

Master's thesis

# Self-assembled $SrRuO_3$ nanowires through selective growth on $DyScO_3$ surface terminations



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# Abstract

Self assembled  $SrRuO_3$  nanowires<sup>1</sup> were grown selectively on one  $DyScO_3(110)$  surface termination by Pulsed Laser Deposition. This selective growth resulted in crystalline nanowires, typically 6 nm high, 80 nm wide and separated by a valley of 100 nm. The physical mechanism which drives the formation of these nanowires on mixed terminated substrates was studies using a Solid-on-Solid model.  $SrRuO_3$  was assumed to have a high diffusivity on DyO terminated areas compared to  $ScO_2$  and  $SrRuO_3$  covered areas. This resulted in nanowire formation on ordered  $ScO_2$  terminated areas. Modelled growth on single DyO or  $ScO_2$  terminated substrates provided an explanation for island and smooth growth respectively. Overall the model is in good qualitative agreement with the deposited films, thus providing a mechanism for nanowire growth. A better understanding of the mechanism leads to more control over the properties and dimensions of these nanowires.

Nanowire physical properties were studied using Microwave Impedance Microscopy and 2point electrical measurements. These indicate a clear contrast between the insulating  $DyScO_3(110)$  substrates and conducting  $SrRuO_3$  wires.

<sup>&</sup>lt;sup>1</sup>Cover image: Scanning Tunnelling Microscopy image of SrRuO<sub>3</sub> nanowires on a DyScO<sub>3</sub>(110) substrate grown using Pulsed Laser Deposition. Lateral dimension  $1 \times 1 \ \mu m$ , wire height approximately 5 nm. More image details are depicted in figure 3.6

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# Abbreviations & symbols

$DyScO_3$	Dysprosium Scandate
$SrRuO_3$	Strontium Ruthenate
$SrTiO_3$	Strontium Titanate
a.u.	Arbitrary units
CM-AFM	Contact Mode AFM
IV curve	Current Voltage curve
MBE	Molecular Beam Epitaxy
MIM	Microwave Impedance Microscopy
NC-AFM	Non-Contact mode AFM
PLD	Pulsed Laser Deposition
RHEED	Reflection High-Energy Electron Diffraction
SEM	Scanning Electron Microscope
SOS	Solid-on-Solid
SPM	Scanning Probe Microscopy
STM	Scanning Tunnelling Microscopy
TM-AFM	Tapping Mode AFM
u.c.	Unit cell
UHV	Ultra High Vacuum
UPS	Ultraviolet Photoelectron Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
$\alpha$	Characteristic jump distance [nm]
$\gamma_f$	Films surface free energy [J]
$\gamma_s$	Substrates surface free energy [J]
au	Adatom residence time before desorption [sec]
v	Hopping attempt frequency [Hz]
a, b, c	Lattice constants [nm]
$a_p$	Psuedo-cubic lattice constant [nm]
$E_A$	Activation energy for diffusion [eV]
$E_B$	Step-up energy barrier per unit cell [eV/cell]
$E_D$	Diffusion barrier [eV]
$E_N$	Nearest neighbour bond energy [eV]
$E_S$	Substrate bond energy [eV]
$E_{add}$	Additional step-up energy barrier [eV]
h	SOS height [cell]
$h_n$	SOS neighbour height [cell]
k	Hopping probability
$k_0$	Attempt frequency for hopping [Hz]
$k_B$	Boltzmann's constant $[eV K^{-1}]$
$k_x$	Hopping probability in direction x

L	Total SOS hopping probability
$l_D$	Diffusion length [nm]
$l_t$	Terrace width [nm]
r	Random number between 0 and 1 $$
S	Normalized step density
Т	Temperature $[^{\circ}C]$ or $[K]$

