of four growth modes is depicted. Three of these modes (a-c) are often used to describe the nucleation and growth from a thermodynamic point of view.

Wetting of the deposited film and a two-dimensional layer-by-layer or Frank van de Merwe [3] growth mode, see figure (2.2b), is expected if relation (2.1) is valid.

$$\gamma_s > \gamma_f \quad (2.1)$$

No significant wetting and a three-dimensional island or the Volmer Weber [4] growth mode, see figure (2.2a), is expected if relation (2.2) is valid.

$$\gamma_f > \gamma_s \quad (2.2)$$

This thermodynamic model to describe the thin film morphology evolution is only valid for small or moderate supersaturations.

In heteroepitaxial* growth the surface morphology evolution also depends on the elastic strain in the deposited film due to a difference in lattice mismatch. This influences the surface morphology evolution. A change from two-dimensional layer-by-layer into a three-dimensional island growth mode can occur after a critical thickness, see figure (2.2c). In this growth mode, generally referred to as the Stranski-Krastanov [5] growth mode, the lattice of the first atomic layers will match the substrate lattice due to wetting. The result is that the stress[†] increases with the layer thickness. After a critical layer thickness misfit dislocations are introduced, which changes the growth mode. Dislocations are introduced to relieve the strain. This strain is incorporated in the interface energy, which is often added in relation (2.1) and (2.2) to distinguish the above described three growth modes.

Nucleation and growth from a kinetic point of view

In the kinetic model the important parameters to describe the surface morphology evolution are the adatom surface diffusion coefficient (D_s), the energy barrier to hop from lattice site to lattice site E_T and energy barrier to hop towards a lower terrace E_S . The distance an adatom or cluster can diffuse on the surface before it is trapped is mostly influenced by the diffusion coefficient. This rms surface diffusion distance l_d of an adatom from the arrival site can be expressed by equation (2.3).

$$l_d = \sqrt{D_s \tau} \quad (2.3)$$

In this equation, D_s is the surface diffusion coefficient and τ the adatom or cluster residence time before desorption or the time before an adatom is trapped at a step or island edge [6]. The expression for the surface diffusion coefficient is equation (2.4).

$$D_s = \nu \alpha^2 \exp\left(\frac{-E_A}{k_B T}\right) \quad (2.4)$$

In this equation E_A is the activation energy, k_B the boltzmann's constant, T the temperature, ν the attempt frequency and α the characteristic jump distance.

* If the deposited material is identical to the crystalline substrate in composition, orientation and crystallographic structure, the growth is generally referred as homoepitaxial growth otherwise it is referred as heteroepitaxial growth.

† The lattice of the first atomic layers will match the substrate lattice and therefore strain is introduced.

Parameters such as the substrate material and surface bonds influence the diffusion coefficient and therefore the average diffusion length l_d .

To describe the surface morphology evolution with the kinetic model also three different growth modes (a,b,d) are generally distinguished, based on the relative rate of the inter- and intralayer mass transport. These three growth modes will be discussed in the next section.

Intralayer mass transport: diffusion of adatoms or clusters on a terrace.

Interlayer mass transport: diffusion of adatoms or clusters to a lower terrace.

A deposited thin film will have a layer-by-layer morphology evolution if no second layer nucleation and growth takes place, see figure (2.2b). In this surface morphology evolution the adatom diffusion length is such that two-dimensional islands will grow on the terraces and eventually coalesce to form a closed layer. To have a layer-by-layer surface evolution, adatoms that are deposited on the growing islands, should have enough intra- and interlayer mass transport to diffuse to the lower terrace.

A qualitative description of the surface morphology evolution during two-dimensional growth is given by Voigtländer [7]. In this description four atomic processes are used:

1. deposition of atoms on the terrace surface;
2. diffusion of adatoms on the terrace surface;
3. nucleation of two-dimensional islands;
4. growth of two-dimensional islands.

These processes are used to explain the surface morphology evolution of metal epitaxy [8,9], but can also be used qualitatively for other material systems such as metal oxides. At first, the island density drastically increases as a function of the deposition coverage until approximately 0.05 atomic layers. The next phase is that adatoms will attach to the two-dimensional islands and a so called capture zone is formed around each island. In this zone adatoms attach to an island and there is a low probability that nuclei are formed [10,11]. Further increase in the coverage leads to the coalescence of the two-dimensional islands into a continuous layer. However, perfect two-dimensional growth does theoretically not exist, since second layer nucleation starts just before one layer is closed. This can be comprehended by the fact that during the coalescence phase the adatom diffusion distance l_d (intralayer mass transport) to move towards a lower terrace (interlayer mass transport) increases. This increases the probability of second layer nucleation.

Step flow growth is a special case of two-dimensional growth and only occurs with pre-existing steps on the surface. During step flow growth the diffusing adatoms reach the step edge and are trapped before the nucleation of two-dimensional islands can occur. The fast intralayer mass transport results in propagating steps, generally referred as step flow growth. A deposited thin film will have a step flow growth surface morphology evolution if the adatoms diffusion length l_d is larger than the terrace width l_T .

A deposited thin film will have island or a multilevel two-dimensional surface morphology evolution if second and multiple layer nucleation and growth occurs before the islands have coalesced. In this mode intralayer mass transport is insufficient to prevent nuclei nucleation on a terrace and two-dimensional islands. The adatoms surface diffusion length is such that the adatoms are not able to find an existing step- or island edge.

2.3 Diagnostic instruments to monitor the nucleation and growth

At present there are several diagnostic instruments to characterize the micro- and macroscopic structure and composition ex-situ, whereas the number of in-situ instruments to monitor the deposition is limited. This section briefly describes the diffraction and imaging instruments to follow the nucleation and growth during physical and chemical vapor deposition. Diagnostic information during deposition of materials such as metal oxides is currently mostly derived from diffraction methods [7] such as Reflection High Energy Electron Diffraction (RHEED) [12], Surface X-Ray Diffraction (SXR) [13] and Low Energy Electron Diffraction (LEED) [14].

These diffraction based instruments measure the periodic arrangement of the surface atoms. However, the local surface morphology such as the island density, the island size distribution and island shapes can not be directly measured on a microscopic scale as opposed to imaging techniques such as SPM. Nevertheless, these instruments are mostly used to study the deposition process in-situ*, since they are compatible with most deposition techniques, surface sensitive, non-invasive and have a rather high time resolution.

Real-space imaging instruments, such as Low Energy Electron Microscopy (LEEM), Transmission Electron Microscopy (TEM), Reflection Electron Microscopy (REM), Scanning Electron Microscopy (SEM) and SPM [15,16], can be used to image the surface morphology directly. At present LEEM [17,6] and REM [18] are already used to study the local surface structure during synthesis. With these instruments the local surface morphology, such as the island density and distribution at specific sites can be measured. TEM and SPM are

* With in-situ is meant that the surface structure can be followed real-time during synthesis.

instruments with a high spatial resolution, but are usually not^{*} combined with deposition techniques and therefore merely used ex-situ[†]. This hampers quantitative studies to describe the nucleation and growth since:

- observing the surface morphology evolution ex-situ is time-consuming;
- it is difficult to measure the evolution of the same microscopic surface location;
- the surface morphology evolution could be influenced by the cooling procedure to room temperature, ambient exposure and ex-situ sample preparation.

With SPM the local surface morphology such as island sizes, densities and capture zones can be directly measured without sample preparation as opposed to TEM. However, at present the number of instruments with which the nucleation and growth can be monitored with SPM during or shortly after deposition is limited [7]. In this thesis the possibility to study the local surface morphology evolution during Pulsed Laser Deposition (PLD) with in-situ SPM is described. In the next section PLD will be introduced.

2.4 Pulsed Laser Deposition

A schematic view of a typical PLD setup is given in figure (2.3). In this schematic drawing the vacuum chamber and optics are depicted. Furthermore, the target, heater with on it a substrate, plasma plume and laser beam are visible. Typically a pulsed laser[‡] beam is focused on a rotating or scanning target, at an angle of 45° with respect to the target normal. During laser-target interaction electromagnetic energy is rapidly (20 nanoseconds) converted into thermal energy which evaporates the bulk target material. Furthermore, evaporated material adsorbs the laser energy which results in a dense and hot plasma plume with ablated species like atoms, particles and clusters. This plasma will expand[§] towards the substrate surface and atoms and clusters impinge on the substrate surface if the substrate is placed near the plasma. The period between two consecutive deposition pulses can be as long as many seconds. In this period

* Although there are attempts to combine TEM and deposition this is not commercially available.

† After the deposition is finished and the sample is removed from the deposition chamber.

‡ For PLD a pulsed excimer (ArF, KrF, XeCl) or solid state Nd:YAG lasers operating at repetition frequency of 0.1-100Hz are commonly used.

§ During plasma expansion high energetic species decelerate due to interactions with the background gas and emit photons which give the plasma its characteristic luminosity.

Figure 2.3: Schematic view of a PLD setup with the vacuum chamber and the used optics.

adatoms and clusters can rearrange themselves on the surface when they overcome the energy barriers as discussed above, see also figure (3.7). In figure (3.7) the deposition and growth periods are schematically depicted. Unique for PLD is that the deposition and growth are separated in time. Thin film synthesis with PLD is for a number of reasons different, compared to other physical vapor deposition techniques such as Molecular Beam Epitaxy (MBE). The main differences are that:

- the deposition is pulsed and in between the pulses no deposition takes place, see also figure (3.7);
- the peak deposition rate and therefore the supersaturation is orders of magnitude higher;
- the kinetic energy of the arriving species can be tuned over a wide range (0.1-100eV);
- inert and reactive background gasses such as argon and oxygen can be used during deposition at a relatively high pressure, oxygen is typically used to deposit metal oxides such as SrRuO_3 and SrTiO_3 ;
- the stoichiometric transfer from target to thin film is relatively easily obtained.

In PLD several deposition parameters, such as flux per pulse, number of pulses, background pressure and substrate temperature can be independently

changed to manipulate the growth mode. The two-dimensional growth mode is often preferred for thin film devices, since this mode can be used to control the growth rate and obtain smooth interfaces. To have sufficient intra- and interlayer mass transport for two-dimensional growth the substrate temperature is usually increased*.

A transition from a layer-by-layer to a step flow growth regime can be established by adjusting several independent experimental parameters, such as by decreasing the laser repetition rate, the flux per pulse and the substrate terrace width l_T . All these parameters influence the intra- and interlayer mass transport and therefore the thin film surface morphology evolution. Since PLD is a flexible deposition technique and can be used to deposit almost any inorganic material it is often used for research purposes. The main reason this synthesis technique is not widespread in industry and mainly applied in research facilities is that with PLD the deposited area is typically limited to $10 \times 10 \text{ mm}^2$.

2.5 In-situ growth monitoring during PLD: current status

So far diffraction instruments such as Surface X-ray Diffraction (SXRD) and Reflection High Energy Electron Diffraction (RHEED) are typically used to follow the nucleation and growth during PLD. Nowadays, RHEED [19,20] is typically used for in-situ growth monitoring†. RHEED was used in this work to find the deposition parameters for several material systems such that the nucleation and growth could be followed “quasi” real-time with SFM. A study of these material systems are described in chapter five. A schematic view of the used high-pressure RHEED setup is depicted in figure (2.4). In the representation the electron source and phosphor screen are located such that it does not disturb the deposition process and an additional plate, not depicted in the representation, is placed between the plasma and screen to minimize material deposition on the phosphor screen.

* This can also be achieved by depositing a single monolayer in a short period, which is generally referred to as interval deposition. This increases the nucleation density and therefore decreases the distance of adatoms, deposited on top of two-dimensional islands, to a step-down. A similar effect can be obtained by lowering the substrate temperature during the nucleation and increasing the temperature during growth. This increases the initial nucleation density and the intra- and interlayer mass transport during growth.

† SXRD is not widespread since it requires a powerful x-rays source, only available at a synchrotron.

Figure 2.4: Schematic representation of the PLD assisted high pressure RHEED setup.

Although the diffraction pattern can also be used to estimate the surface structure this technique is mostly used to control the growth rate and growth mode. To control the growth rate the intensity of the specular spot is followed. Details about this RHEED assisted PLD setup can be found elsewhere [21]. With the RHEED data, ex-situ measured surface morphology data and Monte Carlo simulations, images of the surface morphology during deposition are typically reconstructed.

In figure (2.5) typical RHEED intensity oscillations are depicted, as well as the corresponding reconstructed surface morphology evolution. Figure (2.5a) corresponds with a two-dimensional layer-by-layer growth, whereas figure (2.5b) corresponds with a multilevel two-dimensional growth. The topography images are an artist impression* of the surface morphology during homoepitaxial SrTiO_3 growth. In figure (2.5a,b) it can be seen that the real-time RHEED data is coupled to the step density, S . The latter is related to the two and multilevel two-dimensional island density n_x and terrace step density. So far, it is not possible to image the surface morphology during deposition as is depicted in the artist impression. However, as mentioned above and visualized in figure (2.5)

* These images are based on ex-situ SFM and Monte Carlo simulations.

Figure 2.5: Artist's impression of the surface evolution during the homoepitaxial SrTiO_3 growth and RHEED intensity oscillations (shown in the insets): (a) for two-dimensional island growth; (b) a multi level two-dimensional growth. The images in this impression are, among other things, based on SFM images measured *ex-situ*.

measuring the surface morphology with high spatial resolution is important to understand the surface evolution. This thesis describes how the local surface morphology can be measured “quasi” real-time with a SFM while minimizing the effect on synthesis processes such as PLD. Our choice to use a Scanning Force Microscope (SFM) instead of a Scanning Tunneling Microscope (STM) was based on the fact that also non-conducting surface can be measured with SFM. In chapter three it is shown that one of the problems in combining SFM with PLD* is the presence of the plasma plume. Notice in figure (2.3 and 2.4) the position of the plasma plume. Important to remember is that there is so far no equipment to image the local surface morphology such as depicted in figure (2.5) during PLD.

2.6 Summary and conclusions

In this chapter the elementary microscopic processes, surface morphology evolution models and in-situ techniques to study vapor phase deposition and more in particular PLD are described. Although the description of the nucleation and growth is over simplified†, it shows that imaging the local surface structure during synthesis with for example a SPM is important to further understand and optimize the synthesis process. Furthermore, it highlights the deposition parameters that influence the nucleation and growth. For example the nucleation

* Standard or typical PLD conditions for compounds such as SrTiO_3 or TiO_2 are a substrate temperature of 750°C and a pressure of 10Pa oxygen.

† For example in practice the growth modes are often mixed.

density n_x on a vicinal substrate is determined by the amount of atoms or clusters arriving on the substrate and the distance an adatom can travel. The first is related to the deposition rate or flux F and the second to the deposition parameters such as the substrate temperature. From this chapter it is also learned that:

- in PLD the deposition and growth are separated in time;
- the actual deposition rate and therefore the supersaturation is in PLD orders of magnitude higher compared to other deposition techniques such as MBE;
- for deposition techniques such as PLD, with a high supersaturation it is recommended to describe the surface morphology evolution with the kinetic instead of the thermodynamic model;
- detailed images of the surface morphology evolution are required to increase our fundamental understanding of the deposition process and test nucleation theories [1]. A SFM is a suitable instrument to capture such images even with atomic resolution.

2.7 References

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Chapter 3

Scanning Force Microscopy

3.1 Introduction

Scanning Force Microscopy (SFM) is a relatively new technique to characterize surfaces with atomic resolution. It was introduced by Binnig, Quate and Gerber in 1986 [1] and is generally referred to as Atomic Force Microscopy (AFM). In this thesis, this technique will be referred as Scanning Force

Figure 3.1: Schematic drawing of a rectangular cantilever in side view. These cantilevers have a width w , thickness t , length l and a tip height h . The distance between tip and sample is d_{ts} . This d_{ts} is referred to as the tip-sample distance in this thesis.

Microscopy. This microscope is based on the tip-sample interaction forces F_{ts} which are a function of the tip-sample distance d_{ts} . To map the three-dimensional surface topography (x,y,z) , the tip is raster scanned in x and y over the surface and the interaction force is measured at each raster point. The measured force can be used to map the surface topography qualitatively^{*} (x,y,F_{ts}) or fed into a feedback circuit to map the surface topography quantitatively[†] (x,y,z) . In this latter mode, the tip-sample distance d_{ts} is controlled such that the force between tip and sample, is constant.

In SFM a sharp tip is mounted on a force sensor. At present two kinds of force sensors are available, the cantilever and needle sensor, the latter is generally referred to as the tuning fork. Cantilevers are typically made out of silicon and silicon nitride, whereas the tuning fork is made out of quartz. In this work only rectangular cantilevers have been used. A rectangular cantilever beam with at the end of the cantilever beam a sharp tip with height h , see figure (3.1), has a torsional k_T and normal spring constant k_N [2,3]. These are expressed by equation (3.1) and (3.2).

$$k_T = \frac{Gwt^3}{3h^2l} \quad (3.1)$$

$$k_N = \frac{Ywt^3}{4l^3} \quad (3.2)$$

Furthermore, the cantilever has a resonance frequency f_0 [4], which can be expressed by:

$$f_0 = 0.162 \frac{t}{l^2} \left(\frac{Y}{\rho} \right)^{\frac{1}{2}} \quad (3.3)$$

In dynamic mode the cantilever is deliberately oscillated such that it starts to resonate at its resonance frequency. Related to the resonance frequency are the oscillation amplitude and phase (relative to the driving signal), which can also be used to measure the surface in constant-height or constant-force mode. In figure (3.2 c,d) the amplitude and phase versus the frequency are depicted.

SFM is one of the most used Scanning Probe Microscope (SPM) techniques. The first SPM, based on the quantum mechanical tunneling current I_{ts} between tip and sample, was introduced in March 1981 [5] by Binnig, Rohrer, Gerber and Weibel. This microscope is called the Scanning Tunneling Microscope (STM). To measure the tip-sample interaction force F_{ts} the cantilever deflection was initially detected with a STM [1]. Although at present other detection methods

* This is generally referred to as constant-height mode.

† This is generally referred to as constant-force mode.

Figure 3.2: Schematic of the cantilever bending (a) in static mode and an oscillating (b) cantilever in dynamic mode. The other graphs are the oscillation amplitude (c) and phase (d) versus frequency. The latter two are often used in dynamic mode to probe the surface.

[6,7,8,9,10,11,12,13,14,15] are usually applied, the principle of scanning and controlling the tip-sample distance are comparable with the first STM. STM and SFM [16,17,18,19] are able to resolve surfaces with atomic resolution. However, it has to be mentioned that atomic resolution [19,20] with SFM is less straightforward [21,6].

Nevertheless, the number of publications in which SFM is mentioned surpassed the number of publications in which STM is mentioned within 10 years after its invention, see figure (3.3). Remarkably the number of publications in which SFM or STM is mentioned started to increase simultaneously after 1990. The use of SFM and STM, as a research tool, by a large scientific community is probably correlated with several scientific breakthroughs* [22,23] and the introduction of the first commercial SFM tips [24] and SPM-systems [25] in the late '80 and early '90. As can be derived from the number of publications, the use

* The manipulation of atoms on conducting surfaces with STM by Eigler and Schweizer, the increase in resolution as discussed above and the fact that AFM and STM could be used simultaneously are three of these scientific breakthroughs worthwhile to mention.

Figure 3.3: Number of publications in which SFM (■) or STM (○) is mentioned in the web of science.

of SFM surpassed the STM in the scientific community after 1998, which is probably due to the fact that: STM requires a conducting surface whereas SFM can image almost any surface. Besides this SFM is a more versatile technique compared to STM because besides topography other surface properties such as magnetic and tribologic properties can often be measured simultaneously.

For these reasons a SFM is also used to monitor the growth during PLD instead of a STM. As mentioned in chapter two detailed images of the surface morphology evolution are required to increase our fundamental understanding of the deposition process and a SFM is a suitable technique to capture such images. The outline of this chapter is as follows. In section 3.2 an overview of the different SFM operating modes is given. Besides this it describes dynamic mode spectroscopy curves and the procedure to extract the chemical and van de Waals interaction potential from the frequency shift versus distance curves. Dynamic mode spectroscopy was used in this thesis to study qualitatively the tip-sample interaction.

Section 3.3 describes, which dynamic feedback schedule is the most suitable to image the surface morphology in deposition conditions. Furthermore it describes three geometries to image the surface morphology during PLD. Section 3.4 summarizes this chapter with some concluding remarks.

3.2 Operating modes in SFM

The tip-sample interaction force F_{ts} bends the cantilever beam. This bending is used in static mode SFM to measure the surface topography. Besides the vertical bending, also the torsion of the cantilever can be used. This provides frictional information between the scanning tip and surface [26,15]. In this thesis friction data was used to study the surface termination of SrTiO_3 (001) substrates. To image the surface in static mode SFM the cantilever properties should be such that the cantilever deflection can be measured without tip or sample deformation [21]. In dynamic mode SFM, the cantilever is deliberately oscillated near or at its resonance frequency. The shift in resonance frequency f_0 , amplitude A_0 and phase γ_0 are used in dynamic mode SFM to depict the surface morphology. An advantage of dynamic mode SFM is that the lateral forces between tip and sample are reduced and therefore tip and sample deformation is limited compared to static SFM. The two detection schemes for dynamic SFM are Amplitude Modulation (AM-SFM) [10,14,15,16] and Frequency Modulation (FM-SFM) [27,5]. In the following part these two detection schemes will be briefly discussed.

3.2.1 Amplitude Modulation SFM

In Amplitude Modulation (AM-SFM) the cantilever is oscillating with a fixed drive frequency f_{drive} near its free resonance frequency. Due to tip-sample forces F_{ts} the resonance frequency f_0 will shift, which changes the amplitude $A=A_0\pm\Delta A$ at the drive frequency. This deflection signal is fed in the feedback loop to keep the oscillation amplitude and therefore the average force* constant. AM-SFM can be performed in the attractive, intermittent and repulsive tip-sample force regime. Dynamic mode SFM in the intermittent regime is often referred as Tapping Mode [28] and used in this thesis for ex-situ measurements. The minimum detectable force gradient in AM-SFM and FM-SFM is given by equation (3.4) [27].

$$\partial F_{\min} \approx \sqrt{\frac{2k k_B T B}{f_0 Q A^2}} \quad (3.4)$$

In this expression k is the cantilever spring constant, $k_B T$ is the thermal energy, B is the measurement bandwidth, Q is the quality factor of the cantilever, f_0 the resonance frequency and A the mean amplitude. It can be derived from equation (3.4) that the minimum detectable force depends on the

* This is the average force in one oscillation cycle.

cantilever properties (k, f_0, A, Q), bandwidth (B), temperature ($k_B T$) and measurement environment (Q). In this work silicon cantilevers with spring constants between 1- 80N/m and resonance frequencies between 70-300 kHz were used with free amplitudes varying between 5-200nm.

3.2.2 Frequency Modulation SFM

In Frequency Modulation (FM-SFM) [27], the cantilever is oscillating at its free resonance frequency. This is achieved by phase shifting the deflection signal (amplitude) by 90° and feeding it back in the modulation device that excites the cantilever. The cantilever can be excited with a constant excitation amplitude (CE) or constant amplitude (CA). To illustrate the difference of a cantilever excited in the CE and CA-mode the frequency shift Δf , amplitude A and excitation amplitude signal as a function of tip-sample distance d_{ts} of a cantilever excited in the CE and CA-mode are depicted in figure (3.4). In figure (3.4a) two graphs are depicted for the CE and in figure (3.4b) two graphs for the CA-mode. Both the frequency shift and the amplitude versus the tip-sample distance are illustrated. These graphs are so-called spectroscopy curves and the tip-sample distance d_{ts} is regulated by the scanner displacement (called z-piezo movement in figure (3.4)). In the graphs, taken from a paper published by Schirmeisen [29], four measurements are depicted. The difference in these measurements was the used oscillation amplitude. The plateau in the frequency shift and amplitude curves is a regime with no tip-sample interaction force. This corresponds to a relatively long tip-sample distance. In these figures it can be observed that:

- the frequency shift changes from negative, at relatively long tip-sample distances, to positive at small distances in both modes;
- the frequency shift is different for a different free oscillation amplitude;
- the frequency shift as a function of distance is different in both modes;
- the oscillation amplitude decreases in the CE-mode proportional to the tip-sample distance;
- the excitation amplitude increases in the CA-mode proportional to the tip-sample distance.

The latter two are expected, since dissipative forces decrease the cantilever oscillation amplitude with a decreasing tip-sample distance. It is important to notice that in the CE-mode this change in oscillation amplitude reduces the effective distance between tip and sample d_{ts} and can therefore be used to approach the sample surface gently. Notice the scale difference in the graphs, measured in the CE and CA-mode.

Figure 3.4: Spectroscopy curves measured with a silicon tip on HOPG in vacuum at room temperature. (a) Frequency shift Δf and amplitude curves as a function of the z-piezo movement obtained in the CE-mode. The free oscillation amplitude ranged from 23.4 to 39.9 nm. (b) Frequency shift and excitation amplitude curves as a function of z-piezo movement obtained in the CA-mode for amplitudes ranging from 23.4 to 38.6 nm. Notice that in the CE-mode the z-piezo movement is 15 nm, which is for a tip-sample interaction distance relatively long. This graph is taken from Schirmeisen [29].

Tip-sample interaction

These spectroscopy curves can be used to study the tip-sample interaction qualitatively and quantitatively. In the quantitative studies the different forces between tip and sample which corresponds with the change in the frequency shift are estimated, see figure (3.5). This figure (3.5) is taken from a paper published by García and Pérez [30]. The frequency shift in these spectroscopy curves is typically normalized to make the frequency shift independent of the cantilever oscillation amplitude. The normalized frequency shift is used in the CE as well as the CA-mode. For the CE-mode the basic formula is comparable [29] to the CA mode [30] for which it is expressed by equation (3.5).

$$\gamma(d_{ts}) = \frac{kA_0^{3/2}}{f_0} \Delta f(d_{ts}, k, A_0, f_0) \quad (3.5)$$

In this expression $\gamma(d_{ts})$ is the normalized frequency shift, A_0 is the free oscillation amplitude, k is the spring constant and Δf is the frequency shift. This expression is only valid for amplitudes A_0 larger than the typical range at which tip-sample forces F_{ts} occur. Notice that the frequency shift has an $A_0^{3/2}$ dependence which is also qualitatively observed in figure (3.4). The total normalized frequency shift consists of several contributions expressed in equation (3.6).

$$\gamma = \gamma_{chem} + \gamma_{vdW} + \gamma_{electrostatic} \quad (3.6)$$

In this expression γ_{chem} , γ_{vdW} , $\gamma_{electrostatic}$ are the normalized frequency shifts due to respectively the chemical, van de Waals and electrostatic force between tip and sample.

In figure (3.5) the above mentioned forces are expressed in a normalized frequency shift versus distance and depicted. The values for the normalized frequency shift are computed for a cantilever with a tip radius $R=10\text{nm}$, spring constant $k=30\text{N/m}$, amplitude $A=20\text{nm}$, $h=0\text{nm}$, $\alpha=100^\circ$, the geometric mean of the Hamaker constants of tip and sample $H=4 \cdot 10^{-19}\text{J}$, the tip sample potential difference V_{ts} , the contact potential V_c , $V_{ts}-V_c=1\text{Volt}$ and with equations (3.7-3.9). In figure (3.5) it can be seen that for tip-sample distances above 1-2nm merely long range electrostatic and van de Waals forces are contributing to the frequency shift with slopes of respectively 0.5 and 1.5.

Figure 3.5: Schematic representation of the tip and sample (a) and the computed distance dependence of the Chemical (Chem), Van de Waals (VdW) and Electrostatic interaction force expressed in the normalized frequency shift $\Delta f/f$ versus the tip-sample distance d_{ts} . The latter is referred here as the separation s . In the schematic representation $d=d_{ts}$ which is the distance between the tip and sample surface. Graph taken from [30].

To extract the chemical and van de Waals interaction from the frequency shift first the tip-sample potential has to be adjusted such that the electrostatic contribution can be neglected. The resulting van de Waals and chemical tip sample interaction potential has a negative and positive interaction energy, corresponding to an attractive and repulsive force at respectively long and short tip sample distances.

This van de Waals interaction and short range (<2nm) chemical potential can be fitted with respectively a Lennard-Jones potential and Morse potential. The electrostatic, van de Waals and chemical normalized frequency shift [30] are expressed by respectively equations (3.7), (3.8) and (3.9).

$$\gamma_{electrostatic} = \frac{-\pi\epsilon_0 R (V_{ts} - V_c)^2}{(\sqrt{2}d_{LR})^{1/2}} \quad (3.7)$$

$$\gamma_{vdW} = \frac{-HR}{12\sqrt{2}d_{LR}^{3/2}} \quad (3.8)$$

$$\gamma_{chem} = \frac{-U_0\sqrt{2}}{\sqrt{\pi\lambda}} \exp\left(-\frac{d-d_0}{\lambda}\right) \quad (3.9)$$

From these equations the normalized frequency shift $\gamma=(\Delta f/f_0)A_0^{3/2}$ can be determined with the assumption that $d_{LR} < R$ and $A > d_{LR}$. In these expressions the distance $d_{LR}=d+h_{nanotip}$ and R is the tip radius, see figure (3.5). In equation (3.9) U_0 , d_0 and λ are parameters that define the strength, position of the potential minimum and the range of the chemical interaction. The chemical potential is modeled with $U_0=2.25\text{eV}$, $d_0=2.35$ and $\lambda=0.079\text{nm}$. The used model, graphs and a more detailed description can be found in the review work of García and Pérez [30].

To image the surface morphology evolution during PLD long range van de Waals forces and especially electrostatic forces are typically unwanted. The latter can be eliminated by adjusting the tip-sample potential.

3.3 Combining SFM with PLD

The detection scheme and geometry to use a SFM for in-situ growth monitoring during PLD are described in this section. Most surfaces in this work were imaged with dynamic mode SFM in vacuum. In dynamic mode SFM there are two detection schemes based on amplitude and frequency modulation. The

* Magnetic and adhesion forces are neglected.

feedback response times for AM and FM are respectively τ_{AM} , τ_{FM} and expressed by equations (3.10) and (3.11).

$$\tau_{AM} \propto \frac{2Q}{f_0} \quad (3.10)$$

$$\tau_{FM} \propto \frac{1}{f_0} \quad (3.11)$$

In these expressions Q is the quality-factor and f_0 is the resonance frequency. In AM-SFM the response time is quality-factor dependent, whereas in FM-SFM it is independent. The background pressure during PLD is typically between $1\text{-}10^{-6}$ mbar and below 1 mbar, the quality-factor for a cantilever increases a few orders of magnitude [31]. Therefore the response time and frame rate for AM also increases several orders of magnitude. For this reason AM detection is not used in this pressure regime to image the surface morphology. In figure (3.6) the resonance frequency as a function of the background pressure is depicted. In this graph it can be seen that the resonance frequency increases as is the quality-factor from ambient towards 1 mbar after which it is more or less constant. The latter regime corresponds with the background pressure typically used in PLD. Notice that in both modes (AM and FM) an increase of the quality factor decreases the width of the frequency versus amplitude (figure 3.2c) and therefore increases the measurement resolution, see also equation (3.4).

Figure 3.6: Resonance frequency versus the background pressure measured in vacuum for a rectangular cantilever (uncoated silicon cantilevers Nanosensors NCL).

Geometries to image the surface with SFM during PLD

To measure the local surface morphology with a SFM during the PLD synthesis there are basically three options:

- (1) change the SFM or deposition geometry such that the plasma plume species can be deposited on the surface, without moving sample or force sensor;
- (2) move the force sensor temporarily towards the sample to measure with the SFM in a period with no deposition;
- (3) move the sample temporarily towards the SFM in a period with no deposition.

Option 1: change the deposition geometry

SFM can be combined with PLD by modifying the deposition geometry such that the plume is at an angle θ instead of normal to the sample surface. However, a disadvantage of this configuration is that part of the plasma plume is blocked and deposition on the SFM can not be prevented. Furthermore and maybe even more important, the nucleation and growth during deposition such as PLD can not be compared with the nucleation and growth in the standard deposition geometry [32].

Figure 3.7: Representation of the time schedule of the PLD-process. The grey area represents the deposition pulse $\sim 100\mu\text{sec}$. Nucleation and growth results in a decay of the adatom density (represented by the line). The vertical arrows indicate the period in which SFM measurements are planned. In the lower graph the deposition and growth periods are again depicted. Notice that the deposition and growth are separated in time.

Option 2 and 3: Moving the sample or SFM

In PLD the deposition and growth are separated in time. Therefore the local surface morphology can in principle also be measured with SFM without disturbing the deposition process, if the sample can be characterized by SFM between two deposition pulses, see figure (3.7). In this figure the time schedule of the PLD-process is schematically depicted. The two gray bars represent the deposition pulse ($\sim 100\mu\text{sec}$). These bars have been exaggerated for clarity in figure (3.7). The increase and decay in the adatom density is also depicted. After the deposition pulse the growth still continues. By separating the SFM-position in space from the PLD-position, the standard geometry for both SFM and PLD can be maintained and material deposition on tip and cantilever as well as other parts of the SFM is prevented. However, the sample or SFM has to be moved to continue or start imaging in a period with no deposition. As will be shown in chapter four, imaging can continue or start within seconds after the last deposition pulse. Capturing the surface morphology between two deposition

Figure 3.8: Literature overview of the SPM frame rate evolution. Calculated for (256x256 points) static mode (■) and dynamic mode SPM(*). In the graph the authors and years are depicted. For example in 1992 Quate presented a paper in which a frame rate above 100 images/sec is presented. Kuipers and Frenken [33,34], Quate [35], Norio Ookubo [36], Viani [37], Viani [38], Schitter [39], Ando [40], Humphris [41], Rost [47] Kodera and Toshio Ando [42] Humphris [43], Picco [44]. Besides this the typically used SFM frame rate (x) is depicted in the same graph.

pulses is in principle also not limited by the frame rate. The frame rate in this thesis is defined as the number of topography images per minute consisting of 256x256 pixels. In figure (3.8) it can be seen that since the SPM invention the frame rate of prototype research instruments in static as well as in dynamic mode increased by respectively two and four orders of magnitude, but it can also be seen that the frame rate of commercially available equipment kept almost constant. At present, frame rates of 10^3 and 10^4 in respectively dynamic and static mode SPM are the state of the art and companies such as Infinitesima [45] and Leiden Probe Microscopy [46,47] already sell equipment to image surfaces with several frames a second.

If high speed imaging can continue or start within seconds after the last deposition pulse the nucleation and growth can be monitored “quasi” real-time during PLD.

3.4 Concluding remarks

In this chapter SFM is briefly described which was introduced by Binnig, Quate and Gerber in 1986 [1]. SFM is an imaging technique to depict the surface morphology, but so far not used for in-situ growth monitoring during PLD. One of the problems in combining SFM with PLD* is the presence of the plasma plume. In this chapter it is shown that there are three geometries which can be used to combine SFM with PLD. With option (2) and (3) the growth can be followed in-situ when the SFM can continue imaging seconds after the last deposition pulse. From this chapter it is also learned that:

- FM-SFM is the most suitable dynamic operating mode to image the surface morphology in $1\text{-}10^{-6}$ mbar;
- the CE-FM-SFM mode can be used to approach the sample surface gently;
- imaging the surface morphology between two consecutive deposition pulses is in principle not limited by the frame rate;
- besides imaging the SFM can also be used as spectroscopy tool to study the tip-sample interaction.

The next chapter describes the hardware that was developed to extend the operating conditions for SFM and combine SFM with pulsed laser deposition.

* Standard or typical PLD conditions for compounds such as SrTiO_3 or TiO_2 are a substrate temperature of 750°C and a pressure of 10Pa oxygen.

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Chapter 4

Imaging with SFM during Pulsed Laser Deposition

4.1 Introduction and outline

In this chapter the developed hardware to combine Scanning Force Microscopy (SFM) with Pulsed Laser Deposition (PLD) and its performance are described. This equipment is intended to monitor the surface morphology during pulsed laser deposition. As mentioned in chapter three, there are basically three options to measure the local surface morphology with a SFM during the PLD synthesis, see also figure (4.1);

1. change the SFM or deposition geometry such that the plasma plume species can be deposited on the surface;
2. move the force sensor temporarily towards the sample to image the surface morphology in a period with no deposition;
3. move the sample temporarily towards the SFM to image the surface morphology in a period with no deposition.

Option (1) is in this thesis referred to as the theta configuration and option (2) and (3) are so-called parallel configurations. Option (1) and (3) have been build in this work. Of these two configurations, the parallel configuration was actually used and fully tested^{*}. The setup and hardware will be described in section 4.2. Section 4.3 describes the procedure to image the surface morphology,

^{*} The theta configuration resembles the typically used geometry of an SFM setup and was only used in this thesis to test the resolution and several high temperature sample stages. So far, the theta configuration has not been used during deposition. The theta configuration has not been tested during the deposition, to avoid the risk that the deposited material contaminates the SFM-head such that it became useless.

Figure 4.1: Schematic representation of the three options (1-3) to combine SFM with PLD. Option (1) is referred to as the theta configuration and options (2 and 3) are referred to as parallel configurations. In option (2) the SFM is moved towards the PLD-position in a period with no deposition. In option (3) the sample is moved back and forward.

within two consecutive deposition pulses, using the parallel configuration. The advantage of the parallel configuration is that deposition on tip and cantilever, as well as other parts of the SFM, is prevented. Furthermore and maybe even more important, the surface morphology can be imaged while using the generally used deposition geometry. To monitor the nucleation and growth of metal oxides such as TiO_2 , SrTiO_3 and SrRuO_3 , atomic step resolution is required at deposition conditions. Atomic step resolution is defined as the vertical resolution to observe atomic terrace steps. For complex oxides these steps are typically 0.1-0.4nm. Imaging a surface with atomic step resolution is possible if the vibration levels, which introduce mechanical noise, are low enough. In section 4.2 it will be demonstrated that this has been achieved. Another challenge was to design the SFM such that it can be used to monitor the surface morphology evolution at deposition conditions.

For oxides, such as SrTiO_3 and SrRuO_3 the PLD, deposition pressure generally ranges between $1\text{-}10^{-6}\text{mbar}$ and the substrate temperature between 500-850°C. Hardware was developed or modified to measure in this regime. Warming up of heat sensitive elements, such as the piezo-scanner, limit for example the maximum SFM operating temperature, which is typically 500°C in vacuum and 250°C in ambient conditions. To extend the operating temperature the piezo-scanner in the SFM-head was shielded from the heated surface and the thermal load on the SFM-head was minimized. In section 4.4 this hardware is described. In section 4.5 the performance of the modified SFM-head including the high temperature heating stage is demonstrated. The last section summarizes chapter four.

Figure 4.2: Artist's impression of the parallel configuration. SFM-head (1), sample (2), target (3), piezo-motor (5), support frame (6), stepper motor (11), sample-stage (10), linear slider (12) and belt (13). The piezo-motor (5) is used to move the SFM-head along the second linear slider (14) towards the sample surface.

4.2 Hardware to combine SFM with PLD

As mentioned in the introduction, the theta and parallel configuration have been build and tested in this thesis. In the parallel configuration the sample stage is transferred between the PLD and SFM-position. The choice to transfer the sample instead of the SFM-head was based on the fact that the sample stage can be transferred faster* between the two positions. In figure (4.2) an artist's impressions of the parallel configuration (option 3) is depicted. The position of the plasma plume in the parallel configuration is visible in figure (4.3b and c). To adjust the tip-sample distance the SFM-head (1) was moved along a linear slider (14) towards the sample (2). The SFM-head was moved by a piezo-motor (5)

* The sample stage can be constructed such that it has less inertia compared to the SFM-head, used in this work. An object with less inertia can be moved faster.

ANPY-100 from Attocube. To transfer the sample from the PLD towards the SFM-position the sample-stage (10) was also moved along a linear slider (12). It is transferred by a belt (13) which was driven by a stepper motor (11). The used SFM was an inverted fiber SFM (SIS ultraobjective) based on optical interference*. Details of the SFM can be found in section 4.4.

Figure 4.3: Photograph (a) and schematic drawings of the setup side view (b) and top view (c), with the parallel configuration. In the schematic drawings also the SFM-head (1), sample (2), target (3) and plasma plume (4) are depicted. In the side view and photograph, the air damped pods (7) and active damping elements (8) are visible. Above these damping elements respectively the vacuum chamber and the translation stages(x,y,z) were mounted. The latter were connected to the tube (9) which was used to rotate and translate the support frame.

* 4% of the laser light is reflected from the cleaved fiber-end. The other 96% of the light exits the fiber and impinges on the cantilever, reflects partly and travels back into the fiber. For optimal interference the angle between cleaved fiber-end and cantilever should be 8°. This insures that minimal light is reflected from the cleaved fiber-end back to the cantilever. The total optical power reflected back through the fiber depends on the phase difference between the fiber-end reflection and the cantilever reflection. Noise in the interferometer can come from thermal noise of a cantilever, stray reflections and frequency noise of the laser diode.

Atomic step resolution with the parallel configuration

To obtain atomic step resolution, the support frame was damped and the system was placed on a so-called VC-D floor. The general Vibration Criteria curves (VC-curves) [1,2,3] are used to describe the floor quality which ranges from VC-A to VC-G the latter describes a high quality floor with a minimal amount of noise in a range of 1 and 80Hz. In figure (4.3), the main damping systems are depicted. It can be seen in figure (4.3a,b) that the vacuum chamber was mounted on air pods and the support frame, on which the SFM-head was mounted, was actively damped with anti-vibration elements (Halcyonics MOD2). In figure (4.3b) the setup, with inside the vacuum chamber the parallel configuration, is depicted. In this drawing the active damping (8), passive damping elements (7), the sample (2), target (3), plasma plume (4), and tube (9) are visible. The tube was connected to the support frame. In figure (4.3c) a top view of the vacuum chamber is depicted. In this drawing the position of the plasma plume is visible. The support frame (6) could be rotated and translated to replace the sample, target or SFM-head and align the KrF excimer laser (248nm) laser on the target. It is important to notice that the SFM-head was placed horizontal. For optimal performance, the SFM-head should be placed vertical since the active and passive damping are optimized in this direction.

The effect of vibrations and the damping stages on the SFM-measurements was tested in vacuum by imaging a vicinal SrTiO_3 surface. In figure (4.4) two topography images are depicted which were captured with the parallel configuration in vacuum. In these images the surface morphology of SrTiO_3 ,

Figure 4.4: Topography images of a Nb-doped SrTiO_3 surface measured in vacuum without (a) and with (b) active damping activated. In the insets the effect of deactivation on the image resolution is visible. If the active damping was turned off scan and noise lines appear in the image. The images were measured with the parallel configuration.

which has terrace steps of 0.4 nm, is visible, while the active damping was turned on in figure (4.4b) and off in figure (4.4a). It can be seen that the atomic steps are observed in both images, however in figure (4.4a) several scan and noise lines are present opposed to figure (4.4b). In the inset a small part of the two images is zoomed in and several noise and scan lines are visible when the active damping is deactivated. This illustrates the effect on the images when active damping was on or off. Important to remember from this section is that with the parallel configuration atomic step resolution is achieved at room temperature if it is placed on a VC-D floor. On this floor atomic step resolution is obtained with both configurations. More information about the floor quality, as well as the damping properties of the system, can be found in appendix 4A.

4.3 Parallel configuration: Imaging between the deposition pulses

If the surface can be imaged between two consecutive deposition pulses the PLD synthesis is essentially not disturbed. Notice that after every laser pulse a plasma plume develops, which is referred in this thesis as a deposition pulse. To image the surface morphology between two pulses five steps should be completed. This section describes the procedure to integrate step 2 and 4 in the sample-stage transfer such that imaging can continue almost immediately after the last deposition pulse. The five steps are:

1. move the sample towards the SFM position in an interval with no deposition
2. approach the SFM towards the sample surface
3. measure the surface morphology with atomic step resolution
4. retract the SFM from the sample surface
5. move the sample away from the PLD position during deposition

The period between two consecutive deposition pulses typically varies from 0.1-25 seconds, whereas the time to capture an image with SFM is far more. Furthermore it requires typically even more than a minute to load the sample, to approach and to retract again. Notice that the time to approach and also the required time to capture an image are both two orders of magnitude larger than the period between two deposition pulses. However, as is described in chapter three, it should in principle be possible to increase the frame or imaging rate by two orders of magnitude such that the imaging period, step 3, can be neglected. This means that it would be feasible to image the surface morphology between two deposition pulses if steps 1, 2, 4 and 5 can be finished within 0.1-25 seconds. In the parallel configuration the SFM and PLD-position are separated by ~60mm and transferring the sample stage, step 1 and step 5, within a second over 60mm is not an issue. The only problem was to quickly approach the tip towards the

Figure 4.5: Schematic representation of the setup to integrate the approach and transfer procedure. The movement in the X-direction is used to transfer, retract and approach. The angle α is exaggerated for clarity.

sample surface, step 2, without sample or tip deformation. In this thesis step 1 and 2, as well as 4 and 5, were integrated such that the total transfer and approach time and also the retract and transfer time can be decreased.

The way this was done is as follows: the sample was mounted under an angle α ($0-5^\circ$) and approached and retracted sideways, instead of in the direction normal to the sample surface, see figure (4.5). In this figure, the sample is depicted in the SFM as well as in the PLD-position. By mounting the sample under a small angle α , a coarse movement in X results in a fine movement in Z. With this setup and procedure, mechanical positioning is less critical. For example a transfer repositioning error* $\Delta X = 1000\text{nm}$ changes the tip-sample distance only by $\Delta Z = 17\text{nm}$ for $\alpha = 1^\circ$. By keeping the SFM scanning in the constant-force mode during transfer, ΔZ is automatically adjusted. In this procedure, the initial approach is done by moving the SFM towards the sample surface. To reduce tip and sample deformation the SFM was operated in CE-FM-SFM. In this mode the effective distance, between tip and sample d_{ts} , is reduced and therefore used here to approach the sample surface sideways [4,5], see also chapter three.

* The reposition error Δx can in principle also be used to reposition the sample surface location in the transfer-direction such that the same microscopic surface location can be followed.

Important to remember from this section is that during transfer of the sample from the PLD-position towards the SFM-position the tip is automatically approached, and during transfer from SFM towards deposition the tip is automatically retracted. To demonstrate the procedure an image is depicted, in figure (4.6), in which the sample was transferred while scanning. The SFM was imaging a SrTiO_3 surface with $\sim 0.4\text{nm}$ high terrace steps. At T_1 the stepper motor moved the sample towards the PLD-position and, almost immediately, the tip lost contact with the sample surface (retraction). At T_2 (approach) the SFM continued imaging the SrTiO_3 surface with atomic step resolution. In the period $T_{1 \rightarrow 2}$ the sample is switched from the SFM towards the PLD and back towards

Figure 4.6: SFM-topography while imaging a treated SrTiO_3 (001) substrate surface with 0.4nm high terrace steps, during imaging the sample was moved from the SFM towards the PLD-position and back. At T_1 the sample was moved towards the PLD position and the tip is retracted. At T_2 the SFM continued imaging after the sample was transferred back towards the SFM-position. The SFM was scanning between $T_{1 \rightarrow 2}$.

the SFM-position. Obviously in this period the surface morphology is not visible.

From this section it is important to remember that the scanning SFM almost directly continues imaging, after transferring the sample from the PLD towards the SFM-position, without moving the SFM-head by the piezo-motor. During these experiments the angle α was typically 1° . To transfer the sample from the deposition towards the SFM-position and visa versa, the sample was moved along linear sliders (ERO fuhrungen type SM30.105.080) with a spindle or belt in

combination with a stepper motor^{*}. The parallel configuration in figure (4.2) is only depicted with the belt.

The main difference between the two mechanisms, to transfer the sample, is the step size and therefore also the total time $T_{1 \rightarrow 2}$. As can be seen in table 4.1, the maximum step size of the spindle drive is $\sim 4\mu\text{m}$, whereas the belt drive has a minimum step size of $\sim 24\mu\text{m}$.

In figure (4.6) the sample was transferred with the spindle drive and a step size of 600nm. The sample stage had a low velocity at the SFM and PLD-position, which was correlated to the motion profile of the stepper motor. In figure (4.7) the step/second for the stepper motor as a function of time is depicted. Notice that the time is related to the number of steps and the

Figure 4.7: Example of a typically used motion profile for the stepper motor with the settings: starting speed 10, acceleration 5% and top speed 250. The sample stage velocity profile has a comparable shape. The sample stage has a low velocity at the SFM and PLD-position. Graph taken from Mocon-ST1 manual [6].

steps/second to the stepper motor revolutions. It can be derived from figure (4.7) that the sample stage is transferred such that it had a relative low transfer speed at the SFM-position. In the following pages the performance of both the spindle and belt drive will be described.

* The spindle was connected to an AML model C17.1 L025-076 UHV motor and the specific hardware elements for the belt drive are taken from an Epson(830) printer. To drive the motors a labview program (MOCON-ST1 from Mulder-Hardenberg BV in the Netherlands) was used.

Table 4.1: Sample stage step size with the belt and spindle drive.

Stepsize	Spindle drive [μm]	Belt drive [μm]
Minimum	0.3	24
Maximum	4	192

4.3.1 Transfer with the spindle drive

In figure (4.8) a marker is placed in the topography evolution images after depositing indium oxide* using 3, 5 and 10 deposition pulses. As can be seen in image (a-c), the marker can be followed after the subsequent deposition pulses. In the images terraces of the used SrTiO_3 substrate, are visible as well as three-dimensional islands. It can also be seen that atomic step resolution can be

Figure 4.8: SFM topography images. Surface morphology evolution of deposited indium oxide on top of Nb-doped SrTiO_3 followed at room temperature. As a guide for the eye a marker is placed in the images after 3 deposition pulses (a), after 5 deposition pulses (b) and after 10 deposition pulses (c). Notice that in these topography images atomic substrate steps (0.4nm) with on top indium oxide islands are visible which density and size increases.

maintained. Positioning of the sample stage was regulated by simply stopping the motor after n steps. The minimum period $T_{1 \rightarrow 2}$ could be reduced to 18 seconds, which results in an average transfer and approach speed of 6.6mm/sec. Maybe even more important is the lateral shift in the images of $\pm 500\text{nm}^\dagger$. Notice that the surface morphology is slightly shifted in the images. This shift is within the range of the SFM-scanner ($15 \times 15 \mu\text{m}^2$) such that the same surface location can in

* The SFM measurements as well as the deposition was done in a background pressure of 0.7mbar at room temperature, a fluency of 3Jcm^{-2} and a substrate target spacing of 50mm. This results in a deposition rate around 0.1nm/pulse. This pressure was chosen such that three-dimensional islands were formed on the SrTiO_3 surface.

† The obtained reposition accuracy is comparable with the motor stepsize ($\sim 600\text{nm}$) used in this experiment.

principle be monitored. The ability to follow the same surface location is often a problem in surface science studies and therefore valuable. This can for example be used to study the evolution of unique nanostructures.

4.3.2 Transfer with the belt drive

To reduce the time $T_{1 \rightarrow 2}$ even further a mechanism was tested in which the sample stage was connected to a belt drive. To measure the repositioning accuracy ΔX , of this mechanism, a calibration sample was used. The surface of this sample consists of physically etched micrometer sized structures with a height of 6-12nm. In figure (4.9) six images are depicted. It can be seen that a clear structure is visible and that between $T_{1 \rightarrow 2}$ there is no topography information. In these images, the total time $T_{1 \rightarrow 2}$ decreases from image (a) to image (f).

As is mentioned above, the sample is transferred towards and from the PLD-position in $T_{1 \rightarrow 2}$. It can be seen that in images (a-d) a round marker and in images (e,f) a square marker is placed. This is done, as a guide for the eye, to

Figure 4.9: SFM topography images to demonstrate the transfer procedure. In the images the period $T_{1 \rightarrow 2}$ decreases from 10 seconds (c) to 2 seconds in (e and f). To visualize the repositioning a round marker is placed in (a-d) and a square marker in (e) and (f). Notice the shift in the marker if $T_{1 \rightarrow 2} < 4$ seconds. During imaging the sample was moved towards the PLD-position and back to the SFM-position to continue imaging.

follow the repositioning error after the transfer. It can be seen that by increasing the sample stage velocity, and therefore decreasing $T_{1 \rightarrow 2}$, the shift in the marker increases. This is clearly visible below $T_{1 \rightarrow 2} < 4$ seconds, see images (e,f). In these images the square marker shifts several micrometers from image (e) to image (f) in contrast to the marker in images (a-d). A large shift in the markers means a large repositioning error ΔX .