# Introduction

Complex oxide a materials like DyScO<sub>3</sub> and SrRuO<sub>3</sub> are an interesting class of materials which comprise a large range of physical properties such as superconductivity  $(YBa_2Cu_3O_{7-x}[1])$ , itinerant ferromagnetism (SrRuO<sub>3</sub>[2]) and ferroelectricity  $(PbZr_xTi_{1-x}O_3[3])$ . Patterned microstructures of these complex oxides, for example derived from sol-gels[4], create additional applications. Other techniques, for example Pulsed Laser Deposition[5] (PLD) allow for coherent growth of thin films consisting of these materials. During PLD growth the film thickness and stoichiometry can be controlled artificially. Creating patterned PLD grown films results in coherently grown functional complex oxides which can be used in devices. For example conducting nanowires or ordered arrays of nanodots can be created[6]. The physical properties and nano structural control of these materials are being studied in great detail and are very promising for future electronic applications. Moreover nanowires provide a method for studying the fundamental properties of materials at a small scale, for example by quantum confinement in one dimensional platinum chains[7].

In this report nanowire fabrication by self assembly is studied. Perovskite material SrRuO<sub>3</sub> is grown on a DyScO<sub>3</sub> substrate using PLD. A perovskite like DyScO<sub>3</sub> can have two types of surface terminations: DyO and ScO<sub>2</sub>. SrRuO<sub>3</sub> grows selectively on one of these terminations. This selective growth behaviour results in SrRuO<sub>3</sub> nanowire formation when the substrate shows ordered areas of both surface terminations. The goal of this research is to investigate the physical phenomena which drive the self-assembly of SrRuO<sub>3</sub> on DyScO<sub>3</sub> chemical terminations during PLD growth. A Solid-on-Solid (SOS)[8] model is used to simulate the growth on an atomic scale in order to better understand nanowire formation. The model is modified to allow for areas to have different hopping barriers and it incorporates a basic form of hetroepitaxy.

In chapter 1 the theoretical background required to study growth behaviour of perovskites during PLD growth is discussed. An overview of the equipment and conditions used to fabricate the films and the tools used analyse them is given in chapter 2. In this section the model is described as well. The experimental results are given in chapter 3. In chapter 4 the model and experimental data are compared and discussed. Chapter 5 contains the conclusions and a few recommendations. Appendix A includes part of the SOS C++ code used for simulating wire growth, appendix B contains some additional data and a few types of interesting growth behaviour, which could be studied in more detail in the future.

# Chapter 1

# Perovskite crystal growth

In this chapter the theoretical background required to study nanowire growth during Pulsed Laser Deposition (PLD) is explained. Since both SrRuO<sub>3</sub> and DyScO<sub>3</sub> are perovskite crystals, first perovskite crystal and the kinetic model which describes their behaviour during growth are discussed. Secondly PLD-RHEED growth is explained, the RHEED measurements are compared with theoretical growth modes. Finally the theory behind Solid-on-Solid Monte Carlo simulations is discussed.

#### **1.1** Perovskite crystals

Both DyScO<sub>3</sub> and SrRuO<sub>3</sub> are complex oxide materials which are part of the perovskite ABO<sub>3</sub> crystal class. A cubic perovskite is drawn schematically in figure 1.1a, it contains oxygen anions and two types of cations of different size, A and B. The cations can have a charge ranging from +1 to +5, for example  $A^{2+}B^{4+}O_3^{6-}$ . The B-site cation is surrounded by an oxygen octahedron, drawn in figure 1.1a as well. ABO<sub>3</sub> perovskite materials consist of alternating layers of AO and BO<sub>2</sub>, drawn schematically in figure 1.1b. If the A-site cation has a charge of 2+ and the B-site cations are 4+, these layers are charge neutral. In the case of  $(A^{3+}O)^+$ ,  $(B^{3+}O_2)^-$  the layers are polar. DyScO<sub>3</sub> is a 3+/3+ perovskite.