By using the belt drive the transfer- and approach- time was reduced to two seconds with a sample repositioning accuracy of $\pm 2\mu\text{m}$. This error ΔX is such that the same surface location can be measured several times if the SFM is used to compensate the error. The value of $\pm 2\mu\text{m}$ suggests that the error was caused by slipping of the mechanical system and not by an error^{*} of the stepper motor. If that was the case at least an error of $24\mu\text{m}$ is expected, see also table (4.1). Increasing the repositioning accuracy by further tuning the setup, mainly the belt and sliders, is maybe possible although difficult.

The minimum transfer and approach time could be reduced to 0.5 second. This results in an average transfer and approach speed of 120mm/sec and a $T_{1 \rightarrow 2} \sim 1$ second.

So by simply integrating the several steps listed above, $T_{1 \rightarrow 2}$ is decreased by two orders of magnitude. The above mentioned procedure can also be integrated with a high frame rate SPM. In high speed SPM equipment the load and approach time, instead of the time to capture several frames, will be the time limiting process. With the above described procedure the load and approach period can be reduced to several seconds. It is expected that the combination of a fast load and approach can be used to make a high throughput SPM tool.

4.4 Extending the SFM operating range to study metal oxides

To monitor the nucleation and growth of oxides such as SrTiO_3 and SrRuO_3 at deposition conditions, the SFM should be able to measure surfaces at temperatures between 500-850°C and in pressures between 10^{-6} -1mbar. Imaging with high spatial resolution at these conditions was a challenge for a number of reasons. For example warming up of the SFM-head has to be limited, since the piezo-scanner can depolarize. A second problem in imaging hot surfaces was that the images can become distorted[†] and the cantilever properties drift when the

* With an error of the stepper motor is meant that instead of n-steps (n+1) or (n-1) steps are made.

† In SPM the measurement is based on the piezo-electric-scanner feedback in the three orthogonal directions x y and z. Piezo properties like the displacement-voltage are temperature dependent and to measure accurately the scanner has to have a constant temperature. Furthermore warming up of the setup can induce lateral and vertical drift in the images due to thermal expansions of the system.

temperature is not constant. For example the resonance frequency, amplitude and cantilever deflection change if the temperature is not constant. This makes the characterization of the surface topography with atomic step resolution at elevated temperatures more difficult with SFM compared to STM.

To monitor hot surfaces the SFM piezo-scanner was shielded from the heated surface and a small high temperature sample stage was used. The latter was developed to reduce the thermal load on the SFM-head. In the following pages the hardware to extend the operating conditions is described. This hardware was used to monitor the surface morphology during the deposition of material systems such as SrTiO_3 and SrRuO_3 at deposition conditions.

4.4.1 A scanner for the PLD pressure range

Before describing the hardware to extend the SFM operating temperature, the piezo-scanner^{*}, which was designed such that it can be operated between $1\text{-}10^{-6}\text{mbar}$, will be described. Measuring with SFM in $1\text{-}10^{-6}\text{mbar}$ is difficult since, electrical breakdown can distort the measurement by changing the offset potential of the piezos [7]. In the segmented SFM-scanner the distance between the scanner electrodes is around 1mm and the maximum voltage was limited to 330Volts. This was designed such that electrical breakdown[†] is circumvented. In figure (4.10) the breakdown voltage or spark potential for different gasses is depicted. In this figure the PLD pressure regime for this scanner is also visualized. It can be seen that the sparkpotential [8] is not reached for the maximum deposition pressure (1mbar), since the maximum potential is only 330Volts at 10^{-4}cm atm . This means that measuring in the above mentioned pressure regime is not difficult if the potential across and layout of the piezo-tube are such that the sparkpotential is not reached. Empirically SFM imaging in a pressure range of $1\text{-}10^{-6}\text{mbar}$ was achieved without any discharge problems.

4.4.2 A scanner for elevated temperature operation

The maximum sample temperature on which a SFM can image the surface morphology is called the maximum SFM operating temperature. As mentioned above this temperature is often limited [9] due to the excessive heating of heat sensitive elements in a SFM-setup, such as the piezo-scanner. At present, lead zirconium titanate (PZT) is mostly used as a piezoelectric material to scan the

* With the tube-scanner, piezo-tube and piezo-scanner the same is meant in this work.

† The potential at which electrical breakdown starts is the so-called sparkpotential and depends on the type of gas, the background pressure, the electrode material and the spacing between the electrodes.

Figure 4.10: Breakdown voltage versus pd for different gasses. The distance between the electrodes is d and p is the background pressure. The pd -values for the typically used PLD-regime is depicted, 10^{-4} cm·atm corresponds with the maximum deposition pressure. Graph taken from [11].

surface, since it has a high displacement-voltage [10]. To prevent scanner depolarization and measurement distortions* the scanner has to be operated at a constant temperature well below the Curie temperature. This is around 150°C for the used PZT-scanner.

Although other classes of piezoelectric materials, such as lithium niobates and bismuth titanates, can be used to extend the maximum operating temperature, the applicability of these materials in scanners is limited, since their displacement voltage is compared to PZT orders of magnitudes lower.

In this work a typically used tube-scanner (EBL#2) was shielded from the hot surface with a Macor-tube. Before describing this shielded scanner some results will be presented, which have been used to design this SFM-head. First a dummy-SFM was build to estimate how much shielding was required. This dummy-SFM consisted of a tube scanner with on top a 20mm long Macor insulation tube. This assembly will be referred to as the dummy-SFM. To test the

* In SPM the measurement is based on the piezo-electric-scanner feedback in the three orthogonal directions x y and z . Scanner properties like the displacement-voltage have to be constant to measure accurately.

Figure 4.11: Temperature profile image (a) and line scan (b) of the dummy SFM in air. The image and profile were measured with a thermoelectric camera at different heater temperatures. The numbers in the line scan across the dummy correspond as following: heater(1), Macor-tube(2), middle of the Macor-tube(3), Macor-piezo interface(4) and piezo (5).

dummy-SFM, a heater was pressed against the top of the Macor-tube and the temperature profile was measured, see figure (4.11). The heater (Heatwave labs. Inc., model 101491 UHV/O₂) required around 28Watt to reach 500°C in vacuum and had a comparable diameter as the Macor-tube. The used thermal load on the SFM-head has been decreased during this work to approximately one Watt. In section 4.4 the present used low power heating stage is described in detail.

Although currently the thermal load on SFM-head is different, the following experiments and data are still important and will be used later in section 4.5. In figure (4.11) an image recorded with a thermoelectric camera [12] and the corresponding line profile, measured in ambient conditions, are visualized. In the image the Macor-tube (3) and piezo-tube (5) of the dummy-SFM are depicted. The temperature profile of figure (4.11b), was captured with a thermoelectric camera after calibrating the emissivity values* with a thermocouple. The temperature profiles in figure (4.11b) were taken at different heater temperatures. Notice that the numbers in the line profile correspond with the numbers in the image of figure (4.11a). It can be seen in figure (4.11b) that there is a relatively large temperature gradient at the Macor-piezo interface. A gradient is expected, but this transition is probably not representing the true interface temperature, since in this test the thermal contact between the Macor-tube and piezo-tube was

* $\epsilon \sim 0.7$ for the piezo-tube $\epsilon \sim 0.90$ for the macor shielding and $\epsilon \sim 0.9$ for the alumina holder.

not well defined. This was different for the dummy-SFM compared to the currently used SFM because old components were used, which were damaged at the Macor-piezo interface. Nevertheless, it can be seen that the Macor-piezo interface temperature was less than 150°C with the heater at 400°C . Therefore it was expected that it should be possible to scan on this heater without depolarizing the piezo-scanner up to heater temperatures of 400°C .

The piezo-Macor interface temperature was also measured^{*} as a function of the background pressure with the top of the Macor tube heated up to 600°C . This temperature was reached by pressing the dummy-SFM on the heater. In vacuum the maximum temperature was set to 600°C to prevent fluorine out gassing[†]. As can be seen in table 4.2, the maximum interface temperature was 78°C at a pressure of $2 \cdot 10^{-1}\text{mbar}$. Since this is well below 150°C , it can be concluded that the Macor tube is long enough to shield the piezo scanner up to 600°C in a background pressure up to $2 \cdot 10^{-1}\text{mbar}$.

Table 4.2: Temperature measured at the Macor-piezo interface at different background pressures with the dummy-SFM pressed on the ceramic heater.

Temperature heater [$^{\circ}\text{C}$]	Pressure [mbar]	Temperature Macor-piezo interface [$^{\circ}\text{C}$]
600	$1 \cdot 10^{-5}$	57
600	$1 \cdot 10^{-2}$	65
600	$2 \cdot 10^{-1}$	78

SFM hardware

In figure (4.12) the SFM assembly, the cantilever holder and the SFM-head are depicted. The base plate was connected to the bottom of the SFM-housing to protect the SFM-assembly. On top of this base plate the piezo-tube, Macor-tube and fiber holder were glued. The optical fiber was glued into the fiber holder, which was mounted on the Macor-tube. The aluminium cantilever holder contains a pre-aligned cantilever, which was placed on top of the fiber holder, such that the micron sized cavity between the cleaved monomode fiber (785nm) and cantilever could be tuned [13]. To tune this cavity a second piezo[‡] was located directly beneath the cantilevers. This piezo was used to actively tune the

^{*} Infrared transmitting vacuum windows like BaF_2 were not available to measure the profile non invasively with the thermoelectric camera

[†] www.almath.co.uk/macor.htm

[‡] This element is used to actively tune the interferometer and to excite the cantilever in dynamic mode.

Figure 4.12: Schematic representations of the SFM-head and its components. The SFM-assembly was mounted in the SFM-head. The aluminum pre-aligned cantilever holder was mounted on the fiber holder. This is removed, in the top view of the SFM-head.

interferometer and to excite the cantilever in dynamic mode. Notice that this piezo is not shielded from the hot surface.

To characterize the thermal properties of the SFM-assembly, and especially the piezo-tube, the temperature profile was measured in air and vacuum. The distance between the heater and SFM-assembly was 1-3mm and the metal housing was removed. In figure (4.13) the temperature profiles of the SFM assembly are depicted at different heater temperatures. Notice that the part numbers in figure (4.12) correspond to the same part numbers in figure (4.11) and (4.13). As can be seen in figure (4.13), the Macor-piezo interface temperature was less compared to the measured values at the dummy-SFM. This can be expected, because the gap reduces the total heat transfer. Furthermore, it can be seen in figure (4.13b) that the maximum scanner temperature was well below 150°C, while the heater temperature ~400°C. In vacuum it is expected that the heat transfer, and therefore the total thermal load on the SFM-head, further decreases. To verify this, the temperature evolution profile was measured in 10Pa^{*}, with a constant heater power, see figure (4.14). At three locations thermal contact with a thermocouple could be established. As can be seen from figure (4.14), the temperature in the middle of the Macor tube was ~75°C after ten minutes. Furthermore, it can be seen that after ten minutes the temperature

* In PLD typical background pressures are 10Pa and therefore this pressure was also chosen in this experiment.

Figure 4.13: Temperature profile image (a) and line scan (b) of the SFM-assembly in air. The image and profile are measured with a thermoelectric camera at different heater temperatures. The numbers in the line scan across the SFM correspond as following: g heater (1), Macor tube (2), middle of the Macor tube (3), Macor-piezo interface (4) and piezo (5).

gradients $\Delta T_{1-2}^* \sim 230^\circ\text{C}$ and $\Delta T_{1-3} \sim 415^\circ\text{C}$. The total temperature gradient between the top and middle of the Macor-tube is $\sim 125^\circ\text{C}$, which means that the piezo-tube was well below 75°C . From these measurements it can be concluded that the piezo-scanner was sufficiently shielded, such that tests could be performed with the used heater up to 700°C in vacuum and 400°C in ambient conditions without risking that the scanner depolarizes.

In section 4.5 it is shown that the cantilever was only heated up to 90°C with the currently used high temperature sample stage at 750°C in 10^{-2}mbar . This means that with the current thermal load on the SFM-assembly ($\sim 1\text{Watt}$ is required to reach 500°C) the piezo-tube is warmed up by only a few degrees. Notice that the temperature profiles of the SFM in vacuum were measured for a heater that required 28Watts to reach 500°C . By decreasing the thermal load on the SFM-head also several other issues faced by operating the SFM at elevated temperatures were reduced, such as thermal drift due to lateral and vertical thermal expansions, excessive heating of heat sensitive SFM elements, as well as the resonance frequency drift of the cantilever. These issues will be described in

* ΔT_{1-2} is the temperature gradient between the heater (1) and the cantilever body (2).
 ΔT_{1-3} is the temperature gradient between the heater (1) and the middle (3) of the Macor tube.

Figure 4.14: Temperature profile measured in 10Pa oxygen at several SFM-assembly locations while the heater temperature is increased at $t=0$ seconds from 20°C to 415°C at $t=40$ seconds and up to 490°C after 600 seconds. The heater power was kept constant at 28W. $\blacktriangle$ In the middle of the Macor tube (3), $\circ$ cantilever body (2), $\blacksquare$ Interface fiber holder cantilever holder (2-3).

section 4.5. The next section describes the high temperature sample stage, which was used to test the SFM performance at elevated temperatures.

4.4.3 A high temperature sample stage for elevated temperature operation

To extend the maximum operating temperature for scanning probe microscopy several academic groups have developed small thermal mass heating stages [14,15,16,17,18,19,20] to minimize the input energy. At present, the highest SFM operating temperature in ambient is obtained with a hot stage fabricated by M. Dibattista et al. This $350\mu\text{m}$ diameter heater ($2.7^{\circ}\text{C}/\text{mW}$) can heat the surface up to 800°C and image up to 400°C in ambient conditions, without damaging the scanner.

Heaters designed, fabricated and calibrated by Gregor Whiche from MAT Berlin were comparable with the ones used by Dibattistata et al. With these heaters and the above described SFM-head, images up to 800°C at ambient conditions were captured, see appendix 4B. To our knowledge this is the highest operating temperature at ambient conditions, although the applicability of these membrane heaters for SFM is limited. This is limited, because it is difficult to mount a sample on top of these heated membranes (several microns thick). Therefore a substrate as SrTiO_3 can not be used as a template.

At present, a high temperature sample stage is used, on which samples can be mounted relatively easily. This high temperature sample stage can be operated in different gas environments, such as oxygen with a pressure ranging from ambient to UHV. This high temperature sample stage is depicted in figure (4.15).

In figure (4.15), which is not on scale, the SFM-head in combination with the high temperature sample stage is depicted. The latter is also visualized in top and side view. In figure (4.15a) the different components of the SFM-head can be seen. Notice that the piezo, mounted in the cantilever holder, is not shielded from the hot surface. In this high temperature sample stage a filament (Pt200 resistor), embedded in a rigid ceramic plate ($2 \times 4 \times 1.2 \text{ mm}^3$), was used to heat a $2 \times 2 \text{ mm}^2$ area. In the high temperature sample stage the rigid connection wires were used to suspend the heated area ($2 \times 2 \text{ mm}^2$) almost freely and therefore the heat losses were minimized. In the above mentioned hot stages, the used membranes are also suspended. In this way, the above described membrane heaters of Dibattista and Gregor Whiche resemble the high temperature sample stage, although the thermal load of our hot stage is somewhat larger.

An advantage of our stage is that samples with dimensions up to ($2 \times 2 \text{ mm}^2$) can be mounted on top of the heated area. Here, this was done with thermally conducting Platinum paint. The paint was used to improve the temperature

Figure 4.15: Side view of SFM-head and heater configuration (a) with a zoom on the high temperature sample stage in top view (b) and side view (c). 1: sample 2: piezo 3: Macortube 5: Piezo-tube. The ceramic plate (Al_2O_3) with the embedded heater filament is clamped in the support block.

homogeneity and to minimize the temperature gradient between the heater and sample surface. Furthermore, it has a high melting point and does not sublime up to 850°C, in contrast to the commonly used silver paint (Leitsilber 200) which sublimates above 500°C in vacuum, see appendix 4C. The filament resistance (Pt200) is directly related to the filament temperature and reliable up to 850°C with an accuracy of $\pm 15^\circ\text{C}$. Therefore no additional thermocouple or pyrometer was required. To measure the resistance a voltmeter (Keithly 197) was placed parallel and an amperemeter (HP 34401A Multimeter) in series with the resistor. This stage has several advantages listed below compared to other designed and tested heating stages. In appendix 4B more information about the build and tested heating stages can be found.

- The temperature read-out is integrated in the heater.
- The drift while imaging due to lateral and vertical thermal expansions is minimized since warming up of the SFM setup is minimized.
- Samples up to $2 \times 2 \text{ mm}^2$ can be characterized.

To characterize the heater performance several properties were measured such as the input power. The required input power to reach a stable heater temperature as a function of pressure is given in figure (4.16). In this figure the difference between the total input power to heat a SrTiO_3 substrate measured in 10^{-4} and 10^{-2} mbar is limited. It can also be seen that the input power increases above 10^{-1} mbar and is as expected higher in ambient conditions. Since there is almost no input power difference below 10^{-2} mbar, it can be concluded that

Figure 4.16: Heater temperature as a function of input power and pressure ■ 10^{-4} mbar ▲ 10^{-2} mbar ● 10^{-1} mbar ○ atmospheric pressure. Notice that below 10^{-2} mbar there is almost no difference in input power versus temperature.

radiation and conduction are the two main contributions to the total heat loss from 10^{-2} - 10^{-6} mbar. The difference in input power to reach a heater temperature in air and vacuum can be attributed to convection. In the following page a model is described to estimate the contribution of radiation, conduction and convection to the total heat loss of the heater. These values can be used to further reduce the thermal load on the SFM-head by decreasing the heater input power.

4.4.3.1 Thermall losses of the high temperature sample stage

To estimate the heat losses a model was fitted to the data measured at 10^{-4} mbar. The model calculates Q_{total} which is expressed by equation (4.1). The model will be described after treating the results. From the fit of the data in figure (4.17) it can be concluded that:

- the conduction losses through the wires and the radiation heat losses from the heated area are almost equal at relative low temperatures and radiation starts to dominate above 450°C ;
- the temperature of the connection wires is limited (less than 250°C while the heater is above 750°C);
- to further decrease the thermal load on the SFM-head the radiation heat losses have to be further minimized.

Figure 4.17: Estimated values for the conduction and radiation heat losses of the heating stage. Heat losses as a function of heating stage temperature, the depicted curves are as follows: (■) measurement data taken in 10^{-4} mbar, (○) fitted data calculated with Q_{total} . (▲) Fitted radiation calculated with Q_{hob} , (△) fitted conduction losses through the wires calculated with $Q_{\text{conduction}}$, (□) fitted radiation losses calculated with $Q_{\text{conduction}}$ and Q_{cold} . These were calculated after fitting T_l such that the fit approximates the measurements. T_l $T_c \sim 200\text{K}$ with the heating stage temperature at 1000K .

In a typical high temperature UHV STM setup around 4W [18] is needed to directly heat a semiconductor-slab up to 500°C. Advantages of the above described high temperature sample stage compared to this directly heated semiconductor-slab are that:

- the input power is a factor of four less;
- it can be applied in different environments such as vacuum, ambient and even into liquids;
- it is relatively easy to mount samples on.

This description of the heating stages is also helpful to comprehend that the total heat loss can be further decreased if the heated area reduces, although it has to be mentioned that by decreasing the surface area, the required skills for sample handling increases.

Model

$$Q_{total} = Q_{radiation} + Q_{conduction} \quad (4.1)$$

In this expression Q_{total} is the total heat loss, $Q_{radiation}$ is the heat loss due to radiation and $Q_{conduction}$ is the heat loss due to conduction. In the model only radiation and conduction are taken into account and the heat losses due to convection are neglected. Since the filament (Pt200 resistor) was embedded in a rigid ceramic plate (2x4x1.2mm³) of which 2x2mm² was only heated, the radiation is expressed by equation (4.2).

$$Q_{radiation} = Q_{hot} + Q_{cold} \quad (4.2)$$

In this expression Q_{hot} is the radiation energy from the hot area^{*} and Q_{cold} is the radiation energy from the plate surface directly outside the hotspot in which there is a temperature gradient. The irradiative heat losses are expressed by equations (4.3) and (4.4).

$$Q_{hot} = \sigma \varepsilon A_{hot} (T_h^4 - T_c^4) \quad (4.3)$$

$$Q_{cold} = \sigma \varepsilon A_{cold} (T_l^4 - T_c^4) \quad (4.4)$$

In these equations σ is the constant of Stefan Boltzmann, ε is the emissivity, A_{hot} is the hotspot area, A_{cold} is the plate area in which there is a temperature

* The substrate surface, the backside surface and edge surfaces

gradient, T_h is the heatingstage or hotspot temperature, T_l is the temperature of the cold part of the heatingstage and T_c is the environmental temperature. The emissivity value for the heating stage and SrTiO_3 was set at 0.7 [21,22]. In this model the radiation contribution of the connection wires was neglected because it was expected that the wires were at a relative low temperature. To model the conduction equation (4.5) was used.

$$Q_{\text{conduction}} = 2 \left[\frac{kA(T_l - T_c)}{l} \right] \quad (4.5)$$

In this expression k is the thermal conductivity A , is the cross sectional area of the platinum wire, l is the length of the platinum wire before it is clamped to the heat sink (6mm), T_l is the temperature of the cold part of the heatingstage and T_c is the environmental or heat sink temperature in Kelvin.

T_l was determined in a simple procedure with a fixed emissivity and using the heating stage temperature to calculate Q_{hot} such that Q_{total} approximated the measurement data. In the model $k=72\text{W/m}^2$ and $T_c=293\text{K}$.

4.5 SFM performance at metal oxide PLD conditions

The period for the SFM-head, setup and heating stage to reach a workable thermal equilibrium such that the surface can measured in dynamic mode with atomic step resolution is defined as the stabilization time. This period after a temperature step depends on the stabilization time of:

1. the cantilever resonance frequency;
2. the interferometer operating point;
3. the cantilever oscillation amplitude;
4. the heating stage;
5. the mechanical setup.

The warming up of the cantilever (1) will shift the resonance frequency since the cantilever will expand and the Young's modulus of silicon decreases with temperature. For the used cantilevers the decrease is mostly due to the latter and has a value of 5.2Hz/K [17]. The interferometer operating point* (2) was affected by temperature due to thermal expansions of the SFM which also resulted in

* To control the interferometer operating point the piezo below the cantilever was moved such that the interferometer setpoint was at the maximum slope of the interference amplitude distance curve. This sinusoidal curve has a maximum and minimum interference amplitude corresponding to the distance between fiber-end and cantilever.

vertical and lateral drift during imaging. Furthermore it was changed due to the increase of the piezo displacement-voltage with temperature which also affects the cantilever excitation signal and therefore the oscillation amplitude. Warming up the mechanical setup (5) and heating stage (4) will cause lateral and vertical drift during imaging and has to be minimized. The shift in resonance frequency, due to a small temperature increase, is relatively large in vacuum. Only if the cantilever holder and SFM-head temperature are constant, the cantilever temperature will become constant and the resonance frequency will stabilize. It is expected that the cantilever resonance frequency takes the most time to stabilize and the heater temperature is the fastest. To estimate the stabilization time, the resonance frequency and heater resistance were measured, after increasing the heater temperature from room temperature to 750°C, see figure (4.18).

In figure (4.18a) the temperature of the heating stage is depicted in ambient

Figure 4.18: a) Thermal response of the heating stage in ambient ($\circ$, Δ) and 10^{-4} mbar ($\bullet$, $\blacktriangle$). b) Shift of the cantilever resonance frequency after a temperature increase from room temperature to 750°C at $t=0$ sec. Inset the frequency change as a function of time. The resonance frequency was measured in 10^{-4} mbar the time for the heater to stabilize was less than 1 minute.

and vacuum during quenching and heating. In figure (4.18b) the change in the resonance frequency is visible during heating up to 750°C in vacuum. The inset shows the frequency drift in Hz/min. It can be seen in figure (4.18a) that the heater temperature was stabilized within a minute, whereas the resonance frequency requires a stabilization time of at least 30 minutes after the

temperature step^{*}. Notice the difference in time scale (minutes and seconds) between the two figures. The difference in response time can be explained by the difference in thermal mass of the heating stage and SFM-head. As mentioned above the cantilever temperature will become constant if the SFM-head is stabilized. Empirically imaging can start after stabilizing at least 30min while heating a sample up to 750°C. From figure (4.18b) this can also be expected, because after 30min the resonance frequency becomes stable.

In figure (4.18) it can also be seen that the sample can be quenched, down to room temperature, within two minutes in vacuum and 75 seconds in ambient conditions. These two different quenching times can be explained by the fact that the heat loss in vacuum, at relatively low temperatures, has to come from the conducting losses through the platinum wires while at ambient conditions also convection has to be taken into account. In chapter five and six this high temperature sample stage will be used to quench the sample after stopping the deposition. In this way the surface morphology was “frozen”.

An important set of images will be described in the next page. This will demonstrate that with the modified SFM-scanner and heating stage the operating temperature is extended in vacuum.

Two experiments, in which the sample was heated during imaging, are presented to prove this. In figure (4.19) several images are selected from dynamic mode measurements that were carried out at 750°C in 10⁻²mbar oxygen. In these topography images a vicinal SrTiO₃ surface with SrTiO₃ two-dimensional islands was monitored for ninety minutes. In the images, a marker is placed as a guide for the eye to follow the lateral drift. Furthermore the terrace steps are highlighted in the first image. The islands and terrace heights correspond to the SrTiO₃ unit cell lattice constant (0.3905~0.4nm).

From these measurements it is concluded that the resolution of the equipment is such that islands with a size above 50-100nm² can be seen up to 750°C. In this experiment the initial lateral drift was ~80nm/min. This reduced to 7nm/min after stabilizing over 24 hours. This is comparable to the room temperature drift. Increasing the heater temperature from room temperature to 750°C and 600°C in respectively a background pressure of 10⁻⁴mbar and 1bar, resulted in a resonance frequency shift of 450 Hz, see appendix 4C. This frequency shift corresponds to an increase of the cantilever temperature of ~90°C. With this assumption and the thermal properties of the scanner it can be concluded that the scanner was warmed up at most by a few degrees, see also section 4.4.2. This prevents measurement distortions, since the piezo-scanner properties are still comparable to those at room temperature. Even though the cantilever temperature increase is

* To characterize the stabilization time the voltage across the heater filament was increased at t=0seconds and the filament temperature was measured.

Figure 4.19: SFM topography images of a SrTiO_3 surface, measured at 750°C in 10^{-2} mbar O_2 . In the first image the substrate step-edge is colored white as a guide for the eye. Furthermore markers are placed in the subsequent images to visualize the lateral drift during 90 minutes.

less in vacuum compared to ambient, SFM measurements in vacuum are more sensitive* to temperature variations.

This sensitivity can be probably decreased by using quartz cantilevers or tuning forks since these force sensors, compared to the micro machined cantilevers have a better frequency stability $\partial f_0/\partial T$ [23], although this has to be tested. To demonstrate that after a relatively small temperature step a SFM-measurement is quickly stabilized, figure (4.20) is depicted.

* The full width at half maximum (FWHM) of the resonance peak decreases with pressure and therefore cantilever temperature variations should be limited to avoid unstable SFM performance at low operating pressures. Typically a FWHM of ~ 50 Hz is found at a pressure of 10^{-1} mbar.

Figure 4.20: Demonstration of the lateral thermal drift while imaging a calibration grid with a vertical step. During imaging (512 x 512 points) the sample temperature was increased three times by 10°C. The estimated drift was around 60nm/K.

In this experiment a vertical oriented step was used to demonstrate the lateral drift after increasing the heater temperature in steps of 10°C while scanning. As can be seen a temperature increase of 10°C has a lateral shift of 300nm and is stabilized within ~60 scan lines. This demonstrates that this high temperature SFM can even be used for variable temperature experiments if the temperature step is limited. In this section images with atomic step resolution are depicted measured in dynamic mode. It can be concluded that non-coated silicon cantilevers are suitable to measure SrTiO₃ surfaces up to 750°C with atomic step resolution. For a brief analysis of the influence of the temperature on the measurement resolution and cantilever properties, see appendix 4C. Furthermore above data proves that the high temperature sample stage in which the hot surface was suspended by platinum wires can be used to extend the SFM operating temperature.

4.6 Concluding remarks

From this chapter it is learned that:

- With a simple transfer mechanism the same area can be studied during deposition processes such as PLD;
- It is possible to continue imaging the sample surface within seconds after the last deposition pulse;
- Measuring in a background pressure of 1-10⁻⁶mbar is not an issue with a proper scanner layout;

- By minimizing the heat input on a SFM the operating temperature can be extended, for example with a SiC based membrane heater SFM measurements up to 800°C in ambient conditions were carried out;
- A cylindrical insulation tube placed on top of the scanner and a low power sample stage are sufficient to perform dynamic mode SFM measurements in air and vacuum up to respectively 600°C and 850°C, see also appendix 4E;
- The resolution of the equipment is such that islands with a size above 50-100nm² can be seen up to 850°C in dynamic mode.

Important to remember from this chapter is that it should be feasible to follow nucleation and growth processes between two consecutive deposition pulses for oxides such as SrRuO₃. This is feasible by combining the fast transfer- and approach procedure with a high speed SFM and the hardware to extend the operating temperature and pressure.

The hardware specifically designed to combine PLD with SFM can also be a used as a guideline to combine other techniques with SFM and SPM in general. For example the high temperature heating stage can also be used to extend the operating range in other SPM equipment and enables to study phase transitions, diffusion and nanofriction at high temperature as proposed by Zykova-Timan et al. [24]. The high temperature sample stage can be useful in many applications and fields because all kinds of samples can be mounted on it, it decreases the thermal mass and it can be operated in a wide range of environments. In our own laboratory it is already applied in different other applications.

The procedure to transfer the sample between two or several positions is maybe even more relevant since this can be used to combine SFM and SPM with other deposition and analyzing techniques to monitor the same surface area after several modifications. Furthermore it can be used to make of SPM a user friendly and high throughput tool.

4.7 References

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Chapter 5

Model systems for in-situ growth monitoring

5.1 Introduction

This chapter describes several studies, which were done to select several model systems for in-situ growth monitoring during Pulsed Laser Deposition (PLD). The nucleation and growth of the selected materials were studied with the developed in-situ SFM. This will be described in chapter six.

In chapter four it was shown that imaging at elevated temperatures was achieved after using the small high temperature sample stage. At present two-dimensional islands, with a lateral size above 50-100nm², can be measured with atomic step resolution up to 850°C. As is described in chapter two the two-dimensional island size is related to parameters such as the substrate temperature and substrate terrace length l_T . The larger the two and three-dimensional island size the easier it becomes to measure it. To increase the two-dimensional islands size, during two-dimensional island growth, the terrace length l_T should be larger than the diffusion length l_d , which should be as large as possible. In this chapter a study of indium oxide, indium tin oxide (ITO), gold, TiO₂, SrTiO₃ and SrRuO₃ is described. To select several model systems the island size and surface morphology evolution during deposition were studied. Of these materials ITO and gold are typically deposited at low substrate temperatures (20-100°C) and have a three-dimensional island growth. TiO₂, SrTiO₃ and SrRuO₃ are typically deposited at high substrate temperatures (500-850°C) and have an epitaxial two-dimensional island growth on SrTiO₃ (001) substrates.

TiO₂-terminated SrTiO₃ (001) surfaces were used as a substrate in this thesis. This substrate can be prepared such that a surface with smooth terraces and atomic steps (~0.4nm) can be reproducibly obtained. This treated substrate was used as a reference to check the SFM resolution. The SrTiO₃ (001) substrate is

often^{*} used in homo- and heteroepitaxial growth studies and these results were used to compare the in-situ RHEED as well as the in-situ and ex-situ SFM measurements. Section 5.2 gives an overview of the preparation treatments for SrTiO₃ (001) substrates and describes the preparation treatment to obtain a TiO₂-terminated surface. This preparation treatment consists of a selective etching and post-annealing step. The detailed processes during these two steps were not well understood, in particular the formation of circular features that are often observed [18]. In this chapter the etching as well as the post-anneal process are described. Three routes were tested to optimize the treatment for low miscut substrates ($l_T > 500\text{nm}$) and to verify the description of the etching and post-annealing step. In these routes, the effect of post-annealing, the etch time and pre-annealing were studied with ex-situ SFM.

Section 5.3 and 5.4 describe the pre-study of the low and high temperature model systems for in-situ growth monitoring. It also motivates that the studied materials are interesting from an application point of view. These systems will be further described in chapter six. The last section summarizes this chapter with some conclusions.

5.2 SrTiO₃ substrates

SrTiO₃ has a cubic crystallographic structure above 105K with a lattice constant of 0.3905nm at room temperature, and a thermal expansion coefficient of $9 \cdot 10^{-6} \text{ K}^{-1}$. It is often used as a substrate for complex oxides since it is chemically stable and has a small lattice mismatch with other oxides such as SrRuO₃, TiO₂ and YBaCuO_x. The SrTiO₃ (001) surface can be prepared such that it has a SrO, TiO₂ or mixed termination. In this work only TiO₂-terminated SrTiO₃ substrates were used since this substrate surface is in general regarded as stable [1] and atomically smooth.

Before describing the used preparation method, the preparation methods to obtain a SrO and mixed termination will be shortly described. The different preparation methods to obtain a SrO-termination consist respectively of a 1-propanol cleaning step and subsequent annealing in oxygen [2], deposition of [3,4,5] SrO, SrRuO₃, SrTiO₃ [6,7] or reactive ion etching [8]. A mixed terminated surface [2,9,10] with at the surface SrO and TiO₂ areas and a clear terrace structure forms after annealing as-received SrTiO₃ (001) substrates. In figure (5.1a) the unit cell of SrTiO₃ is depicted as alternating $\text{Ti}^{4+}(\text{O}^{2-})_2$ and Sr^{2+}O^2

* SrTiO₃ (001) is often used since it is chemically stable, atomically smooth and has a small lattice mismatch with oxides such as TiO₂ and SrRuO₃.

planes. These planes are charge neutral. Nevertheless, the SrO-terminated surface is slightly polarized [11] and therefore chemically unstable.

To obtain a stable substrate surface with smooth TiO₂-terminated terraces, see image (4,5) in figure (5.1b), a preparation treatment can be used in which selective chemical etching is used to remove the SrO surface plane. The total preparation procedure* consists of:

- ultrasonically soaking an as-received substrate in analytical grade and demineralized water for >10 min;
- shortly (~30 s.) dipping the substrates in a BHF solution to etch the SrO [18,15];
- post-annealing the etched substrates at 900-950°C in 1 atm oxygen.

In this procedure soaking the as-received substrate in demineralized water is important to hydroxylize SrO, which dissolves faster in a buffered HF-solution (NH₄F:HF=87.5:12.5 pH=5.5) compared to TiO₂. In figure (5.1b) the surface morphology after etching and post-annealing is depicted. In this figure four images in top view are depicted one of an as-received substrate (1), one after etching (3), one after post-annealing (4) and an image (2) in which the etched surface is illustrated.

In image (1) a schematic representation of the as-received substrate surface morphology is depicted. The surface has half and one unit cell deep holes as well as half and one unit cell high islands on the terraces. These islands and holes have either a SrO or TiO₂ surface termination. In image (1) only the holes and islands are depicted for the most left terrace. As can be seen, before etching the terraces have small holes, islands and a rough terrace edge.

Hydrolyzing: as-received substrates (I)

The first step in the treatment, as listed above, is to hydroxylize the SrO. Sr(OH)₂ is formed on top of the SrO-terminated surface as well as at the edges of the terraces, islands and holes.

* In the experiments the substrates were placed on a Teflon holder and soaked in Demi-water for at least 20 minutes and subsequently ultrasonically agitated in a buffered HF solution, four times rinsed with water and once with ethanol to facilitate the drying with N₂-gas. Substrate annealing was performed in a tube oven with an oxygen flow of 200ml/min, the annealing times were exclusive the 3 minutes warming up to ~930°C and 120 minutes cooling to room temperature. The commercially obtain SrTiO₃ (001) substrates are referred to as as-received substrates and were commercially obtained from Surfacenet GmbH in Germany.

Figure 5.1: a) The cubic unit cell of SrTiO_3 depicted as planes of SrO and TiO_2 . The height of the unit cell is $\sim 0.4\text{nm}$. b) Surface morphology evolution to describe the surface treatment this is illustrated with five images. Image 1) as-received substrate surface, 2) surface evolution during etching, 3) surface morphology after etching, 4,5) morphology after post-annealing. In image (1) the one and half unit cell high islands ($0.2\text{-}0.4\text{nm}$) on the terrace and the holes ($0.2\text{-}0.4\text{nm}$) in the terrace are depicted on the most left terrace. Notice also the rough terrace step edges of the as-received substrate. During etching the SrO -plane below the TiO_2 -surface plane is also etched sideways at an edge. This means that the small holes in the as-received substrate are etched sideways and therefore their diameter increases. It also means that the unit cell high TiO_2 -terminated islands on top of the surface are etched from aside and removed (the SrO -plane below the TiO_2 -plane is etched). In image (2), the etched area is depicted for the two most left terraces, this area is etched sideways and leaves a smooth TiO_2 -terminated surface behind, see image (3). It is important to remember that during etching the small holes as well as the terrace step are etched sideways, the etch direction is illustrated with an arrow in image (1). In the etched area the holes and etched step merge and coalesce. In image (3) the typically observed holes, after etching near a step down, are depicted which are 0.4nm deep (one unit cell). In images (4,5) the typical surface morphology after post-annealing is depicted.

Etching $\text{Sr}(\text{OH})_2$ (II)

During the second step $\text{Sr}(\text{OH})_2$ is etched. In image (3) the cross section of a unit cell deep hole is depicted. It is proposed here that during etching the SrO -plane below the TiO_2 -surface plane is also etched sideways at an edge besides the SrO on top of the surface. This means that the holes in the as-received substrate, are etched sideways and therefore their diameter increases. As can be seen in image (2,3) the holes are one unit cell deep and appear near a terrace step down. In image (2) the etched area is visualized for the two most left terraces. In the etched area the etched holes and terrace step coalesce and leave a closed and atomically smooth TiO_2 -terminated surface layer behind, see image (3).

This process will be referred in this thesis as two-dimensional etching since it is the reverse of two-dimensional growth. To our knowledge this is the first time two-dimensional etching is mentioned to describe this etching process. During this process the terrace is etched sideways over a distance l_{etch}^* . The shift in the terrace ledges between image (1) and (2,3) corresponds with l_{etch} .

It is important to remember that in the etched area of image (2), holes coalesce with the terrace step. According to this model all holes merge during etching with the terrace step if the terrace width l_T is smaller than l_{etch} . This results in smooth terraces without holes after etching. With this model it can be predicted that a terrace will contain holes after etching if

$$l_T > l_{\text{etch}}$$

and no holes if:

$$l_T < l_{\text{etch}}$$

In these expressions l_T is the terrace width and l_{etch} is the average lateral distance which is etched. The holes, often observed [18] after etching near a step down, can be explained with this model.

Post-annealing the etched substrate (III)

The last step in the preparation treatment is to anneal the substrate surface. In this post-anneal step, the surface re-crystallizes and the holes typically disappear if $l_T < 500\text{nm}$, see figure (5.1b) images (4 and 5). It is proposed here that during post-annealing, step edge diffusion transports material along the terrace ledge to minimize its surface energy. This process results in straightened terrace edges. To illustrate the processes during post-annealing of a low miscut substrate figure (5.2) is depicted. In image (1) the surface is schematically

* This can be compared with a capture zone in two dimensional growth. In figure (5.9) the capture zone for TiO_2 deposited on SrTiO_3 is illustrated. In this zone, this is an area around a terrace step or hole, no stable islands are nucleated. In the images depicted in figure (5.1b), the etched area contains no holes and has a TiO_2 -termination after etching.

Figure 5.2: Surface morphology evolution according to the post-annealing model. Image (1) low miscut substrate after etching, (2) during post-annealing, (3) after post-annealing. In image (1) rough terrace step edges and holes (~ 0.4 nm deep) are depicted. It is proposed here that during post-annealing step edge diffusion transports material along the terrace step to minimize its surface energy. This results in straightened terraces, round holes and a decreasing hole density. During post-annealing the terrace straightened and holes coalesce with the terrace edge, see image (2). In image (3) the surface is imaged after extensive annealing. In this picture the steps are straightened, but still some holes are visible. Because the surface or edge energy is minimized the remaining holes do not coalesce with the terrace if the annealing period is prolonged.

depicted after etching. As can be seen it still has a relatively rough terrace edge and several holes. During post-annealing the terrace ledge straightens and holes coalesce with the terrace edge, see image (2). In image (3) the surface is imaged after extensive annealing. In this picture the steps are straightened, but still some holes are visible. Because the surface or edge energy is minimized the remaining holes do not coalesce with the terrace, not even after prolonged annealing.

Testing the two models to describe the etching and post-annealing procedure

To verify the proposed etching and post-annealing model, the surface morphology evolution during the preparation treatment will be described in the next pages. It starts by describing the treatment for typically used high miscut substrates. In figure (5.3) the imaged as-received, etched and post-annealed surfaces are depicted, for a substrate with a terrace width of l_T 120nm, *sample 1*. Besides this, the surface morphology after etching and after post-annealing is

depicted for a substrate with a terrace width of l_T 240nm, *sample 2*. The surface after post-annealing (f) is zoomed in and will be discussed later.

In both images, captured directly after etching, some holes are visible and l_{etch} is 100-300nm. It has to be mentioned that the islands on top of the surface, visible after etching, originate from the etch solutions. These are not $SrTiO_3$ islands. It can also be seen in the images after the post-anneal step, that the holes and etch contaminants are removed and that the terrace edge has straightened. For substrates with a terrace length $l_T \gg 500$ nm, one unit cell deep holes were not completely removed during post-annealing*. As mentioned in the introduction

Figure 5.3: SFM topography images of sample 1 and 2 a) as-received b) directly after etching c) after post-annealing d) after etching sample 2 e) after post-annealing f) zoom in of post-annealed substrate.

the larger the island size the easier it becomes to image it with SFM. To have two-dimensional island growth instead of step flow growth holes are unwanted, since they reduce the effective terrace width l_T and therefore decrease the average island size. These holes were typically removed during post-annealing for terraces with $l_T \ll 500$ nm and remained for $l_T \gg 500$ nm. In the following pages three

* Vicinal substrates 0.2° - 0.5° can be post-annealed 1-3 hours at 900 - 930°C to obtain a smooth and closed terrace.

routes that have been explored to smoothen the surface for $l_T \gg 500\text{nm}$ are described. In the first route the post-annealing time and temperature were increased. In the second route the etch time was varied, so far all substrates were etched for 30 seconds. If the model to describe the etch procedure is valid, the hole diameter and etched area will increase proportional with the etch period. The third route was to pre-anneal the substrates. If the post-annealing model is valid, the terrace edge will straighten during pre-annealing. Re-crystallizing the as-received surface could help to decrease the hole density.

Figure 5.4: *SrTiO₃ topography images after subsequent post-annealing at 900°C.*

Effect of post-annealing on the surface treatment

In figure (5.4) the surface morphology evolution is depicted after post-annealing at 900°C. It can be seen that the mean hole diameter is constant, whereas the hole density decreases in time. This indicates that the holes do not merge and on average no material is moved towards the holes. Furthermore it can be seen that the terraces steps straighten and that the holes become rounder. In the second image, after two hours of post-annealing, a terrace step with a hole is schematically depicted.

The two arrows indicate the direction, step up and step down, for a hole. It was found that holes, which are located at a distance of a several hundred nanometers ($>400\text{nm}$) from a step down, do not move towards a step not even after extensive* annealing. The proposed post-annealing model describes that material diffuses along the terrace ledges to straighten the terrace steps. Once the terrace steps are straightened the hole density becomes constant. With this model it can be understood why the holes are not disappearing for low miscut substrates. For example it is not likely that all holes merge with the terrace after six hours in figure (5.4). To accelerate step edge diffusion the post-annealing temperature was increased up to 950°C. This increased the straightening process

* With extensive annealing is meant annealing at 900°C for more than 24 hours.

and therefore decreased the hole density, but resulted in a mixed surface termination. A mixed termination is also seen by Frangento in substrates annealed at 950°C [13]. From our observations it is recommended to post-anneal the substrates below 950°C to prevent SrO enrichment at the surface. The substrates used in this work were typically annealed at 930°C.

Effect of etch times

To study the influence of the etch time, this period was varied (30-120 seconds). After etching the surface morphology was directly imaged. From these images the average hole diameter was extracted, see table (5.1). It can be seen that the hole diameter increases with the etch time. The increase in the hole diameter supports the proposed model in which the holes are etched sideways.

Table 5.1: Average hole diameter measured after etching an as-received SrTiO_3 substrate.

Etch time [sec]	Diameter [nm]
30	54 ± 44
60	150 ± 100
120	250 ± 100

Effect of pre-annealing

In figure (5.5) the measured images of an as-received, a pre-annealed substrate, etched and a post-annealed substrate, with $l_T = 1500\text{nm}$, are depicted. It is difficult to see, but the as-received substrate has terraces. Furthermore, after a detailed analysis islands (0.2-0.4nm high) on top and small holes in the terraces are visible. During pre-annealing the terrace steps will straighten according to our model and the holes become rounder. In the image measured after pre-annealing, terraces with islands on top and small holes in the terraces are clearly visible. Furthermore it appears that the ledges have straightened and the holes became rounder after the pre-anneal step. The holes became squarer after etching the pre-annealed substrate although this is again difficult to see. The last image depicts the surface morphology after post-annealing. It can be seen that the surface has terraces with smooth wide areas, islands and a rough terrace step. This modified treatment is promising, but could not be further investigated during this thesis because high quality low miscut substrates were not available anymore. According to the post-anneal model further annealing will straighten the terrace step and therefore most of the holes will coalesce with the terrace step. From the above routes it is recommended to investigate the pre-annealing in combination with a longer etching and post-annealing period. I expect that by increasing the pre-annealing and post-annealing period the steps will further straighten and therefore the probability to observe a hole near a step down decreases. Closed TiO_2 -

Figure 5.5: Surface topography measured with *ex-situ* SFM a) *as-received* substrate b) *pre-annealed* 3 hrs at 950°C c) 60 sec *etched* d) *post annealed* for 2 hours at 950°C.

terminated terraces, with $l_T > 1\mu\text{m}$, can perhaps become available if the pre-annealing, etching period and post-annealing are further optimized. This kind of surfaces would be helpful to monitor the nucleation and growth with the in-situ SFM.

Surface termination and stability

The surface stability is discussed here even though it is a slightly different subject from the other part of this section which describes the SrTiO_3 substrate treatment. Nevertheless, it is added since our observations explain the results obtained in several papers and could be important for others. In the images, measured after the treatment, a surface roughness was observed which increased in time. In figure (5.6) four images are depicted. The images were captured in ambient conditions after the preparation treatment as is listed above. Images (a,b) were measured directly after the post-anneal step and images (c,d) several weeks after the treatment. A peak to peak surface roughness of 0.2nm was measured directly after the post-anneal step on the terrace surface. This has also been observed in the images captured after post-annealing in figure (5.2). It has to be mentioned that these observations were done with sharp tips*. After storing, the treated substrates for several weeks, the roughness increased. It can be seen in figure (5.6) that islands are present on the terrace surface in images (a-d). This observation indicates that the surface is not stable and perhaps not even TiO_2 -terminated. It has to be mentioned that this has not been noticed before in our laboratory, although SrTiO_3 substrates are generally used for experiments in which their termination is important. Vonk et al. [12], Fragneto et al.[13] and Lopez et al. [14] also observed a 0.2nm layer on top of the TiO_2 -terminated surface after post-annealing. Vonk measured the atomic structure with Surface X-

* For the dynamic mode *ex-situ* SFM measurements silicon coated cantilevers (330kHz, 43Nm^{-1}) with a tip radius $<10\text{nm}$, and non-coated cantilevers (330kHz, 43Nm^{-1}) with a tip radius $<2\text{nm}$ have been used.

Ray diffraction (SXRD) and explained the 0.2nm roughness with an oxygen overlayer model. In their model the shortest O-O distances was close to 0.2nm and might be clarified by the presence of hydrogen. Fragneto measured the atomic structure with SXRD and SFM. Fragneto found similar results as Vonk. Lopez et al. investigated the surface with High Resolution Electron Energy Loss Spectroscopy (HREELS) and found only O-H bonds if sodium was present. This contamination makes the neutral TiO_2 -surface positively charged such that these molecules can attach to the surface.

To clarify the nature of the surface roughness, the contamination on an etched substrate is compared with two annealed substrates, see table (5.2). From this analysis it can be concluded that the thermal treatment contaminated the substrates with sodium and magnesium. Notice that the surface roughness and contamination, measured in this work, correspond with the observations of Lopez. Therefore it is likely that the 0.2nm surface roughness, measured directly after post-annealing, is probably due to the presence of sodium on the surface. Vonk

Figure 5.6: SFM topography images measured directly (a,b) and a few weeks (c,d) after post-annealing, measured in ambient conditions.

and Fragneto characterized a surface after treating the SrTiO_3 substrates with the same procedure and the same contaminating oven^{*} and therefore these substrates were probably also contaminated. It is expected that the effect, of this contamination, on the nucleation and growth is limited since the H_2O and Na contamination sublimates in vacuum above respectively 80 and 500°C [14], although it is not possible to exclude it.

^{*} The presence of sodium on the surface after the thermal treatment is probably due contact of human perspiration with the ceramics and glassware of the oven.

Table 5.2: Relative element concentration as found by X-ray Photo Spectroscopy (XPS) analysis. Sample 1 and 2 were treated as listed above, sample 3 was an etched substrate. It has to be mentioned that this has not been measured at the time the surface roughness was measured with SFM, but several years later.

Sample	Ti 2p	Sr3d	NaKLL	Mg1S	O1S	C1S
1	16.31	17.16	2.18	1.81	55.01	7.53
2	13.80	16.27	4.04	0.73	55.22	10.95
3	11.86	14.01	0.00	0.00	48.67	25.45

5.3 Low temperature model systems

Indium oxide, indium tin oxide (ITO) and gold are polycrystalline or amorphous and have a three-dimensional growth, if they are deposited on SrTiO_3 at low substrate temperatures. To monitor the nucleation and growth of amorphous or polycrystalline materials diffraction techniques such as RHEED give no information. Polycrystalline thin films however, are often used in multilayer thin film devices and therefore important. To monitor and control the nucleation and growth of these materials an in-situ SFM, which is able to measure the surface morphology during growth, would be an outcome. Indium tin oxide (ITO) is a Transparent Conducting Oxide (TCO). This material is typically deposited at low substrate temperatures and commonly used as transparent electrode in Organic Light Emitting Diodes (OLEDs), solar cells and display technology. The Indium Tin Oxide properties* depend on the doping concentration and deposition conditions such as pressure [15]. To correlate these properties with the surface morphology and film structure, ex-situ experiments were done. In figure (5.7) the surface morphology, after depositing a ITO thin film at room temperature, is depicted. It can be seen in figure (5.7) that the peak to peak surface roughness is significantly higher for a thin film which was doped with Sn than without doping. The trend in these ex-situ measurements is that the surface roughness and film crystallinity decreases proportional to the doping concentration.

* It is known that PLD synthesized ITO thin films at room temperature on polymer substrates such as PET can have a optical transmittance above 85% and a resistivity below $4.1 \cdot 10^{-4} \Omega\text{cm}$. For example the resistivity increases with the Sn-doping concentration. See also the references in [15].

Figure 5.7: Ex-situ SFM images of an ITO film deposited on polyethylene substrates at room temperature. Graph taken from [15].

In figure (5.8) four TEM images are depicted. These images were captured after the sample was removed from the deposition chamber. The difference in these thin films was the grain size. In the images a marker is placed to highlight the trend in the grain size. It can be seen that the grain size changes from $\sim 100\text{nm}$ towards $\sim 10\text{nm}$ with respectively a Sn-doping concentrations* of 0, 2, 5 and 10%. ITO deposited on SrTiO_3 is used to test the SFM equipment. It is expected to observe islands with a height of at least one nanometer and a lateral size of $\sim 100\text{nm}^2$, for undoped ITO. Notice that three-dimensional growth is different from multilevel two-dimensional growth. In chapter six the in-situ growth monitoring experiments on ITO as well as gold deposited on SrTiO_3 will be described. At low substrate temperatures gold forms nanoparticles or three-dimensional islands. These islands are, in contrary to bulk often not considered as inert and therefore interesting for catalytic applications [16]. It is known that gold has a high mobility and that the gold surface changes from a smooth surface to a surface with gold-grains [17] if the temperature is increased. It is expected that this change can be observed with our instrument. It is also expected that diffusing gold clusters can be observed at relatively low temperatures. Au and ITO have almost no epitaxial relation with the SrTiO_3 substrate. Nevertheless these substrates were used since they have a reproducible surface with smooth terraces and atomic steps, which can be used as a reference to check the vertical SFM resolution.