Figure: 1.1: Cubic ABO<sub>3</sub> perovskite (a) and alternating layers AO, BO<sub>2</sub>, AO (b) are drawn schematically

DyScO<sub>3</sub> is not cubic, it has a distorted orthorhombic structure with Sc-O-Sc angles between 139-144°[9]. The orthorhombic structure contains four formula units per full cell. An orthorhombic DyScO<sub>3</sub> structure is drawn schematically in figure 1.2. The Pnma lattice constants of DyScO<sub>3</sub> are  $a = 0.5720 \ nm$ ,  $b = 0.5442 \ nm$  and  $c = 0.7890 \ nm$  which correspond to a psuedo-cubic lattice constant of  $a_p = \frac{1}{2}\sqrt{a^2 + b^2} \approx \frac{c}{2} = 0.3945 \ nm$ . This pseudo-cubic cell is drawn in figure 1.2 as well. DyScO<sub>3</sub> (110) direction has a square lattice with lattice constant  $a_p$ . One must keep in mind that the DyScO<sub>3</sub> (110) pseudo-cubic cell is only square in the (110) direction not in other directions. All Figures and text in this report refer to the pseudo-cubic crystal where the pseudo-cubic c-axis lies parallel to the growth direction (110) unless specifically defined otherwise.



Figure: 1.2: Orthorhombic DyScO<sub>3</sub> crystal structure (Pnma) showing two psuedo-cubic subcells inside the orthorhombic unit cell. [9]

SrRuO<sub>3</sub> also is an orthorhombic perovskite with psuedo-cubic lattice constant  $a_p = 0.393 nm$ . The lattice mismatch between DyScO<sub>3</sub> and SrRuO<sub>3</sub> is small [9], which allows for coherent growth. Another close match to SrRuO<sub>3</sub> is SrTiO<sub>3</sub> (cubic a = 0.3905 nm) which is commonly used as a substrate material. The SrRuO<sub>3</sub> strain with respect to DyScO<sub>3</sub> is tensile while the strain is compressive with respect to SrTiO<sub>3</sub>. The topmost layer of a perovskite crystal can be either one of the alternating layers. This surface termination is known to vary locally on the substrates surface. In the case of SrTiO<sub>3</sub>, SrO can be chemically etched[10] using a buffered HF solution to acquire only TiO<sub>2</sub> termination. During the final stages of this master project a method to create single terminated DyScO<sub>3</sub> surfaces was developed using a NaOH treatment [11].

### 1.2 Crystal growth theory

Crystals can be created artificially, using for example PLD. During PLD growth material is evaporated onto a substrate. What happens at the substrate depends on many factors, like the type of substrate and the type of material being evaporated, but also the temperature and the rate at which the material is evaporated. Two ways of describing crystal growth are possible. In equilibrium the surface morphology can be described by thermodynamics[12]. However to describe nanowire formation during growth, not in equilibrium, a more detailed method for analysing surfaces is required. Kinetic theory provides this description of the physical mechanism which governs nanowire formation.

#### 1.2.1 Atomistic view on crystal growth

Kinetic theory studies the motion of single atoms or individual perovskite unit cells on a crystal surface. A crystal surface is vicinal, in other words it is tilted with respect to the desired crystal direction by a certain miscut angle. This tilt results in steps of unit cell (u.c.) height separated

by flat terraces. Such a terrace and all possible movements for a single cell are depicted in figure 1.3. Cells or atoms arrive at the surface and can adsorb (stick) to the surface (a,f). Once at the surface they can diffuse (b), nucleate (c), form islands (d), detach from islands (e), step up/down islands or steps (g) or detach from the surface (j).



Figure: 1.3: Schematic representation of the atomic process during growth: (a) deposition of an adatom on a terrace; (b) diffusion of an adatom 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 island; (g) step-down diffusion of an adatom; (h) diffusion along a stepedge; (i) attachment of an adatom at a step; (j) desorption from a terrace. [13]

In the kinetic model surface morphology evolution is determined by a surface diffusion coefficient  $D_S$  which relates the diffusion distance  $l_D$  to  $\tau$ , the adatom residence time before desorption or incorporation at a step edge. This relation is given by equation 1.1.

$$l_D = \sqrt{D_S \tau} \tag{1.1}$$

The expression for the surface diffusion coefficient is given by equation 1.2. Where v is the hopping attempt frequency,  $\alpha$  the characteristic jump distance,  $k_B$  Boltzmann's constant and T the temperature.  $E_A$  represents the activation energy for diffusion.