* To change the doping concentration, an ITO target is used, which corresponds with the above concentrations.

Figure 5.8: TEM images measured after the deposition of an ITO thin film at room temperature. The insets show the corresponding electron diffraction patterns of the area. Graph taken from [15].

5.4 High temperature model systems

It is known that TiO_2 , SrTiO_3 and SrRuO_3 deposited on SrTiO_3 substrates have a two-dimensional growth if the substrate during deposition is $500\text{--}850^\circ\text{C}$. In two-dimensional growth the surface morphology changes from atomically smooth at a coverage $\theta \sim 1$ into a rough surface with relatively large islands at a coverage of $\theta \sim 0.5$. This change in surface morphology might be such that it can be monitored with our developed SFM. To investigate whether the homoepitaxial SrTiO_3 and heteroepitaxial TiO_2 and SrRuO_3 growth can be monitored in-situ, a pre-study was done. In this pre-study several deposition parameters such as the substrate temperature were varied to study the average islands size as a function of the coverage. It was known that SrTiO_3 and SrRuO_3 have a two-dimensional growth mode and the two-dimensional islands have a height of $\sim 0.4\text{nm}$. This islands height corresponds with the unit cell height of SrTiO_3 and SrRuO_3 . RHEED and ex-situ SFM have been used to follow the surface evolution during PLD.

The deposition parameters such as fluency, which have been kept constant are depicted in table (5.3).

Table 5.3: Deposition parameters of TiO_2 , SrTiO_3 and SrRuO_3 .

Material	Fluency [J/cm ²]	Repetition rate [Hz]	Deposition oxygen pressure [10 ⁻² mbar]	Substrate target distance [mm]
TiO_2	1.3	0.25	13	50
SrTiO_3	1.3	1	3	50
SrRuO_3	2.5	1	3	50

5.4.1 TiO_2

TiO_2^* is one of the most investigated materials in surface science and used as heterogeneous catalyst, but also as protective, insulating and optical coating. To investigate whether TiO_2 deposited on SrTiO_3 is a good model system, the dependence of the deposition parameters such as substrate temperature on the surface morphology was studied. Preliminary experiments with PLD and ex-situ SFM measurements [18] showed that TiO_2 deposited on SrTiO_3 surfaces at 850 °C formed two-dimensional islands, see figure (5.9). This SFM image was measured after depositing less than 1 monolayer at 850°C. The height of the two-

Figure 5.9: SFM topography images after less than 1 monolayer TiO_2 deposited at 850 °C on SrTiO_3 .

* TiO_2 crystallizes in three major different structures: rutile (tetragonal, $a = b = 4.584$ Å, $c = 2.953$ Å), anatase (tetragonal, $a = b = 3.782$ Å, $c = 9.502$ Å) and brookite (rhombohedral, $a = 5.436$ Å, $b = 9.166$ Å, $c = 5.135$ Å) [13].

dimensional islands* are comparable to the substrate steps. In the images several capture zones, around holes in the terrace, are depicted. In such a zone no two-dimensional islands are observable and the deposited material is attached to a pre-existing step. The average distance of a zone with islands, the so-called island zone, to a step down and up was respectively 180nm and 140nm. In image (5.9a) the island zone is highlighted. The latter difference in distance might be attributed to the growth of the substrate step by 20nm. To have two-dimensional island growth instead of step flow growth holes are unwanted, because they reduce the effective terrace width l_T and therefore decrease the island size. Smaller islands as well as step flow growth makes it more difficult to observe a clear difference in the surface morphology during deposition. In figure (5.9a) it can be seen that in areas with several holes in the terrace no islands were visible. From these images it is tempting to conclude that TiO_2 appears to be a perfect model system. However, other experiments prove that it is less suitable to test the equipment. The main reason for this statement is that the substrate temperature is too high to have islands with a measurable size.

5.4.2 SrTiO_3

In this section a pre-study of the homoepitaxial SrTiO_3 growth will be described. For this study RHEED and ex-situ SFM was used, to investigate the dependence of the deposition parameters such as substrate temperature on the surface morphology evolution. To heat the substrates, the high temperature sample stage as described in section (4.4), was used. In figure (5.10) three intensity oscillations of the specular spot are depicted. These oscillations correspond to a two-dimensional layer-by-layer growth. Notice that this RHEED data was measured during the deposition. Two of these thin films have been deposited at a heater temperature of 650°C and one at 850°C. The temperature is the heater temperature and it is assumed that this is almost similar as the substrate temperature. In textbooks it is generally assumed that the second RHEED minimum corresponds with 1,5 monolayer and the second maximum with 2 monolayers (ML).

Testing the influence of a miniaturized heating stage

In our laboratory one kind of heating stage is generally used to regulate the substrate temperature during PLD. It could be that the substrates have a different temperature if a miniaturized heater is used. By comparing the intensity

* This seems to be comparable to the anatase phase, although it is difficult to speak of a phase after less than one monolayer.

Figure 5.10: RHEED intensity oscillations of homoepitaxial SrTiO_3 growth. Substrates were mounted with platinum paint or with silver paint. The SrTiO_3 substrates had a terrace width $l_T \sim 170\text{nm}$.

oscillations of figure (5.10) with other data*, it was concluded that there was no difference in the intensity oscillations. The difference between the thin films mounted on the miniaturized heater with platinum or silver paint was also investigated by looking at the RHEED-data and comparing the surface morphology after deposition. Platinum paint was used in this work since silver sublimates above 500°C and contaminates the SFM-head. In figure (5.10) it can be seen that the deposition rate is slightly different for the substrates mounted with platinum or silver paint, but this is typically the case from deposition to deposition. There is no significant difference in the oscillation pattern or surface morphology for the substrates mounted with platinum or silver paint. From these experiments, it was concluded that the miniaturized heating stage and the platinum paint did not change the typically observed growth mode.

* This is data from experiments that have been done in the same PLD-system with a different heating stage and silver paint.

Surface morphology as a function of substrate temperature

The growth was also monitored with RHEED. To study the surface morphology it was imaged ex-situ. In figure (5.11) the surface morphology, measured after stopping the deposition* in a RHEED minimum, while using a substrate temperature of 650, 730 and 850°C, is depicted.

It can be seen that in the image, captured after the deposition of a thin film on a substrate at 850°C, two-dimensional islands are visible on the terraces. The lateral island size is $\sim 150\text{nm}^2$ and the islands have a height of $\sim 0.4\text{nm}$. It can also be seen that, the island area decreases rapidly with temperature. Below 850°C the islands size was such that it was difficult to determine the island density or size. It has to be mentioned that the lateral resolution of the used ex-SFM is better than the current in-situ SFM resolution. Therefore it is concluded that at least below 850°C SrTiO_3 , is not a suitable model system with the current setup.

Figure 5.11: SFM images after homoepitaxial growth of SrTiO_3 stopped in a RHEED minimum. This data was measured with ex-situ SFM on different substrates.

Surface morphology evolution while depositing at 850°C

To investigate whether SrTiO_3 , deposited at 850°C, was a good model system the island size as a function of coverage was measured. In figure (5.12) the surface morphology is depicted after quenching†. The deposition was stopped in the first RHEED minimum ($\sim 0.5\text{ML}$), first maximum ($\sim 1\text{ML}$) and second minimum ($\sim 1.5\text{ML}$). After the first RHEED minimum two-dimensional islands can be observed, whereas after the first RHEED maximum the surface layer is almost closed and second layer nucleation starts. Remarkably the image measured after stopping the deposition in the second RHEED minimum, appears to be almost

* The sample was directly quenched to room temperature after the deposition.

† The samples were quenched as fast as possible with the high temperature sample stage in deposition pressure. In this way the growth is stopped and the surface morphology was frozen.

closed. It was expected that in this image islands would be visible. From these images, it seems that the diffusion length decreases after the first monolayer.

This could indicate that the surface changes during deposition and therefore the diffusion length. Remember that it was shown that the substrate surface was

Figure 5.12: SFM-topography images after homoepitaxial growth of SrTiO_3 done at 850°C . This data was measured with ex-situ SFM on the same substrate.

contaminated and the influence of this layer cannot be excluded. The surface morphology is also measured after depositing 1.5ML above 850°C . This resulted also in a smooth surface; at least the two-dimensional islands size did not increase. After these experiments we again have to conclude that, to monitor the nucleation and growth with the in-situ SFM, the homoepitaxial SrTiO_3 growth is not a suitable model system for the current setup. It has to be mentioned that it is interesting to further investigate the initial nucleation and growth if the resolution of our setup can be further increased.

5.4.3 SrRuO_3

SrRuO_3^* is chemically stable and one of the best conducting complex oxides. Therefore it is a promising electrode material in oxide hetero structures like ferroelectric random access memories (FeRAM) and Field Effect Transistors (FET). The high temperature sample stage, as described in section (4.4), was used again to investigate the dependence of the deposition parameters, such as substrate temperature, on the surface morphology evolution. Furthermore the surface morphology stability was tested.

* SrRuO_3 has an orthorhombic symmetry at room temperature and changes to a cubic phase above 550°C . This orthorhombic structure can be simplified with a pseudo-cubic perovskite structure with a lattice parameter of $3.930\text{\AA}$ which has a low lattice mismatch with SrTiO_3 .

Surface morphology as a function of substrate temperature

In figure (5.13) three images are depicted. These images were ex-situ measured and reflect the surface morphology after depositing 1,5ML SrRuO_3 at 615, 710 and 760°C. To deposit only 1.5 ML, the deposition was stopped in the second RHEED minimum. After stopping the deposition, the sample was quenched to room temperature and directly imaged at ambient conditions. For

Figure 5.13: SFM-topography images after 1.5ML heteroepitaxial growth of SrRuO_3 . This data was measured with ex-situ SFM on different substrates.

these experiments substrates with different terrace widths ($l_T = 200\text{-}800\text{nm}$) were used, because high quality substrates with one terrace length were not available. This makes it more difficult to compare the results. Nevertheless it can be seen that the surface contains two-dimensional islands and several holes. The large holes (0.4nm deep), in images (a,b) originate from the substrate. Inside these holes some material is deposited and some holes are almost closed except at the edges. At all the terrace edges there is a trench, this is visible near a terrace step after depositing 1,5ML at 710°C and 615°C. Inside this trench no islands are visible. This trench will be discussed later in more detail.

The surface in image (c), measured after quenching from 760°C, has a different morphology. As is discussed in chapter two, this surface morphology corresponds with 1 ML, since it is almost closed and has some second layer nucleation. Apparently the second RHEED minimum is not always corresponding* with 1.5 ML for all materials and conditions. To improve our understanding of the growth and RHEED oscillations it would be helpful to check the surface morphology during deposition. Our in-situ SFM instrument would be for this kind of studies a valuable tool.

* It has to be mentioned that quenching also could influences the growth. This has not been investigated yet.

Figure 5.14: *Ex-situ SFM images captured on different substrates. These images illustrate the measured surface morphology evolution at 700°C.*

Surface morphology evolution while depositing at 700°C

In figure (5.14) several images are depicted, which were captured after stopping the deposition in the first minimum, first maximum and second minimum RHEED intensity. The measured SFM-data corresponding to the first RHEED maximum corresponds to an almost closed surface layer. It is likely that this corresponds to 1 ML, see also chapter two. After 0.5 and 1.5ML several islands are clearly visible. In these images it can be seen that there is a clear difference in island size after $\sim 0.5\text{ML}$ and $\sim 1.5\text{ML}$ of $\sim 500\text{nm}^2$ and $\sim 100\text{nm}^2$, respectively. The difference in lateral island size can be explained with a larger diffusion length l_d for SrRuO_3 on a TiO_2 -terminated surface compared to the SrO -terminated surface. A trench near the step and hole edge is clearly visible in these images. This trench is also observed in figure (5.12) although difficult to see. The trench is visible near a step at a terrace edge and edge of a hole after 0.5 and 1.5ML. Here it is proposed that the low lattice mismatch with SrTiO_3 could induce substrate edge stress, which introduces an additional energy barrier that is hard to overcome. Notice that the difference in the (001) unit cell length* is small.

* SrRuO_3 has an orthorhombic symmetry at room temperature and changes to a tetragonal phase at 550°C and to the cubic phase at even higher temperatures. This

This barrier could explain why SrRuO_3 is not formed at the substrate terrace step edge or hole step edge. It is expected that this trench will be different or not even present if another substrate, with a different lattice mismatch, will be used.

Recommendations for future studies

From the pre-study on SrRuO_3 it is recommended to further investigate if the difference in unit cell size between SrRuO_3 and SrTiO_3 is the reason of the measured trench. It would be helpful to investigate if this trench also appears after 0.5 and 1.5ML deposited on DyScO_3 and NdGaO_3 which have a different mismatch with SrRuO_3 . Furthermore it would be interesting to test if this trench affects the electrical properties.

5.4.4 SrRuO_3 surface morphology stability

In this section it will be shown that that the SrRuO_3 surface morphology stability depends on the background pressure. Since the in-situ SFM will image the surface morphology for a relatively long period at elevated temperatures it is important that the surface is stable. To investigate the conditions at which the surface becomes unstable the RHEED diffraction pattern was studied. The RHEED diffraction pattern was monitored of several 5-10ML thick SrRuO_3 films which were cooled down to room temperature and slowly heated in:

- low vacuum ($\sim 10^{-2}$ mbar) directly after the deposition;
- high vacuum ($\sim 10^{-7}$ mbar) directly after the deposition;
- high vacuum ($\sim 10^{-7}$ mbar) after ambient exposure;
- low vacuum ($\sim 10^{-2}$ mbar) after ambient exposure;

To verify that the thin films were smooth after the deposition, the surface morphology of two reference samples, deposited at a substrate temperature of 700°C , were imaged directly after quenching, see figure (5.15). From these reference samples it can be concluded that the surface layer after 5 or 7 ML SrRuO_3 is almost closed and has a peak to peak roughness of 0.4nm.

orthorhombic structure can be simplified with a pseudo-cubic perovskite structure with a lattice parameter of 3.930Å which is slightly larger than SrTiO_3 .

Figure 5.15: SFM topography images measured ex-situ after hetero epitaxial growth of SrRuO_3 at 700°C . Image (a) measured after 5 monolayers, image (b) after 7 monolayers. The deposition was stopped in a RHEED maximum.

SrRuO_3 surface stability in low vacuum

In figure (5.16) the diffraction pattern is depicted as a function of the heater temperature. In the images four clear spots are visible. The three spots, visualized by (1-3) in image (a) are diffraction spots and (4) is the ongoing electron beam. In figure (5.16) it can be seen that the diffraction pattern was visible up to 820°C and the surface after the experiment was smooth with a peak to peak roughness

Figure 5.16: Diffraction pattern images (a-i) as a function of temperature in 10^{-2}mbar O_2 . Image (a) measured at 20°C after deposition. SFM topography image (j) after stability tested for a 5 ML thick SrRuO_3 film deposited at 700°C in 13 Pa oxygen. Image (a) the specular spot (2) and the other two diffraction spots (1,3) as well as the ongoing electron beam (4) are highlighted.

of 0.4nm, see figure (5.16j). From these observations it was concluded that the SrRuO_3 surface is stable up to 820°C in an oxygen pressure of $8 \cdot 10^{-2}\text{mbar}$.

SrRuO₃ surface stability in high vacuum

In figure (5.17) the diffraction pattern of a SrRuO₃ film is visible as a function of heater temperature in an oxygen pressure of 10^{-7} mbar. It was observed that at

Figure 5.17: Diffraction pattern images (a-i) as a function of temperature in 10^{-7} mbar O_2 . Image (a) measured at $20^\circ C$. Time difference between (d) and (e) is 10 minutes and between (f) and (g) 3 minutes. In image (f) the RHEED intensity is increased. SFM topography image (j) was measured after the stability test. This data was recorded for a 7ML thick SrRuO₃ film deposited at $700^\circ C$.

$465^\circ C$ the diffraction pattern diffuses quickly and more spots appeared in the image. The latter spots corresponded to a surface with three-dimensional or multilevel two-dimensional islands. The measured surface morphology after the experiment had a peak to peak roughness of 3nm, see figure (5.17j). Therefore, it is concluded that the surface is unstable above $465^\circ C$ in 10^{-7} mbar.

Figure 5.18: Diffraction pattern images measured after ambient exposure as a function of temperature in 10^{-2} mbar (a-e) and 10^{-7} mbar (f-i). SFM topography image (j) measured after the heating up to $480^\circ C$ in 10^{-7} mbar.

SrRuO₃ surface stability after ambient exposure

In figure (5.18) the recorded diffraction patterns of a SrRuO₃ film are visible. These images have been measured after ambient exposure as a function of heater temperature in an oxygen pressure of 10⁻² mbar and 10⁻⁷ mbar. As can be seen in image (e) after the relatively short* ambient exposure, the diffraction pattern is visible up to at least 660°C in 10⁻²mbar and started to disappear above 358°C in a pressure of 10⁻⁷mbar, see image (g and h). Ex-situ SFM of the heated thin film up to 480°C in 10⁻⁷mbar showed a surface with a peak to peak roughness of 3nm and three-dimensional islands, see figure (5.18j). From these experiments it was concluded that the exposed SrRuO₃ surface is at least stable below 660°C in 10⁻²mbar and unstable above 358°C in 10⁻⁷mbar. It is expected that in low vacuum the surface is stable up to at least 800°C.

Summary and discussion

From these experiments it is learned that:

- non-exposed SrRuO₃ surfaces are stable in an oxygen environment of 10⁻²mbar up to 800°C;
- the surface starts to decompose below 500°C in 10⁻⁷mbar.

These conclusions are supported by data of Huo lee [19], Halley [20] and Mlynarczyk [21]. Since we found that also the surface of non-exposed samples were chemically unstable in UHV, the model as proposed by Shin et al. [22,23] could be valid, but the surface is probably also instable without ambient exposure. In the model proposed by Shin the surface instability is claimed to be dependent on hydrocarbon contaminations. The most important to remember is that the SrRuO₃ surface is stable and can be imaged for a long period at 700°C when it is kept under deposition conditions.

5.5 Conclusions

The first part of this chapter described the surface morphology of SrTiO₃ (001) substrates before, during and after the treatment to obtain a stable TiO₂-terminated surface. From this section it is learned that:

- the preparation method to obtain TiO₂-terminated SrTiO₃ (001) surfaces can be described by a simple etching and post-anneal model;
- the description of the etching step explains the holes in the terraces after the etching step;

* For an hour in ambient conditions.

- the description of the post-annealing step explains that the holes are merging with the terrace step until the surface or step edge energy is minimized;
- the found peak to peak surface roughness of 0.2-0.4nm after the post-anneal step found by us and others [12,13] is due to sodium contamination.

The second part of this chapter described a pre-study to select a model system for in-situ growth monitoring. From this study it is expected that ITO, Au and SrRuO₃ deposited on SrTiO₃ substrates are good model systems to test the setup designed for in-situ growth monitoring.

5.6 References

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Chapter 6

In-situ SFM characterization

6.1 Introduction

In this chapter, the influence of the SFM operating conditions, as well as the tip-sample materials, on the image quality and imaging stability is described. In chapter five, indium oxide, indium tin oxide (ITO), Au and SrRuO_3 are selected for in-situ growth monitoring. From the pre-study, it is expected that two and three-dimensional islands* can be imaged during deposition. However, the question is whether the selected model systems could be imaged at elevated temperatures. For example, imaging could be hampered if mobile material reacts with or attaches to the tip.

From Scanning Tunneling Microscopy (STM) it is known that the imaging quality depends on the tip-sample materials and measurement conditions. Therefore, a wide variety of tip materials such as tungsten, platinum, platinum alloys and gold are developed for STM. For example, tungsten tips are used to perform stable measurements at room temperature in high pressure CO, whereas tips made out of platinum and platinum alloys Pt/Rh, Pt/Ir, Pt/Au are required for measurements in oxygen and mixtures of CO and oxygen. It is also worthwhile to mention the work described by Kuipers et al. [1,2]. This work describes an STM instrument to measure surfaces at elevated temperatures. Kuipers observed that the measurement time, in which the resolution on the Pb(110) surface was sufficient, decreased with increasing temperature and that the Pb(110) surface could not be imaged above $\sim 50^\circ\text{C}$, even though various other

* The height of these islands is expected to be 1 nanometer or more with a lateral size of $50\text{-}100\text{nm}^2$ or more.

metal and semiconductor surfaces could be measured up to a maximum temperature of $\sim 450^\circ\text{C}$.

Therefore it is likely that the imaging quality in SFM will also depend on the operating and measurement conditions as well as the used tip and studied surface material. Measurement conditions which have been studied are the influence of the sample temperature and background pressure. Furthermore, the influence of the SFM operating mode and the corresponding parameters, such as the oscillation amplitude and resonance frequency, on the imaging stability were investigated. The observations are described in this chapter.

Of the above mentioned model systems we have studied SrRuO_3 the most extensively. SrRuO_3 is typically deposited at high substrate temperatures ($500\text{--}750^\circ\text{C}$) whereas ITO and gold are typically deposited at low substrate temperatures ($20\text{--}100^\circ\text{C}$). In section 6.2 and 6.3, the in-situ SFM measurements on the low and high temperature model systems are described. In these sections the dependence of the imaging stability and image quality on the measurement and operating conditions is illustrated.

Section 6.4 will summarize the most important observations and possible mechanisms that influence the imaging stability. In section 6.5, the tip-sample interaction instability, which influences in-situ growth monitoring, will be explained and compared with literature data. In section 6.6, some concluding remarks as well as some recommendations are presented.

6.2 Indium tin oxide and gold: low temperature model systems

As low temperature model systems indium oxide, indium tin oxide and gold are selected. First, the results concerning indium oxide and 10%-Sn doped indium oxide deposited on a TiO_2 -terminated SrTiO_3 (001) surface are described. 10% Sn-doped indium oxide and indium oxide are referred to in this thesis as doped ITO and undoped ITO, respectively. Subsequently the observations on gold will be depicted. The used deposition settings for gold and indium oxide can be found in table 6.1.

Table 6.1: Deposition parameters

Material	Fluency [J/cm^2]	Repetition rate [Hz]	Deposition oxygen pressure [10^{-2} mbar]	Substrate target distance [mm]
ITO	3	1	3.5	50
Au	5	1	3	50

Imaging indium oxide during pulsed laser deposition

A selection of the topography images*, measured at room temperature during the deposition† of undoped ITO on a treated SrTiO_3 substrate, are depicted in

Figure 6.1: SFM-images measured in-situ during the deposition of In_2O_3 on Nb-doped SrTiO_3 substrates at room temperature.

* The in-situ SFM data is measured in dynamic mode with standard silicon cantilevers tips (radius $<10\text{nm}$, 190kHz , 43Nm^{-1}) and typically an amplitude of $100\text{-}190\text{nm}$ with the amplitude setpoint at 70% regulating in the self excitation-mode on the amplitude.

† In this chapter, the surface morphology evolution, during Pulsed Laser Deposition (PLD), is imaged and characterized in-situ. With the equipment, as is described in chapter four, the surface can be monitored “quasi” real-time between the deposition

figure (6.1). The first two images were captured before deposition and after pre-ablation whereas the other images were measured between two deposition pulses. In all images, the unit cell high steps originating from the SrTiO_3 surface, are visible. No clear change in the surface roughness was observed while depositing at room temperature. The clear difference in surface morphology was observed as a function of doping concentration while depositing at $\sim 300^\circ\text{C}$ instead of $\sim 20^\circ\text{C}$. This is illustrated in figure (6.2). In figure (6.2) images (a,b) were measured ex-situ, after depositing a 110nm thick 10% Sn-doped ITO and a 110 nm thick undoped ITO film at a substrate temperature of 300°C . Image (c) was measured in-situ after depositing $\sim 1\text{nm}$ while the substrate was 300°C . The substrate temperature was increased from 20 till 300°C to increase the adatom mobility and therefore the island size. As can be seen in figure (6.2) the terrace steps are visible in image (a) whereas images (b,c) have a rough surface. Image (c) was measured in-situ after quenching the sample to room temperature. In this image three-dimensional islands are visible. From the pre-study it is expected that one observes such islands during room temperature deposition. The explanation to clarify the difference in surface roughness goes beyond the scope of this chapter. Unfortunately, the undoped ITO surface could not be imaged at 300°C with high resolution. The imaging stability as well as the image quality decreased above a specific temperature ($<300^\circ\text{C}$) and depended on the operating mode and dynamic mode settings, as will be shown next.

Figure 6.2: Surface morphology measured after depositing 110nm ITO on SrTiO_3 at 300°C .

Image quality and measurement stability dependence on the temperature

Figure (6.3) shows several SFM images of a 10%-Sn doped ITO film deposited and imaged in dynamic mode at 400°C directly after deposition. Two images were measured after quenching to room temperature and one to 270°C . As can be seen

pulses. It is debatable if this way of characterizing can be called during or after deposition. In this chapter it is called during deposition or “quasi” real-time.

in the images (a-f), the image resolution was unstable while measuring at 400°C. In images (a,d,f) the terraces are clearly seen, whereas images (b,c,e) have areas which are unclear.

To illustrate the difference in image resolution if the surface morphology was measured below 400°C, images (g-i) are depicted in figure (6.3). In images (g-i) the terrace steps are clearly visible and the image resolution is more or less constant. Also on gold, the measurement stability decreased above a specific

Figure 6.3: SFM images (a-f) were captured at 400°C in dynamic mode after the deposition of 10% Sn-doped ITO on a treated SrTiO_3 substrate. Images (g,h) were measured at room temperature and image (i) at 270°C in dynamic mode.

temperature. Figure (6.4) illustrates the influence of the substrate temperature on the measurement stability, while imaging a few nanometer thick gold film deposited at room temperature. Image (a) was captured at room temperature. In image (b) the temperature was increased from 20 up to 35°C and in image (c) from 35 up to 45°C while scanning. The arrow in image (b) depicts the moment at which the heater temperature was increased.

The resolution in the images decreases in time above a certain temperature. This can be followed in images (f-j), which were measured at 110°C. In image (j) the resolution is such that even the substrate steps are difficult to see. From the above observations we learn that the imaging stability in dynamic mode rapidly decreases for gold above 100°C, for undoped ITO above 300°C and for doped ITO above 400°C.

Figure 6.4: SFM topography images captured of a thin film of Au deposited at room temperature on SrTiO_3 .

Image quality and measurement stability dependence on the operating conditions

The influence of the SFM operating mode as well as the dynamic mode settings such as amplitude on the measurement stability at elevated temperatures is shortly described here. It was in above experiments observed that the imaging stability in dynamic mode was related to the oscillation amplitude. A larger oscillation amplitude increased the maximum SFM operating temperature and improved the measurement stability. At elevated temperatures the SFM was typically operated with oscillation amplitudes of 100-180nm and a resonance frequency of 140-190kHz. In static mode SFM the tip is constantly in contact with the sample surface. If there is a tip-sample reaction it is expected this has a larger influence in static mode compared to dynamic mode. In figure (6.5) three images are depicted which were captured while scanning in static mode at 270°C. As can be seen in images (a-c) blobs appeared on the surface. In dynamic mode the surface was imaged at 270°C without influencing the surface morphology, see image (i) figure (6.3). These results indicate that the tip-sample interaction is important.

Figure 6.5: SFM-images measured after deposition 10% Sn-doped (ITO) at 270°C (a-c). The surface morphology evolution was imaged in static mode SFM at 270°C.

6.3 SrRuO₃: a high temperature model system

As high temperature model systems SrRuO₃ is selected. The surface morphology of SrRuO₃ was followed during the deposition at 700°C on a TiO₂-terminated SrTiO₃ (001) surface. Imaging at 700°C in deposition pressure ($\sim 10^{-2}$ mbar) resulted in images without any details. To image the surface, the heater temperature had to be lowered. In figure (6.6), images (a-f) are depicted, these were captured at different temperatures, after depositing a SrRuO₃ thin film at 700°C and cooling the sample down to room temperature. It can be seen that the terrace steps, originating from the substrate, are visible in all images. Up to 500°C the SrRuO₃ surface was smooth and could be imaged in dynamic mode. Above 500°C the imaging stability in dynamic mode decreased. Images (d-i) were measured after more material* was deposited. In static mode the image quality decreased far below 500°C and after imaging in static mode, blobs were measured while imaging in dynamic mode. These blobs are visible in images (e-i). In image (e) one blob and in image (f) several blobs are highlighted with a round marker. It is expected that these blobs were formed while scanning in static mode.

Influence of the background pressure on the SrRuO₃ surface stability

Figure (6.7) illustrates the importance to keep the SrRuO₃ surface in a high background pressure. In this figure image (a,b) were captured at room temperature after depositing a SrRuO₃ thin film at 700°C. After capturing image

* In total 20 deposition pulses are given in images (d-i) compared with 5 pulses in images (a-c).

Figure 6.6: SFM images measured in-situ after depositing 5 deposition pulses (a-c) and 20 deposition pulses (d-f). The SrRuO_3 was deposited on SrTiO_3 at 700°C and cooled down to room temperature after which it was heated in 3 Pa oxygen to study the imaging stability. Image (e,f) were measured in dynamic mode at 600°C and 700°C after scanning in static mode SFM at 600°C .

(b) the oxygen flow was stopped and the pressure in the vacuum chamber lowered* to 10^{-4} mbar.

Before depositing more SrRuO_3 the sample was again heated up to 600°C in vacuum after which the oxygen flow was activated.

The surface morphology evolution† depicted in images (c,d) contain islands which were formed in high vacuum ($<10^{-4}$ mbar) whereas the surface was stable for hours in low vacuum ($\sim 10^{-2}$ mbar). These images show that the SrRuO_3 thin film surface is stable at 700°C in deposition pressures. Nevertheless it was not possible to image this stable surface.

* The used vacuum pump was in such a condition that it was not good to have a 10^{-2} mbar pressure for several days and therefore the pressure was decreased several times during the experiments in the chamber.

† The exact deposition rate in these experiments was not calculated and therefore the amount of pulses is given however it is expected that 80 pulses corresponds to at least a few nanometers.

Figure 6.7: SFM images of the surface morphology evolution (a-d) of SrRuO_3 after 20 deposition pulses (a), after 40 deposition pulses (b), after 60 deposition pulses (c) and after 80 deposition pulses (d). The latter has been imaged at $\sim 450^\circ\text{C}$ in 3Pa oxygen. The other images were measured at room temperature.

6.4 Summary of the experimental results

From the SFM measurements performed on the low and high temperature model systems it was observed that:

- the imaging stability and image quality measured in dynamic mode depends on the surface material, temperature and operating conditions;
 - The measurement resolution and stability decreased above 100, 300, 400 and 500°C for respectively gold, undoped ITO, doped ITO and SrRuO_3 thin films.
 - A larger oscillation amplitude and scan-speed, increased the maximum SFM operating temperature and improved the measurement stability.
- the measurement resolution re-appeared after cooling the sample down to room temperature for all model systems;
- in static mode large islands or blobs appeared while scanning at elevated substrate temperatures;

The most important observation from this section is that far below the maximum SFM operating temperature (850°C), the surface morphology of ITO, Au and SrRuO_3 could not be imaged for a long period. Apparently, the silicon tip-sample interaction force F_{ts} changes for several materials systems at elevated temperatures such that the cantilever deflection does not represent the surface topography.

The methods and principles used to extend the measurement conditions for STM have also been studied in this work and applied wherever possible. However, imaging at elevated temperatures with SFM is more complicated compared to STM, because in SFM also the cantilever properties such as resonance frequency

change as a function of temperature and an increase in the tip radius directly affects the measurement resolution. Several explanations listed below have been investigated to clarify the imaging instability while measuring ITO, Au and SrRuO₃ at elevated temperatures.

- I. The cantilever is contaminated and material on the cantilever is diffusing towards the tip.
- II. The tip is reacting at elevated temperatures and therefore the radius is increasing.
- III. The cantilever and tip are heated during tip-sample interaction and therefore the frequency and oscillation amplitude shift.
- IV. The tip is reacting with the surface and sticks temporarily to the surface.

Contamination (I)

A possible reason that the tip radius increases or the surface gets contaminated, is due to cantilever contamination. The as-received cantilever can be contaminated [3] due to packaging and shipping and therefore cantilever cleaning procedures have been developed like acid baths [4,5], plasma etching, ozone, thermal [6] treatment and Si-oxidation. To exclude that the measurement instability and expected increase in the silicon tip radius at elevated temperatures originates from cantilever contamination, several cleaning methods for the as-received cantilever were briefly investigated. Several as-received probes, oxidized* and plasma cleaned probes were used to characterize the topography of a SrTiO₃ substrate. This was done to study the influence of these cleaning procedures on the measurement stability. So far, improvement in the measurement stability was not observed and therefore the used cantilevers were not treated in the remainder of this thesis or otherwise mentioned.

Tip radius increases due to heating (II)

To investigate the effect of temperature and gas environment on the cantilever properties, non-coated silicon and silicon nitride probes were heated up to 900°C in oxygen and 1000°C in nitrogen. From these preliminary experiments it turned out that silicon nitride cantilevers deformed at elevated temperatures and were therefore not used in this thesis. Furthermore, it was learned that heating uncoated silicon probes up to 900°C did not decrease the tip radius significantly.

* Annealed for a few hours in 1 atm oxygen at 950°C.

Cantilever properties shift due to increased heat-transfer (III)

As is mentioned in chapter four, the cantilever properties have to be stabilized before a measurement can start. An increase in the cantilever temperature could therefore disturb the measurements. Two examples of a “good figure (6.8a)” and “bad figure (6.8b)” frequency shift versus tip-sample distance curve are shown in figure (6.8). These figures will be described later in more detail. In figure (6.8b) it can be seen that the frequency shift changes over a long distance ($>40\text{nm}$). In appendix 6A spectroscopy data is depicted in which even distances of 100nm were measured, see figure (6A.3). It is known that the convection heat transfer coefficient could be tip-sample distance dependent above 50Pa [7] and is constant below 10^{-2}mbar . This could explain the change in the frequency shift at a large tip sample distance, with a temporarily increase of the cantilever temperature when the system is outgassing*. To test this hypothesis, dynamic spectroscopy data was measured as a function of the background pressure 10^{-6} - 10^0 mbar at elevated temperatures. However, no effect was observed that could explain the spectroscopy data, see figure (6.8b), and therefore it is concluded that a temporarily increase of the cantilever temperature due to a distance dependent heat transfer† is not likely.

In this discussion explanations I-III have been shortly described and excluded. It will be shown below that the imaging stability and image quality decrease above a specific temperature for the studied model systems can be clarified with explanation IV.

6.5 Tip-sample interaction

From the above explanations scenario IV is the most likely. In this scenario, the silicon tip reacts with the studied materials and temporarily sticks to the sample surface. As mentioned previously this is also known for tips used in STM. To improve the imaging stability in oxygen with STM, tips made out of platinum and platinum alloys ~Pt/Rh, Pt/Ir, Pt/Au are often used. It is expected that the measurement stability also increases in SFM by using platinum-iridium coated tips, because platinum-iridium is more inert compared to Si-tips‡.

* Since the measurement instability also occurred below 10^{-2}mbar , the heat transfer coefficient could only increase if the local pressure between tip and sample is effectively increased due to out gassing of the tip and SFM parts.

† The heat transfer from the substrate to the tip and cantilever consist of convection, conduction and radiation. Radiation and conduction contributions are not expected to increase at relatively large tip sample distance and were therefore not considered.

‡ The used PtIr coated tips were: PPP-NCLPt Pointprobe silicon cantilever from Nanosensors, with a Pt/Ir-coating on the tip and detector side ($l=225\pm10\mu\text{m}$ $t=7\pm1\mu\text{m}$ $w=38\pm7.5\mu\text{m}$ $k=21\text{-}98\text{N/m}$ $f=146\text{-}236\text{kHz}$, tip height= $10\text{-}15\mu\text{m}$, radius $<$

To test this hypothesis coated and uncoated tips were used to image oxide surfaces such as SrTiO_3 and DyScO_3 . Furthermore the tip sample interaction was studied with spectroscopy curves. With spectroscopy curves the cantilever deflection such as bending, amplitude and resonance frequency was measured as a function of the tip-sample distance d_{ts} . It turned out that the platinum-iridium coated tips were not suitable to image oxide surfaces such as SrTiO_3 and DyScO_3 above 500°C , whereas with an uncoated tip the terrace steps on the SrTiO_3 and DyScO_3 surface have been imaged up to 850°C .

Two graphs are selected to illustrate the change in the frequency shift versus distance curve in case the measurement became unstable. Graph (6.8a) and graph (6.14b) were measured with a platinum coated tip on a DyScO_3 surface at respectively 400°C and 750°C .

It can be seen that graph (6.8a) has a similar shape as the depicted curve in figure (3.4) opposed to figure (6.8b). The difference in curves (6.8a) and (6.8b)

Figure 6.8: Typical frequency shift versus tip sample distance measured for a Pt coated tip at 400°C (a) and 750°C (b). (■) Tip was approached to the sample (○) Tip was retracted while oscillated. The used oscillation amplitude was $\sim 100\text{nm}$.

indicates that the tip-sample interaction is different above 400°C for this platinum coated silicon tip. A more extensive selection of the measured spectroscopy data, measured at 20, 400, 600 and 750°C , is depicted in respectively figure (6A.1), figure (6A.2), figure (6A.3), figure (6A.4) and figure (6A.5) of appendix 6A. The measurement instability and spectroscopy curve in figure (6.8b) can be explained with an effect called neck formation, in which a material

25nm). The used uncoated silicon probes were: SSS-NCL silicon cantilever from Nanosensors, ($l=225\mu\text{m}$, $k=48/\text{m}$ $f=190\text{kHz}$, radius $< 5\text{nm}$).

bridge is formed between the tip and the sample surface, which is illustrated in figure (6.9). In this figure the formation and breaking up of a neck is schematically depicted.

In image (6.9a) a sharp tip approaches the sample surface. The second image (b) is a snapshot of the moment a neck is formed between tip and sample. In the third image (c) the tip is retracted again and as can be seen in the last image (d) the neck stretches and breaks after a certain retraction height. This will leave a broken neck (blob) behind on the surface. Notice that the numbers in images (a,b,d) correspond with the numbers in figure (6.8b).

As can be understood from figure (6.9), during neck formation the tip-sample interaction is such that the cantilever deflection is not reflecting the sample topography. In figure (6.8b), a measured frequency shift versus distance curves is depicted in which neck formation is likely. At a tip-sample distance depicted by (1) and (2) the tip approaches the sample surface. At position (2) the neck was probably formed while approaching. The frequency shift slope changes sign at position (2), from (3) to (4) there is a sudden jump. It could be possible that part of the neck broke while moving the tip from position (3) to (4). At position (4) the tip was retracted again from the sample surface and the bridge between the tip and sample surface was maintained up to point (5) after which it broke. After a neck breaks, the remainders of the neck were observed on the surface as a blob of material. This neck formation is also observed in STM. In the section 6.5.2 the SFM spectroscopy and topography data will be compared with this STM data. The latter section describes that the imaging resolution and stability in SFM are also likely to decrease due to the formation of a neck in the studied model systems ITO, Au and SrRuO₃.

Figure 6.9: Schematic representation of the neck formation evolution and decay during a tip oscillation. a) approaching the tip (b) spontaneous neck formation (c) neck evolution during stretching (d) breaking of the neck due to retraction. The numbers in images (a,b,d) correspond to the images in figure (6.8b).

6.5.1 Discussion: neck formation

In this section, the measurement instabilities as observed while imaging Au, ITO and SrRuO₃ will be compared with literature. Since dynamic mode SFM spectroscopy data at elevated temperatures is, to our knowledge, not available in literature, the spectroscopy data is compared with STM data. In STM, neck formation over considerable distances [8] has been observed if the tip or the sample surface material tends to wet the other. In the work of Kuipers et al. [1,2], the interaction of a STM-tip with a Pb(110) surface is described as a function of temperature. They observed that STM imaging was not possible above ~50°C, because an electrical short due to neck formation between tip and sample was observed. Kuipers* described that a neck was formed just above room temperature and studied this neck formation and evolution by approaching and retracting the tip. In a paper by Gai and Frenken [2] the formation and re-sharpening of the tip after breaking, are both explained by surface diffusion. They also proposed that the formation and evolution of the neck between tip and sample is proportional with temperature, as can be expected from a diffusion process. Gai and Frenken described the different phases during neck formation. The three main phases they considered are:

- the formation of a material bridge between tip and sample;
- neck growth evolution during stretching;
- spontaneous evolution after stretching;

They concluded that:

- the neck evolution is temperature dependent;
- surface diffusion is responsible for the neck formation;
- the jump to contact, neck formation, is too fast to measure or simulate (pico second regime);
- the direction of neck evolution can be switched from growth to breaking by stretching the neck;
- the evolution of the stretched necks proceeds more than four orders slower than during the growth stage before stretching.

* In the UHV STM experiments performed by Kuipers, a W-wire is used as a tip and imaging above 318K was not possible since there was directly a short circuit between tip and sample. This short was caused by a jump in to contact between tip and surface.

In the following part, the observations of our work will be related to the formation of a neck. By comparing the SFM data with the STM data, depicted in [1,2,10] it can be concluded that they are similar, even though the SFM measurements were done with an oscillating tip. Therefore, it is likely that our observations can also be explained with this so-called neck formation.

Dependence of the imaging stability with temperature and tip-material combination

It was observed in this work that the imaging instability starts for Au, ITO and SrRuO₃ above a specific temperature, which is different for each of the model systems. Furthermore it was observed that the SrTiO₃ and DyScO₃ could be measured up to 850°C with an uncoated silicon tip and only up to 500°C with a platinum coated tip. Because neck formation is a diffusion process and the different materials have different diffusion coefficients this is in correspondence with the formation of a neck.

Restoring resolution after cooling

It is also observed that for Au, ITO and SrRuO₃ measured, with an uncoated silicon probe at elevated temperature, the resolution after cooling down to room temperature restores and the tip radius is as sharp as before. Kuipers, Gai and Frenken also observed that after stretching to a certain degree the tips become sharp again.

Neck size dependence on the temperature vertical, and lateral tip speed

During the experiments performed in this work it was observed that the neck size and breaking length (L) increases proportional with the substrate temperature. This breaking length (L) is in figure (6.8b) the distance between point (4) and (5). By increasing the approach and retraction speed, in this work, the distance between point (4) and (5) in figure (6.8b) could also be influenced. This indicates that the evolution of a stretched neck is measured here. The measured retraction heights of several tenths of nanometer (from point 4 till 5) is relatively short compared to the measured retraction height (L) measured at 450K on Pb(111), which was over 1 μ m with a maximum retraction speed (600nm/sec).

Image quality and measurement stability dependence on the operating conditions

To explain the observed difference between static and dynamic mode the work of Kuipers can be used again. Kuipers observed that by increasing the tip retraction speed neck formation is reduced. It is important to mention that in dynamic mode the tip is oscillating with a certain vertical speed. This speed can

be regarded as a kind of approach and retraction speed. The average tip retraction speed in an oscillation cycle is expressed by equation (6.1).

$$v = 2Af \quad (6.1)$$

In this expression v is the tip speed [m/sec], A is the cantilever oscillation amplitude [m] and f de resonance frequency of the cantilever [Hz]. If the average tip speed increases, it can be predicted that the imaging stability increases, because the probability that a neck forms decreases. This also explains that the imaging instability was less pronounced if large cantilever oscillation amplitudes were used. Typically a free oscillation amplitude of $A_0=140\text{-}190\text{nm}$ was used to improve the measurement stability, even though in general $5\text{-}70\text{nm}$ is used such that $kA > F_{ts}^*$. Maximizing the oscillation amplitude increases the average vertical tip speed[†] and therefore decreases the probability to form a neck. It is now a small step to explain that scanning in dynamic mode SFM, compared to static mode SFM or STM, helps to increase the maximum temperature at which the surface can be imaged. In dynamic mode the tip is oscillated and has a vertical speed opposed to static SFM and STM.

The average vertical tip speed, while scanning in dynamic mode with the used settings, is in the order of 10^7nm/sec which is seven orders higher, compared to the maximum lateral tip speed in static SFM or STM used by Kuipers. The observation that the imaging instability also decreased if the scan speed increased can also be understood, because this increases the lateral tip speed. Increasing the lateral, as well as the vertical tip speed, helps to prevent neck formation.

Origin of the blobs

After approaching and retracting a STM tip several craters and blobs (called hillocks in some articles) were observed on the surface, which resembles the found blobs while imaging in static mode in this work. These blobs have been observed while characterizing ITO, Au, and SrRuO_3 with a silicon probe and are expected to come from broken necks. These necks were formed by surface diffusion of ITO, Au and SrRuO_3 on the tip. The craters and blobs were mainly observed after scanning in static mode at relative low temperatures at which the surface could still be imaged in dynamic mode. Hodel [9], Kuipers [10], Gai and Tomagnini observed comparable craters or blobs left on the surface after the rupture of a neck. Hodel, Kuipers, Gai and Tomagnini studied respectively the Ag-tip, Pb-W tip, Pb-W tip, Pb-Au tip interaction as a function of temperature. The material

* This phenomenon is also referred to as “jump into contact”.

† The period of a single oscillation for the used cantilevers is around $4\text{-}7\mu\text{sec}$ and with an amplitude of 200nm the tip retraction speed is $8 \cdot 10^{-2} \text{ m/sec}$.

blobs, after characterizing SrTiO_3 and DyScO_3 with a platinum coated tip, are probably originating from diffusing platinum towards the substrate surface.

6.6 Concluding remarks and recommendations

In this chapter, it was shown that imaging the surface morphology during PLD was achieved if neck formation could be prevented or limited. To suppress the formation of a neck while imaging, it is recommended to increase the vertical tip oscillation speed in dynamic mode. To increase the average vertical tip speed it is recommended to increase the resonance frequency by at least one order of magnitude. Furthermore it would be helpful to increase the lateral tip speed, which is also required to upgrade the equipment such that the surface can be imaged within a second. This will enable studies in which the growth is not influenced by imaging. It was learned in this chapter that neck formation can be limited or suppressed:

- by increasing the vertical tip speed during scanning;
- by increasing the lateral tip speed;
- by decreasing the temperature;
- by optimizing and selecting specific tip-sample combinations, see also appendix 6B.

The above recommendations will take time to develop because the scanner hardware as well as the feedback electronic system have to be modified. So even though a lot of work is done there is still plenty to explore*, but the first steps are done to image, manipulate and control a new world. This work can be used as a guideline in this journey to image and map the unknown and gives directions:

- to combine deposition techniques with SPM;
- to combine analyzing techniques with SPM;
- to extend the SFM operating conditions;
- to explain measurement instabilities at elevated temperatures;
- to manipulate and control neck formation.

* For example it is recommended to test probes from Anasys to estimate the tip temperature and study the influence of the tip temperature on the deposited thin film surface structure.

6.7 References

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Appendices

Appendix 4A Damping and vibrations

Appendix 4B Different heater designs

Appendix 4C Contamination and out gassing at elevated temperatures

Appendix 4D Measurement resolution at elevated temperatures

Appendix 4E Imaging at elevated temperatures in ambient conditions

Appendix 6A Spectroscopy data

Appendix 6B Selecting a good tip-sample combination

Appendix 4A

Damping and vibrations

To study the surface morphology with atomic step resolution the vertical resolution should be $\sim 1\text{\AA}$. Vibrations from noise sources in a laboratory, especially low^{*} frequency noise, often limit the resolution in sensitive equipment such as FIB, TEM and SFM. To minimize the effect of vibrations on sensitive equipment it is placed at a low vibration spot and several damping systems [1] such as sand boxes, tires, metallic springs, superconducting levitation, eddy-current dampers, optical tables and other devices are applied [2,3,4,5,6]. In general, three mechanical noise sources can be distinguished namely ground, direct force and acoustic noise. Ground noise is due to various sources like people walking on the floor, nearby machinery but even wind blowing on buildings. Direct force noise is caused by machinery, attached to the equipment such as turbo pumps and stepper motors. Acoustic noise is coupled into the equipment by air pressure waves.

The floor “quality” can be described according to the general Vibration Criteria curves (VC-curves) [7,8,9]. These curves are ranging from VC-A to VC-G. The latter describes a high quality floor with a minimal amount of noise in a range of 1 and 80Hz. In general, sensitive equipment such as SEM and SFM requires a VC-E floor. For sensitive instrumentation development even a VC-G floor is recommended. For a particular equipment category the vibration criteria is fulfilled if the measured one-third octave band velocity spectrum lies below the appropriate criterion curve at all frequencies. This appendix (4A) describes the quality of the available laboratory floors, the general applied damping mechanisms in SPM and the used damping systems in the setup.

Experimental equipment to characterize mechanical noise

Accelerometers (Oceano TR1BCN sensors) were used in this thesis to measure quantitatively the vibration levels as a function of frequency of different floors and on several stages in the system. To measure the noise between SFM and sample the SFM itself was used. Vibration data is often expressed in various units like displacement, velocity or acceleration as well as different bandwidths and waveform indices (rms, zero-to-peak, peak-to-peak) [9]. In the measurements vibration data were 50 times averaged and recorded with a fixed bandwidth of 0.48Hz and a one-third octave bandwidth which is 23% of the band center

* Frequencies below 100Hz.

frequency. The latter is more suitable for broadband random energy whereas a fixed bandwidth (0.48Hz was used by us) is better to study relatively pure tone energy.

Floor characterization

To investigate the quality of three different laboratory floors their noise spectrum is characterized and compared to the VC-levels, see figure (4A.1). These three ground floors are all located in the same building and separated in space with at most ~100m.

Floor 1: This ground floor is a concrete slab separated from the main building and created in a room with a VC-C floor.

Floor 2: This ground floor is not separated from the main building.

Floor 3: This ground floor is a concrete slab of (4x4x0.30m) which is placed on 7m long metal poles which are mounted in solid soil. This lab island is created in

Figure 4A.1: Vibration measurement in the three orthogonal directions ($z=\circ$, $y=\square$, $x=\Delta$) for floors 1-3 and the corresponding international VC-levels. The data is plotted per 1/3 octave band with the vertical direction defined as z .

a room with a VC-A floor.

Floor (1) can be characterized as a VC-D floor and is according to international standards suitable to locate sensitive equipment such as a focused ion beam, TEM and SFM. Floor (2) and (3) are classified as VC-C floors and are suitable for processes such as photolithography but not recommended for sensitive equipment such as SFM. The work in this thesis can be regarded as instrumental development for which a VC-G level is recommended. Nevertheless this system has been developed on floor (1) and (2) for practical reasons*. The difference in vibration levels of the measured floors can be addressed to machinery located directly above the floors. This machinery, to circulate the air, is the source of the

* For example to have laser access to an 248nm excimer laser to ablate material.

25, 50 and 100Hz peaks. The improvement in floor quality between floor (1) and (2) is related to the distance to this equipment*. Although the concrete slab (floor (3)) did increase the floor quality from a VC-A towards a VC-C floor the developed system was not located from floor 2 towards floor 3 (concrete slab) since the resonance frequency of the air table and concrete slab (~4Hz) were matching and the vibrations levels were such that instrumental development would be extremely hampered.

Characterization of the main damping stages

To describe the damping properties of a system a transfer function can be used defined by equation (4A.1).

$$T(f) = \frac{A_{output}(f)}{A_{input}(f)} \quad (4A.1)$$

In this expression A_{output} is the amplitude as a function of frequency after the damping stage and A_{input} is the amplitude as a function of frequency before damping. The active damping stages are specified to damp 40dB above 10 Hz and between 5 and 10Hz around 20 dB and state of the art air pods damp 40dB above 10 Hz. However estimating the transfer function between the lab floor and several locations on the system was difficult, because there were several direct connections to the ground floor and the total damping consisted of several damping stages. Furthermore the specifications of the “old” air-pods[†] could not be traced. The transfer function between the VC-C floor (2) and a location on the first platform after passive damping as well as the second platform after active damping is depicted in figure (4A.2). The transfer is not increasing at increasing frequency due to the measurement sensitivity of the used accelerometers. From the transfer it can be stated that the active and passive damping stages reinforce each other. For example at 25 Hz the noise is damped by 50dB which is more than can be expected from merely the passive or active damper elements. As expected, the active elements reduce the vibration levels especially at low frequencies, the damping in the vertical direction is superior compared to lateral directions and the difference in symmetry of the active MOD-2 elements was reflected in the damping difference of the two lateral directions. Furthermore it can be seen that the resonance frequency of the air table is ~4 Hz.

Characterization of the lab-island: a special damping stage

Floor (3) can be considered as a damping stage and has compared to floor (1) and (2) an additional amplitude peak at 4 Hz in the lateral directions and a 12Hz and a broad 25Hz peak in the vertical direction

* The distance to floor (3), (2) and (1) is respectively ~10, ~50 and ~75m.

† These air-pods originate from an old SEM

Figure 4A.2: Transfer function after measuring the vibration spectra at different locations in the system. (a) Transfer in the z -direction of the platform after passive ($\square$) and active ($\circ$) damping. (b) Transfer in x and y on the platform after active damping. The vibration data was taken while all electrical and optical cables were connected and pumps were in operation.

This section will discuss the constructed experimental lab-island since the obtained data, such as the transfer functions, could be valuable for others to damp sensitive equipment or design a new laboratory. To characterize the lab-island the lateral and vertical transfer were measured, see figure (4A.3). This transfer function visualizes that the vertical and lateral damping starts at respectively 3Hz and 7Hz and has no or limited damping between 25-30Hz in the vertical direction. The transfer values in the lateral and vertical direction are in correspondence with the values obtained with a floor ($3 \times 2.5 \times 0.9 \text{m}^3$) mounted on concrete piles and even the 25-30Hz region with no or limited damping has been observed by others in a similar slab constructed directly on the soil [7]. To improve the slab quality the concrete slab should be constructed as described by

Figure 4A.3: Transfer function in the z -direction (c) and in the xy -direction (d) of floor (3).

Amick et al. [10]. In this paper a concrete slab is mounted on dampers instead of concrete or metal piles. Furthermore the mass and area can be increased to improve the damping properties.

At present, mechanical noise on the VC-C floor of 25 and 50 and even 100 Hz cannot be filtered by either the passive or active damping stage. To reduce the vibration levels it is recommended to replace some hardware elements* and to investigate the applicability of a spring system with eddy current damping as well as an additional active damping system.

In-situ characterization of the main damping stages

For practical reasons mechanical noise could not be easily measured with accelerometers at different spots in vacuum such as the SFM-location, sample-location and on top of the frame which support all the main elements. Therefore the effect of noise on the SFM-measurements was tested in vacuum by imaging the surface structure of a vicinal surface with atomic steps, see figure (4A.4). In

Figure 4A.4: SFM-images Al_2O_3 with nanometer steps (a) (inset frequency response), topography of Nb-doped SrTiO_3 (b,e) Topography image of SrTiO_3 at 750°C on top of the high temperature sample stage (c). Surface image measured with (b) and without (e) active damping. While imaging the surface depicted in (d) the active damping is turned off. This experiment was done while the system was located on the described VC-C floor. SrTiO_3 steps measured with the theta-configuration (f). All above measurements are performed in vacuum ranging from 10^{-2}mbar till 10^{-5}mbar .

this manner the mechanical structure of the parallel, theta configuration and

* For example the turbomolecular pump can be replaced by maglev turbomolecular pump or an ion pump and the noise from the water cooling can be reduced by using air circulation.

different sample stages was tested. Notice that the topography images (a-f) were captured in vacuum with a running turbomolecular pump while the system was place on the VC-D ground floor and with the parallel configuration or mentioned otherwise. From the images depicted in figure (4.4A) it can be concluded that atomic step resolution is achieved with;

- both configurations
- two sample stages consisted of a relatively heavy cylinder* and the heating stage as described in chapter four.

Furthermore, it can be concluded that the two main damping stages reinforce each other and that atomic step resolution was only achieved on a VC-D ground floor if both the passive and active damper were properly adjusted. On the VC-C floor vibration noise of 25 and 50 and even 100 Hz could not be completely filtered out by either the passive or active damping stage.

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* This was a 30mm high aluminium or messing cylinder with a diameter of 20mm.

Appendix 4B

Different heater designs

The initial high temperature sample stage consisted of a resistive heating stage which required at least 30W to reach 550°C in vacuum and 4.5W to reach 200°C in ambient conditions. To visualize the heating stage evolution, the size and heater input power to reach 550°C in vacuum and 200°C* in ambient conditions are given in figure (4B.1 and 4B.2).

Figure 4B.1: Selection of the developed and tested heating stages. a) Large original design heating carousel with 4 heaters. b) direct current heating stage of Nb-doped SrTiO_3 c) SiC heating stage with a meander of platinum d) Alumina heating stage with an embedded meander of platinum e) SiC membrane thin film heater with a meander of platinum.

As can be observed in figure (4B.2) the total input power decreased between 1 and 3 order of magnitude. This decrease in power corresponds to the total heated volume, see figure (4B.1) in which a selection of the tested heating stages are depicted. In figure (4B.2) the required input power to reach 550°C in vacuum for a cartridge heater, thin film and free standing ceramic heater are displayed. On these mechanically stable heaters different substrates could be mounted.

Direct current heaters

To pass a current through Nb-doped SrTiO_3 and SrRuO_3 coated SrTiO_3 , substrates ($5 \times 5 \times 1 \text{ mm}^3$) silver electrodes were painted on the sides. Although they could be directly heated up to 550°C in vacuum with a power of ~5W controlling, stabilizing the temperature homogeneity and measuring the temperature was a problem. At that time other heating stages promised better results and therefore no effort was done to investigate this route more thoroughly.

Thin film membrane heaters

Heaters designed; fabricated and calibrated by Gregor Whiche from MAT Berlin had a volume difference of 4 orders compared to the initial heaters. On top of

* A value of 200°C in air is chosen because not all heater structures could be heated further.

Figure 4B.2: a) Required power to reach 550°C of the different heaters in vacuum b) Required power of several heaters to reach 200°C in air.

a) A: resistor heater made by TSST in the Netherlands, B: Heater from Heat wave lab. Inc., C: Peltier element temperature 135°C, D: Nb-doped SrTiO_3 heated by direct current heating the element was glued on a macor block, E: SiC thin film heater with a 100 μm thick $2 \times 2 \text{mm}^2$ substrate was glued on a Macor block, F: SiC thin film heater was mounted on an Aerogel block, G: Wattlow heater hanging freely, H: SiC membrane heater, I: Embedded Pt200 heater.

b) F: Input power of the resistor heater made by TSST to reach 250°C, G: Wattlow heater at 420°C with substrate, H: SiC-heater with Aerogel support, I: Embedded Pt200-heater with SrTiO_3 substrate (1mm thick).

these 2,2 μm thick SiC membrane a platinum meander is structured which is covered with 1 μm SiO_2 to electronically insulate the membrane. This Pt200 resistor was used to read-out the temperature and heat the $1 \times 1 \text{mm}^2$ membrane. These heater membranes were almost freestanding and comparable to the heaters used by M. Dibattista. The temperature homogeneity of these hot plates was fairly good as can be seen from the figure (4B.3).

AFM measurements on these hotplates were performed in static and dynamic mode up to 800 °C in ambient, see figure (4B.3). To our knowledge this is the highest operating AFM temperature in ambient. From these experiments it can be concluded that the SPM operating temperature can be extended if the thermal load on the AFM-head is small.

However, the applicability of these low thermal mass heaters for surface science studies was still limited since there was no method found to mount substrates on such fragile membranes. Nevertheless these hotplates, originally designed for gas sensing applications, could be valuable for a large community if methods will be developed to mount samples on the hotplates. At present hot-plate arrays are already applied in high throughput materials research [1,2,3,4,5,6].

Figure 4B.3 a) SiC membrane thin film heater with a meander of platinum b) image of a thermoelectric camera to visualize the temperature homogeneity c) SFM image captured at 800°C with our SFM in ambient conditions.

Thin film SiC heaters

To mount different substrates, a flat SiC sample (5x5x0.5mm) with a platinum resistor was tested. The best design, to mount such a heater, is a design of L. Kuipers et al. [7] and M. S. Hoogeman [8] in which the thermal drift is minimized in the x,y and z-direction. In this design the sample\heater is pressed on two electrical contacts with a spring. For the prototype heaters such a structure was not available and insulation material like Macor and Aerogel were used to support the heaters. With Aerogel, the best solid insulation material available, a power of 1.5W was required to heat the sample up to 200°C in ambient. A problem in handling Aerogel was its reactivity with water and therefore this route was also abandoned.

Cartridge heater

The obtained results with a so-called cartridge heater (commercially obtained from Wattlow) with integrated thermocouple were also promising because they required around 3W to heat the sample up to 200°C in ambient.

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Appendix 4C

Contamination and outgassing at elevated temperatures

During the first high temperature experiments (up to 700°C) material was deposited on our SFM-head, see figure (4C.1 and 4C.2). From image (4C.2 A) it can be seen that the SFM-head was completely covered. To study this contamination in more detail the cantilever was analyzed with SEM and XPS.

Figure 4C.1: SEM images of the cantilever body and cantilever after a high temperature experiment. A) Overview of the cantilever and the cantilever body, white part is contaminated with silver B) zooming in on the cantilever beam C) zooming in on the clean part of the cantilever body D) Overview of the cantilever body, black area is used to clamp the cantilever E) zooming in at the clean-deposited interface F) zooming in on the middle of the body which is deposited with silver.

Compositional analysis showed that the cantilever surface was contaminated with silver. The images of figure (4C.1 and 4C.2) show that there were areas with and without silver. For example, the cantilever body was completely covered except the part on which the cantilever was clamped and the area which was located directly opposite to the heater.

In the setup two silver sources were present:

- a silver alloy coating with a melting point of 162 °C which was deposited on the electronic contacts (CuBe) of the piezo to excite the cantilever, these contacts were located directly below the cantilever body
- silver paint (Leitsilber 200) used to mount a substrate even though this paint is considered to be chemically stable and widely used in thin film material research up to 900°C-950 °C

Since the silver contamination still appeared after the removal of the coating, it had to be silver paint. To investigate the chemical and thermal stability of the silver paint a clean Si-substrate (10x10mm) was placed in front of the heater*. On top of the heater a small drop of silver paint was placed. Before an experiment, the silver paint was first slowly heated up to 700°C to dissolve all solvents. To determine if silver was deposited on the silicon, it was placed in front of the heater. After heating the substrate was optically inspected and

Figure 4C.2: A) Right: topview of the SFM. 1) Cantilever chip 2) Imprint area of the heated sample 3) Clamp to mount the cantilever in the alignment chip (Nanosensors) 4) body of the aluminum holder. 5) Ceramic part of the scanner-end piece.

Left: Photographs of B) heater with metal oxide crystal C) silicon substrate mounted for the heater with substrate glued with silver paint at 720°C D) with only silver paint at 650°C E) at 770°C.

characterized by XPS. From these experiments it was observed that:

- a large spot or heater structure imprint was visible on the silicon substrate above 500°C, see figure (4C.2), even after a long[†] pre-anneal at 750 °C in vacuum.

* The substrate heater separation was set to 1-2mm and the heater was kept for a few hours at a certain temperature in front of the clean silicon substrate.

† >24hours the heater with a small drop of silver was heated.

- silver is located on the imprint as well as on the spot around it while in an experiment without silver paint no trace of silver was detected.

Remarkably, the cantilever itself seems not been contaminated in figure (4C.1) which can be explained by the fact that the cantilever surface was at a higher temperature compared to the cantilever body and deposited silver was directly re-evaporated. This could also explain why the silver contamination in thin films mounted with silver paint is probably limited. However it has to be mentioned that if the heater substrate gradient was slightly larger than typically used, silver was deposited on the substrate, see figure (4C.3). From the above it can be concluded that the silver paint (Leitsilber 200) was sublimating and forming a silver cloud in vacuum (10^{-2} - 10^{-5} mbar) above 500°C .

To avoid silver contamination the use and applicability of platinum paint was also tested. To investigate the chemical stability of platinum paint (obtained from SPI) similar experiments as for silver have been carried out. From these experiments it can be concluded that platinum is not contaminating up to 850°C . However the adhesion between substrate and heater of commercially platinum paint was such that substrates do not stick on a metal or ceramic heater plate. To improve the adhesion the ceramic heaters can be coated or the paint can be modified. Coating the heaters with noble metals like Au improved the adhesion such that 1 out of 10 samples stayed on the heater. Modifying the paint by adding the solvent used for Leisibler (200) to the platinum paint solution was more successful since this improved the adhesion such that 8 out of 10 samples stayed on. In the remainder of this thesis only this modified platinum paint was used to mount samples or it is mentioned otherwise.

Figure 4C.3: A) Heater setup used in a particular experiment 1: heater 2: silver paint 3: sample. In this particular experiment a second substrate (SrTiO_3) was clamped on top of the first which was mounted with silver paint. B) Example of the top surface (5) after heating up to 880°C in $0.1\text{mbar } \text{O}_2$. The top surface was covered with silver, see (5). Notice also the silver at the edges of (5). A clean surface is also depicted (6) to demonstrate the difference.

Appendix 4D

Measurement resolution at elevated temperatures

Basically the noise sources in dynamic mode SFM which contribute to the overall vertical noise δz are mechanical noise δz_{mech} , amplitude noise δz_A and frequency noise δz_{freq} see equation (4D.1) [1].

$$(\delta z)^2 = (\delta z_{\text{mech}})^2 + (\delta z_A)^2 + (\delta z_{\text{freq}})^2 \quad (4D.1)$$

To measure the local surface morphology with atomic step resolution at elevated temperatures the effect of the above described noise terms as a function of heater temperature are described in this section. From the below described analysis it can be derived that the influence of the heater temperature on these contributions was limited and therefore it was expected that atomic step resolution could still be obtained at elevated temperatures.

Mechanical noise as a function of temperature

To estimate the influence of the temperature on the mechanical noise the heating stage with the two connection wires was modeled as a spring with a heater amplitude A_h . The thermal energy in this spring results in an amplitude and can be expressed with equation (4D.2).

$$A_h \approx \sqrt{\frac{2k_B T}{k_h}} \quad (4D.2)$$

In this expression k_h the spring constant of the heater connection wires, T is the temperature in Kelvin and k_B is the constant of Boltzmann. It can be seen that the heating stage oscillation amplitudes increases with temperature due to thermal vibrations. A second effect is that the spring constant k_h decreases with increasing temperature which can increase the mechanical noise transfer.

For an increase in temperature of 700K the noise increases approximately by a factor of 2 if the decrease in spring constant is neglected. It is expected that this is justified since the temperature increase of the connection wires is limited.

Amplitude noise as a function of temperature

To estimate the influence of the temperature on the amplitude noise δA_0 due to the thermal vibrations of the cantilever equation (4D.3)* is used:

* In this calculation the amplitude noise for CA-FM is estimated since there was no expression for CE-FM.

$$\frac{k(A_0 + \delta A_0)^2}{2} - \frac{kA_0^2}{2} \approx k_B T \quad (4D.3)$$

$$\delta A_0 \approx \frac{k_B T}{kA_0} \quad (4D.4)$$

For an increase in temperature of 700K the noise increases approximately by a factor of four however the amplitude noise δA_0 at room temperature is typically in the order of 10^{-16} m so it can be neglected even though it increases linear with temperature.

Frequency noise as a function of temperature

To relate the frequency noise with the vertical noise an expression for the variation in δd_{ts} that will lead to a shift in the frequency $\delta(\Delta f)$ is used. In this expression the distance between the front atom of the tip and a surface plane is d_{ts} .

$$\delta d_{ts} = \delta(\Delta f) / \left(\frac{\partial(\Delta f)}{\partial d_{ts}} \right) \quad (4D.5)$$

The main frequency noise sources are due to the instrumental or frequency detector noise $\delta(\Delta f)_{\text{instrumental}}$ and the thermal vibration noise $\delta(\Delta f)_{\text{thermal}}$. These two uncorrelated frequency noise sources contribute to the total frequency noise and can be expressed by:

$$\delta(\Delta f) = \sqrt{\delta(\Delta f)_{\text{thermal}}^2 + \delta(\Delta f)_{\text{instrumental}}^2} \quad (4D.6)$$

The two frequency noise source can be estimated in which $\delta(\Delta f)_{\text{instrumental}}$ (0.1Hz_{rms}) for the used instrument and the frequency noise due to thermal vibrations $\delta(\Delta f)_{\text{thermal}}$ can be calculated with the formula of Albrecht[2]:

$$\delta(\Delta f)_{\text{thermal}} = \sqrt{\frac{f_0 k_B T B}{\pi k Q A_0^2}} \quad (4D.7)$$

This frequency term scales with the square root of T. The noise can be estimated: suppose 256x256 pixels are measured with 4 lines a second than the bandwidth B is 4*256=1000Hz with a Q of 10^2 - 10^5 this results in $\delta(\Delta f)_{\text{thermal}} = 22$ mHz at 300K and $\delta(\Delta f)_{\text{thermal}} = 40.9$ mHz at 1000K for the used cantilevers. Since this increases by a factor of two the frequency noise is expected to be almost heater temperature independent.

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Appendix 4E

Imaging at elevated temperatures in ambient conditions

At ambient conditions measurements up to 600°C have been performed in static and dynamic mode, see figure (4E.1). The heater temperature was not further increased to avoid depolarization of the piezo, this piezo was located directly below the cantilever body. At 600°C the cantilever was heated up to an estimated temperature of 100°C. With this thermal load it is possible to estimate, from the data of the scanner shielding, that the piezo-scanner temperature was below 50°C. Although the warming up of the piezo was limited it explains the difference in observed structure width in the six images*. Other effects that have to be taken into account are thermal drift, tip effect and surface stability. Besides scanning up to 600°C it was possible to increase the temperature by 200°C at ambient conditions while scanning the surface. This temperature increase resulted in a lateral shift ($\pm 60\text{nm/K}$) due to thermal expansions of the setup. Although this drift was mostly unidirectional drift no effort was taken to compensate this.

Figure 4E.1: Scanning in ambient conditions on the calibration sample at 20°C (A), 110°C (B), 175°C (C), 250°C (D), 350°C (E) and 475°C (F). The drift was mainly in one direction and was in air $\sim 60\text{nm/K}$ depending on the heater temperature. The step height along the line in image (D) is 6nm.

* A temperature increase, increases the piezo-scanner displacement-voltage which effectively increases the measured structure size.

Appendix 6A

Spectroscopy data

To study the tip-sample interaction for Pt/Ir coated and uncoated tips on a DyScO_3 and SrTiO_3 surface the amplitude and frequency shift distance curves were measured as a function of several experimental parameters such as the free cantilever oscillation amplitude A_0 , the approach and retract speed and the substrate temperature. It has to be mentioned that the effective tip-sample distance is less in the CE-mode and that the distance zero is an arbitrary distance chosen as the maximum tip-sample distance. In this appendix a selection of the measured spectroscopy data will be depicted. In chapter six only two graphs are shown. Some observations are also given at the end of the appendix.

Spectroscopy curves measured with a platinum tip at 20°C on DyScO_3

A selection of the measured spectroscopy data at 20°C is depicted in figure (6A.1). In this figure five graphs are depicted. Graphs (a-d) are frequency shift versus distance curves measured at different amplitudes. Graph (e) depicts the corresponding amplitude versus distance curves. In Graphs (a-d) the black line is the approach curve and the gray the retract curve.

Figure 6A.1: Frequency shift versus distance curves (a-d) and amplitude versus distance (e) measured on DyScO_3 . Curves were measured with a different oscillation amplitude: 200nm (a), 125nm (b), 100nm (c), 40nm (d), the corresponding amplitude distance curves (e). Approach (■) and retract (■) direction in images (a-d).

Spectroscopy curves measured with a platinum tip at 400°C on DyScO₃

A selection of the measured spectroscopy data at 400°C is depicted in figure (6A.2). In this figure six graphs are depicted. Graphs (a-e) are frequency shift versus distance curves measured at different amplitudes. Graph (f) depicts the corresponding amplitude versus distance curves.

Figure 6A.2: Frequency shift versus distance curves (a-e) and amplitude versus distance (f) measured on DyScO₃. Measurements were done with different oscillation amplitudes: 140nm (a), 110nm (b), 80nm (c), 55nm (d), 30nm (e) and the corresponding amplitude distance curves (f). Approach (■) and retract (□) direction in images (a-e).

Spectroscopy curves measured with a platinum tip at 600°C on DyScO₃

A selection of the measured spectroscopy data at 600°C is depicted in figure (6A.3). In this figure six graphs are depicted. Graphs (a-f) are frequency shift versus distance curves which were measured while using different amplitudes. The depicted curves were measured with an amplitude 120-140nm.

Spectroscopy curves measured with a platinum tip at 750°C on DyScO₃

A selection of the measured spectroscopy data at 750°C is depicted in figure (6A.4). In this figure six graphs are depicted. Graphs (a-f) are frequency shift versus distance curves, which were measured while using different amplitudes.

Figure 6A.3: Frequency shift versus distance curves (a-f) measured on DyScO_3 oscillation amplitude 120-140nm.

Figure 6A.4: Frequency shift versus distance curves and corresponding amplitude versus distance (a,b) and (d,e). Frequency shift measured on DyScO_3 with an oscillation amplitude 110nm(c), 55nm (f). Approach (■) and retract (▒) direction in images (a-e).

Spectroscopy curves measured with a pt-tip at different temperatures on SrTiO_3

A selection of the measured spectroscopy data at different temperatures is depicted in figure (6A.5). In figure (a) the frequency shift versus distance is

Figure 6A.5: The approach (■) and retract (○) frequency shift as a function to tip-sample distance on SrTiO_3 a) frequency shift curves measured at different temperatures b) frequency and corresponding amplitude measured at 700°C.

depicted, measured at 20, 500 and 600°C in figure (b) the amplitude and frequency shift versus distance curve measured at 700°C is depicted.

Spectroscopy curves measured with a pt-tip at 750°C on SrTiO_3 .

In this data the approach and retract speed is varied. A selection of the measured spectroscopy data with a free amplitude of 110nm of an uncoated tip and SrTiO_3

Figure 6A.6: the approach (■) and retract (○) amplitude and frequency shift as a function to tip-sample distance on SrTiO_3 a) amplitude at different speeds b) corresponding frequency shifts at different speeds. The free oscillation amplitude was for all 100nm but subsequently shifted by 30nm, 60 and 90nm to put the graphs in one figure. The tip was approached and retracted relatively fast (▲) compared to the curve depicted with the circular (○) symbol.

at 750°C is depicted in figure (6A.6). In figure (a) the amplitude and in figure (b) the frequency shift versus tip-sample distance is depicted.

Observations:

It can be observed from spectroscopy curves measured with a platinum coated tip on DyScO₃ that:

20°C:

- There is a negative and positive frequency shift slope when approaching the tip towards the surface
- The frequency shift as a function of tip-sample distance increases with the decreasing oscillation amplitude
- The negative frequency shift changes over a tip-sample distance of 10-40nm
- The amplitude as a function of tip-sample distance is more or less constant with the oscillation amplitude
- The amplitude starts to decrease at a closer tip-sample distance compared to the frequency shift
- The amplitude decrease has a continuous negative slope

400°C:

- The negative frequency shift changes over a tip-sample distance of 10-20nm
- The frequency shift data is noisy with free amplitudes below 60nm

600°C:

- The frequency shift as a function of tip-sample distance is not reproducible
- The negative frequency shift changes over a tip-sample distance of 40-100nm

750°C:

- The frequency shift as a function of tip-sample distance is not reproducible
- The negative frequency shift changes over a tip-sample distance of 40-100nm
- The approach and retract frequency shift are often hysteretic

On SrTiO₃:

- The negative frequency shift changes over a tip-sample distance of 5-150nm
- At 500°C the first frequency shift change starts relatively far from the surface
- At 20°C the frequency shift changes over a tip sample distance of 10nm
- At 700°C the frequency shift changes over a tip sample distance of 150nm
- The approach and retrace curves are more hysteretic if the measurement speed is increased.

Appendix 6B

Selecting a good tip-simple combination

The silicon tip-sample interface was investigated to comprehend the measurement instability while imaging Au, ITO and SrRuO₃, as well as to find a model system or tip material to decrease this instability. The tip-sample surface is regarded in this work as an interface at which chemical reactions can occur. It is assumed that if the tip-sample interface is thermodynamically stable, also the imaging resolution is stable. The three chemical reactions of a metal oxide MO_x with silicon are given by equations (6.1), (6.2) and (6.3).

A useful scale to predict the course of oxidation-reduction reactions of metals and metal oxides with silicon and silicon dioxide is the oxygen affinity [1]. In table (6.1) the oxygen affinity is depicted. Hubbard and Schlom, [2] also investigated the stability of materials with silicon. They found that several materials form a stable and sharp interface with silicon these materials are depicted with a marker (*) in table 6.1.

As can be seen in table (6.1), the metal oxides with a larger oxygen affinity compared to SiO₂, except for TiO₂, are thermodynamically stable. Hubbard and Schlom also proposed that complex oxides form a stable interface with silicon if they consist of a combination of binary oxides that are thermodynamically compatible with silicon. From table (6.1) it can be predicted that In₂O₃, SnO₂, and SrRuO₃ thin films will all react with the silicon tip at elevated temperatures. The measurement stability* on SrTiO₃ can also be explained, since both SrO and TiO₂ have a higher oxygen affinity as SiO₂. From this analysis it is expected that the imaging stability increases if a substrate is used such as Y₂O₃ or Al₂O₃ since they have a higher oxygen affinity compared to SrTiO₃. However, it is also expected that SrRuO₃, which has a SrO termination, should be stable. To test if

* SrTiO₃ is relatively easy to characterize up to 750°C although according to Hubbard and Schlom also the SrTiO₃- Si interface is not stable at 1000K (G1000° = -19.133kcal/mol) and forms SrSiO₃. Probably the tip is oxidized during operation which increases the measurement stability. The preferred reaction of a Si-SrTiO₃ interface at a 1000K is given by: $3Si + SrTiO_3 \rightarrow SrSiO_3 + TiSi_2$.

with Al_2O_3 coated tips the imaging stability increases this material was deposited on silicon tips. So far the imaging stability while using these coated probes is not tested.

Table 6.1: Oxygen affinity of Metals [1] at 1000K and * materials that are thermodynamically stable with silicon [2.]

Oxide	pO	Oxide	pO	Oxide	pO
Au_2O_3	-5.5	FeO	20.6	SiO_2	36.3
Ag_2O_3	-3.3	WO_2	21.2	TiO_2	44.2
PtO	-1.3	K_2O	23.2	RaO^*	46.3
PdO	-1.1	In_2O_3	24.1	Al_2O_3^*	47.2
Air	0.7	ZnO	25.8	ZrO_2^*	47.2
IrO_2	0.9	$\text{H}_2\text{-H}_2\text{O}$	26.0	HfO_2^*	48.4
Rh_2O	4.2	Ga_2O_3	26.2	Li_2O	48.5
TeO_2	7.2	CO-CO_2	26.8	BaO^*	48.6
Cu_2O	9.6	Na_2O	28.9	Sc_2O_3^*	50.3
BiO	11.4	P_2O_3	29.7	SrO^*	51.2
PbO	12.7	P_2O_3	29.7	BeO^*	52
TcO_2	13.6	Na_2O	28.9	MgO^*	52
ReO_2	13.6	P_2O_3	29.7	Y_2O_3^*	52
As_2O_3	15.3	Cr_2O_3	30.1	Re_2O_3^*	53
NiO	16.2	MnO	32.6	ThO_2^*	55.5
CdO	16.6	Ta_2O_5	33.2	CaO^*	55.5
GeO_2	18.4	NbO	33.7	Ac_2O_3^*	56.4
SnO_2	19.7	VO	34.5		
MoO_2	20.1	B_2O_3	35.4		

Al_2O_3 coated probes

Sapphire is known as wear-resistant and thermal stable. However sapphire coated probes are not commercially available and therefore Al_2O_3 was deposited by PLD on non-coated silicon probes [3]. From initial heat experiments of Si and

Si_3N_4 cantilevers it turned out that only Si-probes were high temperature resistant. Therefore only silicon cantilevers were coated.

Experimental

In these experiments a titanium doped (0.145 wt%) sapphire target was used and ablated with a fluency of 3 J/cm^2 and a repetition rate of (1-5Hz). This resulted in a deposition rate around $0.5 \text{ \AA/pulse}$. Furthermore the target substrate distance (40mm) and deposition pressure ($3 \cdot 10^{-3}$ mbar Argon) were kept constant and only the substrate temperature was varied between $1000\text{-}500^\circ\text{C}$. After deposition the probes were annealed in oxygen and nitrogen at 1 atm.

Results

Figure (6B.1) shows SEM images of an uncoated (a) and a coated silicon tip(b) captured after the deposition and subsequent thermal annealing at a 1000°C in N_2 . The uncoated tip has a smooth surface whereas the coated tip is covered with a layer of fine grains.

The composition on the tip apex is further analyzed by energy dispersive X-ray (EDX). In figure (6B.2) the spectrum of an uncoated and coated tip is displayed. This revealed the presence of Si, Al, O and some C on the coated tip. Carbon is probably originating from airborne contaminants whereas the strong silicon peak originates from the underlying Si. This spectra is the evidence that the coated apex composition is Al_2O_3 . X-ray diffraction (XRD) on the coating was performed to determine the crystallographic structure. In the analysis, no α

Figure 6B.1: SEM imagers of silicon tip(a) and an Al_2O_3 coated silicon tip with a 26-29nm thick Al_2O_3 film.

structure corresponding to the sapphire phase was found besides $\gamma\text{-Al}_2\text{O}_3$. To obtain $\alpha\text{-Al}_2\text{O}_3$ coatings on Si tips a Cr_2O_3 template layer [4,5] was deposited and

† Si_3N_4 deformed completely after an anneal in oxygen at 900°C

Figure 6B.2: EDX-analysis captured at the apex of an uncoated Si tip and a Si tip coated with a 26-29nm thick Al_2O_3 film.

the substrate temperature has been increased up till 1150°C . So far this did not result in the formation of $\alpha\text{-Al}_2\text{O}_3$. To heat up till 1150°C a homemade heater was made. In this heater a tungsten element was heated.

Even it was not proven the tips contained the α -phase, the wear resistance of the uncoated and coated tips were tested on hard nanostructured ZrO_2 sample under different applied loads. The tip radius (30nm) and the initial adhesion force (12nN) were comparable for both probes in the experiments. Figure (6B.3) shows the relative tip area for both coated and uncoated tips as a function of time. The

Figure 6B.3: Tip stability test of the Al_2O_3 coated (solid symbols) and uncoated Si probes (open symbols), performed on hard nanostructures ZrO_2 sample under different load conditions. Data taken from [6].

uncoated tip started to wear at fairly low applied loads (12nN) whereas the coated tip remained stable up to 55nN. So although the exact structure of the Al_2O_3 thin film on the tip is unknown the created coating on Si-probes is wear-resistant.

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Summary

Imaging and mapping “new” land, species, organisms and processes created possibilities to manipulate and control them. Microscopes enabled imaging objects and processes that go beyond the human senses as vision, sense and hearing. This information is required to understand physical and chemical processes such as deposition and growth. Currently, there is also a clear need to monitor the surface morphology during deposition. To image and map (non)conducting surfaces with atomic resolution, Scanning Force Microscopy (SFM) can be used.

With physical vapor deposition techniques such as Pulsed Laser Deposition (PLD) thin films of almost any material such as metal oxides can be deposited. Finding the optimum deposition parameters, for material systems, is traditionally done by trial and error. This can be a tedious and time-consuming process especially when information on composition and morphology is lacking during growth.

Diagnostic information during deposition of materials such as metal oxides is up to now mostly derived from diffraction methods such as Reflection High Energy Electron Diffraction (RHEED), Surface X-Ray Diffraction (SXRD) and Low Energy Electron Diffraction (LEED).

These instruments are based on diffraction and measure the periodic arrangement of the surface atoms. However, the local surface morphology such as the island density, the island size distribution and island shapes can not be directly measured on a microscopic scale as opposed to imaging techniques such as Scanning Probe Microscopy (SPM). This instrument has a high spatial resolution, but is usually not combined with deposition techniques and merely used ex-situ*. This hampers quantitative studies to describe the nucleation and growth because it is difficult to measure the evolution of the same microscopic surface location and the surface morphology evolution could be influenced† by the cooling procedure to room temperature, ambient exposure and ex-situ sample preparation. This thesis describes a setup for in-situ growth monitoring with SFM during Pulsed Laser Deposition (PLD). The setup is designed to study oxide growth during PLD. The choice for oxides is based on the fact that PLD is

* After the deposition is finished and the sample is removed from the deposition chamber.

† For instance, some materials, such as oxides, are deposited in a reactive atmosphere at high temperatures and exposure to ambient conditions as well as cooling to room temperature will influence the surface morphology.

especially suitable technique to deposit oxide[‡] thin films, which have a wide variety of properties. Because of the variety of properties, oxides are often used in thin film devices. The time between two consecutive deposition pulses typically varies from 0.1-25 seconds. If the surface can be imaged with SFM between two consecutive deposition pulses the PLD synthesis is essentially not disturbed and the growth can be monitored.

By separating the SFM-position in space from the PLD-position, the standard geometry for both SFM and PLD can be maintained and material deposition on tip and cantilever as well as other parts of the SFM is prevented. In this thesis a setup is described in which the sample was transferred towards the PLD-position during deposition and moved back to the SFM-position to continue imaging. The procedure to continue imaging, almost immediately (<2sec), after the last deposition pulses is described and demonstrated. Since it is already shown by others that a snapshot of the surface can be captured within a second we have proven that it is feasible to study the nucleation and growth “quasi” real-time during processes as PLD, even though the SFM and PLD-position are separated by ~60mm. The reposition accuracy of the sample after transfer was within the range of the SFM scanner and therefore the same surface area can in principle be monitored during deposition. The procedure to quickly transfer the sample between two positions can also be used to combine SPM with other deposition and analyzing techniques.

To design the SFM such that it is able to image the surface morphology at oxide deposition conditions was another challenge. For oxides, such as SrTiO₃ and SrRuO₃ the deposition pressure generally ranges between 10⁻⁶-1mbar and the substrate temperature between 500-850°C.

To realize “quasi” real-time growth monitoring for oxides such as TiO₂, SrTiO₃ and SrRuO₃, atomic step resolution is required at these harsh deposition conditions. Atomic step resolution is defined as the vertical resolution to observe atomic terrace steps. For oxides these steps are typically 0.1-0.4nm. Imaging surfaces with atomic step resolution in this pressure regime was achieved after damping the mechanical noise sources and designing the setup such that electrical discharge is avoided.

To test our setup at elevated temperatures vicinal SrTiO₃ (001) substrate surfaces were used. This SrTiO₃ (001) surface was prepared such that it has a chemical stable TiO₂-terminated surface with smooth terraces and substrate steps (~0.4nm high). These unit cell high steps were used as a reference to check the vertical SFM resolution. The maximum SFM operating temperature in state of the art equipment is typically limited to 500°C in vacuum and 250°C in ambient

[‡] During deposition a relatively high oxygen pressure can be used and therefore it is relatively easy to incorporate oxygen. Oxides are interesting from an application point of view since their wide variety of properties could be used in existing or novel thin film devices.

conditions. In this thesis the performance of a modified SFM-head including a high temperature heating stage is demonstrated. To show the SFM performance at elevated temperatures on the used heating stage ($\sim 1.5\text{W}$ to reach 750°C) the TiO_2 -terminated SrTiO_3 (001) surface was imaged in dynamic mode up to 850°C in vacuum and up to 600°C in ambient conditions.

TiO_2 -terminated SrTiO_3 was in this thesis also used as a template for growth studies. To obtain a stable TiO_2 -terminated SrTiO_3 (001) surface a selective etching and post-annealing step is typically used. So far, the detailed processes during these two preparation steps are not well understood. In particular, the formation of one unit cell deep holes which are often observed remained unclear. These holes are unwanted for our in-situ growth studies since they reduce the effective terrace width l_T and therefore increase the probability for two-dimensional step flow growth. This growth mode is difficult to monitor while two-dimensional layer-by-layer growth is more straightforward.

In this thesis, the etching as well as the post-anneal process are described by two relative simple models. The model for the etching step explains the holes in the terraces after etching. The model for the post-annealing step describes that the holes are merging with the terrace step until the surface or step edge energy is minimized. With these models it is now possible to predict if there will be holes after the “standard” preparation treatment or that the treatment has to be modified. With the current SrTiO_3 substrate preparation method, one unit cell deep holes remain for $l_T \gg 500\text{nm}$. However, it is now likely that the surface treatment can be modified such that also low miscut substrates ($l_T \gg 500\text{nm}$) without holes can be obtained.

With the current resolution of the setup islands with a lateral size $>50\text{-}100\text{nm}^2$ and a height $>0.2\text{nm}$ can be imaged in dynamic mode up to 850°C in $10^{-6}\text{-}1\text{mbar}$. From a pre-study, it was expected that with the current resolution of the setup two and three-dimensional islands[§] could be imaged during deposition of indium oxide and indium tin oxide (ITO), Au and SrRuO_3 deposited on SrTiO_3 substrates.

However from the in-situ growth monitoring experiments it was observed that far below the maximum SFM operating temperature (850°C), the surface morphology of ITO, Au and SrRuO_3 could not be imaged for a long period. The measurement resolution and stability decreased above 100, 300, 400 and 500°C for respectively gold, undoped ITO, doped ITO and SrRuO_3 thin films.

It is believed that a material bridge was formed between the tip and sample surface while imaging these model systems at these deposition temperatures. In literature, this phenomenon is referred to as neck formation. This neck influences

§ The height of these islands was expected to be 1 nanometer or more with a lateral size of $50\text{-}100\text{nm}^2$ or more.

the silicon tip-sample interaction force F_{ts} such that the cantilever deflection does not represent the surface topography.

To study the tip-sample interaction and the formation and evolution of a neck spectroscopy curves were measured as well. This data and topography images were compared with STM data in which neck formation is discussed such as in the papers written by Kuipers et al. Our observations are comparable with STM data. It was for example observed in the used model systems that the imaging stability and image quality strongly depended on the surface and tip material as well as on the operating conditions and temperature.

Kuipers observed that by increasing the tip retraction speed neck formation is reduced. In this work it was observed that with a larger oscillation amplitude the measurement stability improved at elevated temperatures, near the temperature neck formation takes place. The influence of the SFM operating conditions, as well as the tip-sample materials on this so-called neck formation is described in this thesis.

In dynamic mode the tip is oscillating with a certain vertical speed. To suppress the spontaneous formation of a neck while imaging it is recommended to use dynamic mode SFM and increase the vertical tip oscillation speed. Furthermore it can be suppressed, by optimizing and selecting specific tip-sample combinations. So although a lot of work has been done there is still plenty of room to explore. Nevertheless it can be concluded that this thesis shows that imaging the surface morphology during processes as PLD can be achieved “quasi” real-time. The work described in this thesis can be used as a guideline to improve the setup and gives directions:

- to improve the SrTiO_3 substrate treatment for low miscuts;
- to combine deposition techniques with SPM;
- to combine other analyzing techniques with SPM;
- to extend the SFM operating conditions;
- to explain measurement instabilities at elevated temperatures;
- to manipulate and control neck formation.

Samenvatting

Het vastleggen en in kaart brengen van “nieuw” land, organismen en processen schiep de mogelijkheden om deze te manipuleren en te controleren. Microscopen hebben het mogelijk gemaakt om voorwerpen en processen af te beelden die de mens normaal gesproken niet kan waarnemen. Hieruit kan informatie gehaald worden over fysische en chemische processen zoals depositie en groei. Tegenwoordig is er een duidelijke behoefte om ook de oppervlaktemorfologie te monitoren tijdens zulke processen. Met een Kracht Microscope (KM) kan de oppervlaktestructuur worden vastgelegd in een drie-dimensionale topografische kaart. Dit kan voor zowel geleidende als niet-geleidende materialen tot op atomaire schaal.

Met fysische opdamptechnieken zoals gepulste laser depositie (PLD) kan een grote variëteit aan dunne lagen zoals metaaloxides worden aangebracht. Het vinden van de optimale condities voor materiaalsystemen is traditioneel een trial-and-error proces. Dit kan een langdurig en tijdrovend karwei zijn, met name als er geen informatie beschikbaar is over de oppervlaktemorfologie tijdens het depositieproces.

Diagnostische informatie tijdens het deponeren van materialen zoals metaaloxiden kan tegenwoordig verkregen worden met technieken zoals reflectieve hoge energie elektronendiffractie, oppervlakte röntgenstraling diffractie en lage energie elektronendiffractie. Dit zijn instrumenten gebaseerd op diffractie waarbij de periodische rangschikking van oppervlakte atomen wordt gemeten.

Het nadeel is dat ze de gemiddelde morfologische waarden meten en niet de lokale oppervlaktemorfologie afbeelden zoals wel mogelijk is met raster scanning probe microscopie (SPM). Met deze techniek is het mogelijk om uit de topografische kaarten de eilandafmetingen, vormen en dichtheden te halen. SPM is al erg geschikt om een oppervlak ex-situ in kaart te brengen met een hoge resolutie maar wordt nog bijna niet ingezet om de morfologie te volgen tijdens de depositie.

Het ex-situ afbeelden van een oppervlak belemmert studies om de depositie en groei goed in kaart te brengen. De belemmering ligt met name in het feit dat het moeilijk is om de oppervlaktemorfologie van dezelfde microscopische spot te volgen en dat het afkoelproces de resultaten sterk kan beïnvloeden.

Dit proefschrift beschrijft een opstelling om de depositie en groei te volgen met een krachtmicroscopie tijdens gepulste laser depositie. De opstelling is ontworpen om de groei van metaaloxiden te bestuderen. De keuze voor oxiden is

gebaseerd op het feit dat PLD met name voor deze materiaal systemen erg geschikt is. Oxides zijn interessant vanwege hun rijke spectrum aan eigenschappen die aangewend kunnen worden in tal van toepassingen.

De tijd tussen twee opeenvolgende depositiepulsen varieert typisch van 0.1-25 seconden. Als de oppervlaktemorfologie kan worden vastgelegd tussen twee opeenvolgende depositie pulsen dan zal de PLD synthese in essentie niet worden beïnvloed. In de beschreven opstelling zijn de KM en PLD-positie gescheiden. Door het ruimtelijk scheiden van de KM-positie en PLD-positie kan de standaard geometrie voor zowel KM als PLD worden gehandhaafd. Dit voorkomt ook materiaaldepositie op de tip, cantilever en andere onderdelen van de KM. De afstand tussen de twee posities is ~60mm. Tijdens depositie wordt het monster bewogen naar de PLD-positie. Na de depositie wordt het monster weer terug gezet naar de KM-positie om door te gaan met het afbeelden van de oppervlaktemorfologie. Op deze wijze is het mogelijk de depositie en groei te volgen tijdens PLD. Dit proefschrift beschrijft en demonstreert de procedure om direct te beginnen (<2 seconden) met het in kaart te brengen van de oppervlaktemorfologie na de laatste depositiepuls. Omdat andere groepen al hebben laten zien dat het mogelijk is om de drie-dimensionale oppervlakte meerdere keren af te beelden binnen een seconde is nu dus ook aangetoond dat het haalbaar is om de nucleatie en groei “quasi” real-time te volgen tijdens processen zoals PLD.

Na het herpositioneren van het monster onder de KM is de laterale positioneringsfout zodanig dat deze kan worden gecompenseerd met de KM scanner. Dit maakt het mogelijk om dezelfde spot te volgen.

De procedure om het monster snel tussen twee posities te verplaatsen is niet specifiek voor PLD maar kan evengoed gebruikt worden om SPM te combineren met andere analyse- en depositietechnieken.

Om de KM zo te ontwerpen dat de oppervlaktemorfologie gevolgd kan worden onder depositieomstandigheden was een andere grote uitdaging. Voor metaaloxiden zoals SrTiO_3 en SrRuO_3 ligt de depositie druk typisch zo tussen de 10^{-6} -1mbar en de substraat temperatuur zo tussen de 500-850°C. Om een opstelling te realiseren die de groei en depositie van oxides zoals TiO_2 , SrTiO_3 en SrRuO_3 “quasi” real-time kan volgen is atomaire stapresolutie vereist.

Atomaire stapresolutie is gedefinieerd als de verticale resolutie om atomaire terrasstappen vast te leggen. Voor bovengenoemde oxides zijn deze typisch 0.1-0.4nm hoog.

Het afbeelden van oppervlakken met atomaire stap resolutie in 10^{-6} -1mbar is bereikt na het onderdrukken van de nodige mechanische ruisbronnen en het vermijden van elektronische doorslag. Dit werk beschrijft de opstelling om dit te bereiken. Om de prestaties van de opstelling te testen bij hoge temperaturen zijn SrTiO_3 (001) substraten gebruikt. Deze substraten kunnen zo worden bewerkt dat ze een chemisch stabiel TiO_2 oppervlak krijgen waarop gladde terrassen en

stappen van zo'n 0.4nm hoog aanwezig zijn. De eenheidscel hoge stappen zijn gebruikt om de verticale KM resolutie te verifiëren.

De maximale KM bedrijfstemperatuur is gedefinieerd als de maximale temperatuur om de oppervlaktetopografie te meten. Met de nieuwste KM technologie is dit gelimiteerd tot zo'n 500°C als het oppervlak gemeten kan worden in vacuum en slechts zo'n 250°C als deze gemeten wordt in de buitenlucht. De gebruikte KM is zo aangepast dat de maximale bedrijfstemperatuur kan worden verhoogd. Dit proefschrift beschrijft de prestaties van de aangepaste KM en het kleine verhittingselement om het monster te verwarmen. Met deze configuratie is het behandelde SrTiO₃ oppervlak afgebeeld in vacuum tot 850°C en in de buitenlucht tot 600°C. Dit is gedaan in de zogenaamde dynamische mode. Om het monster te verwarmen met het verhittingselement tot zo'n 750°C in vacuum is ongeveer 1.5W nodig.

Behandeld SrTiO₃ is in dit proefschrift ook gebruikt als sjabloon voor groeistudies. De typisch gebruikte behandelmethode bestaat uit een selectieve etch en post-anneal stap. Tijdens de behandeling vormt er zich een gestapt TiO₂-getermineerd SrTiO₃ (001) oppervlak. Tot op heden zijn de details van deze twee processen niet volledig bekend en begrepen, met name de vorming van de eenheidscel diepe gaten die vaak worden waargenomen. Deze gaten zijn ongewenst voor in-situ groei studies met KM vanwege het feit dat ze de effectieve terrasbreedte l_T reduceren en daarmee de kans op twee-dimensionale step flow groei verhogen. Step flow groei is lastig te meten met KM in tegenstelling tot twee-dimensionale laag-voor-laag groei.

Dit proefschrift beschrijft zowel de ets en post-anneal processen met een relatief simpel model. Het model voor de etsstap verklaart de eenheidscel diepe gaten die vaak worden gezien na het etsen. Het model voor de post-anneal stap beschrijft het proces tijdens annealen. Aan de hand van deze modellen is het mogelijk om te voorspellen of er gaten zullen ontstaan na de standaard preparatie methode of dat de behandeling aangepast moet worden.

Met de huidige behandelmethode zullen eenheidscel diepe gaten aanwezig blijven voor $l_T > 500\text{nm}$. Echter, het is nu mogelijk om de behandeling zodanig te modifieren dat lage miscut substraten ($l_T > 500\text{nm}$) waarschijnlijk ook kunnen worden verkregen zonder gaten.

Met de huidige opstelling kunnen eilanden worden afgebeeld die laterale afmetingen hebben boven de 50-100nm² en een hoogte van >0.2nm. Deze kunnen worden afgebeeld tot 850°C in 10⁻⁶-1mbar.

Uit een voorstudie is gebleken dat met de huidige resolutie die de opstelling haalt de twee- en drie-dimensionale eilandgroei gevolgd kan worden tijdens de depositie van indiumoxide en indiumtinoxide (ITO), Au en SrRuO₃ gedeponeerd op behandeld SrTiO₃.

Echter, tijdens de in-situ experimenten bleek dat voor ITO, Au en SrRuO₃ de evolutie van de oppervlaktetopografie niet voor een lange periode kan worden

gevolgd op typische depositietemperaturen. De gemeten resolutie en stabiliteit namen ver beneden de maximale KM bedrijfstemperatuur (850°C) af. Dit was op ongeveer 100, 300, 400 en 500°C voor respectievelijk goud, indiumoxide, ITO en SrRuO₃ dunne lagen. Een verschijnsel, in de literatuur bekend onder de naam nekformatie leidt er toe dat de gekozen materiaal systemen niet kunnen worden afgebeeld bij hogere temperaturen. Tijdens nekformatie vormt er zich een materiaalbrug tussen de tip en het oppervlak. Deze brug beïnvloedt de tip-monster interactie zodanig dat de cantilever deflectie de oppervlaktemorfologie niet meer weerspiegelt. Om de tip-monster interactie en de formatie en evolutie van een nek te bestuderen zijn naast topografische ook spectroscopische metingen uitgevoerd. Deze informatie alsmede de topografische afbeeldingen zijn vergeleken met STM data waarin nekformatie wordt besproken zoals in de artikelen van Kuipers et al. Het is door ons vastgesteld dat de meetstabiliteit en afbeeldingskwaliteit sterk afhangt van het oppervlak en tipmateriaal alsmede de temperatuur en gebruikte KM-bedrijfswaarden. Onze bevindingen zijn vergelijkbaar met de data beschreven door Kuipers.

Kuipers stelde vast dat de waarschijnlijkheid dat een nek zich zou vormen afnam als de tip terugtreknelheid toenam. In dit werk is vastgesteld dat met een grotere oscillatieamplitude de gemeten stabiliteit verbeterde, vlakbij de temperatuur waarbij nekformatie plaats vindt. De invloed van de KM-bedrijfswaarden alsmede de tip-monster materialen op de vorming van deze zogenaamde nekvorming zijn beschreven in dit proefschrift. In de dynamisch mode oscilleert de tip met een bepaalde verticale snelheid. Om de spontane nekformatie te onderdrukken tijdens het meten is het aanbevolen om de KM in de dynamische mode te gebruiken en de verticale tipsnelheid te maximaliseren. Dit strookt ook met de resultaten van Kuipers omdat ook het oscilleren van de tip kan worden beschouwt als het naderen en weer verwijderden van de tip. Daarnaast kan de formatie van een materiaalbrug worden onderdrukt door het kiezen van de juiste tip-monster combinatie.

De belangrijkste conclusie van dit proefschrift is dat het “quasi” real-time afbeelden van de oppervlaktemorfologie tijdens processen zoals PLD mogelijk is. Echter, ondanks de gemaakte stappen is er nog genoeg ruimte voor verbeteringen. Dit proefschrift kan een leidraad zijn om de gebouwde opstelling te verbeteren en het geeft mogelijkheden en richtingen om:

- de SrTiO₃ substraat behandeling voor lage miscut substraten te verbeteren;
- SPM te combineren met depositietechnieken;
- SPM te combineren met andere analysetechnieken;
- het temperatuur- en drukbereik van SPM te vergroten;
- de meetinstabiliteiten bij hoge temperaturen te verklaren;
- nekformatie te manipuleren en te controleren.

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Dit is het einde van het boekje, dat van de meeste aio's en oio's vele vrije uren heeft gekost en slechts door een handvol mensen gelezen zal worden. De pagina's die ik nu beschrijf wil ik graag gebruiken om terug te blikken op de afgelopen jaren. Mijn passie voor onderzoek is aangewakkerd tijdens mijn stage in het zonnige Stanford (Californië) waar ik het voorrecht had om te werken met onder andere Ted Geballe. De drive die ik daar opdeed hebben me mede geholpen om deze promotie met succes af te ronden. Deze stage zou niet mogelijk geweest zijn zonder Dave, dus bedankt hiervoor! Eenmaal terug in het mooie Twente heb ik gewerkt aan mijn afstudeerproject dat ik afrondde op 10 april 2003. Merkwaardig genoeg zal ik mijn promotie verdedigen op 10 april 2008. De afgelopen jaren heb ik kunnen werken in de twee leukste vakgroepen, LT en IMS, van de faculteit Technische Natuurkunde. Aangezien ik iemand ben die meestal kiest voor en het ene en het andere, was ik dan ook zowel bij de gezellige LT en IMS uitjes te vinden.

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Let's surf the waves that pass!