$$D_S = \upsilon \alpha^2 e^{\left(\frac{-E_A}{k_B T}\right)} \tag{1.2}$$

#### 1.2.2 Growth modes

From a thermodynamic point of view two types of growth can be distinguished depending on the relationship between the substrate surface free energy  $\gamma_s$  and the film surface free energy  $\gamma_f$ . If  $\gamma_s > \gamma_f$  three dimensional growth occurs also known as Volmer-Weber growth mode, depicted schematically in figure 1.4a. If  $\gamma_s < \gamma_f$  the substrate is easily wetted by the film resulting in 2D layer-by-layer growth also known as Frank- van der Merwe growth mode(b). A combined growth 2D/3D growth mode also exists when growing on misfit substrates called Stranski-Krastanov(c). Two dimensional growth can be divided into two group by the kinetic model. If the diffusion distance  $l_D$  is small compared to the step width  $l_t$  atoms will coalesce 1.3(c),(d) to form islands on the terrace, growing in a layer-by-layer fashion (a). If  $l_D$  is large compared to  $l_t$  adatoms will nucleate on the step edges instead of forming islands (d). This growth mode is referred to as step-flow-growth.



Figure: 1.4: Surface morphology evolution scenarios during growth: (a) threedimensional island growth, Volmer-Weber; (b) two-dimensional layer-bylayer growth, Frank-van der Merwe; (c) Stranski-Krastanov growth (d) two-dimensional step flow growth. [13]

### 1.3 Crystal growth by Pulsed Laser Deposition

Pulsed Laser Deposition (PLD) is one of the physical vapour deposition techniques used to grow perovskite thin films. Material is ablated from a target and transferred to a substrate. Both the target and substrate material are placed in a vacuum chamber. The background pressure and gas mixture in the chamber can be controlled and monitored. Material is ablated from the target by a high intensity laser. The laser pulse generates a dense plasma of target material which expands away from the target towards the substrate. At the substrate part of the arriving material will adsorb onto the substrate. The substrate can be heated to allow for better sticking of the arriving species. The amount of material ablated from the target depends on the laser energy and the spot size. The background pressure, target-substrate distance and the substrate temperature determine the amount of material deposited on the substrate by each pulse.

A schematic drawing of a PLD system is depicted in figure 1.5. A target holder capable of holding multiple targets allows for sequential deposition of different materials. During growth the substrates surfaces is monitored using an electron beam, RHEED[5]. The RHEED tube and corresponding CCD-camera are drawn as well.

#### 1.3.1 Reflection High-Energy Electron Diffraction

Reflective High Energy Electron Diffraction (RHEED) can be used during PLD growth. The RHEED signal can be recorded over time during deposition, because RHEED is used with a low angle of incidence. Due to this low angle of incidence RHEED is very surface sensitive and allows for in-situ monitoring of the surface during growth. The diffraction pattern as a result of interference of electrons with the crystal lattice is indicative of the crystal surface. An example 2D RHEED pattern is depicted in figure 1.6a. The specular spot is indicated by a square box.



Figure: 1.5: Schematic impression of a Pulsed Laser Deposition set-up. A laser beam ablates material from a target onto a substrate. During growth the substrates surface is monitored using RHEED[13].

This patterns shows the direct beam on the left side and several 2D spots. Figure 1.6b shows an example 3D RHEED pattern showing many spots.



Figure: 1.6: Example 2D(a) and 3D(b) RHEED patterns. The square box indicates the specular spot.

The growth modes depicted in figure 1.4 can be distinguished by the RHEED signal. In case the samples surface contains small islands the electron beam will penetrate the islands and fulfilment of the Bragg condition leads to additional spots, called 3D spots. These spots indicated Volmer-Weber like growth during PLD.

In case of layer-by-layer growth, the surface roughness changes while the RHEED pattern remains 2D. After half a layer of material is deposited, the film is relatively rough. Completion of a monolayer will results in a smooth film and a maximum specular spot intensity. So the growth of a single monolayer is indicated by one oscillation. The RHEED signal can be used to tune film thickness during growth. Directly after each laser pulse adatoms are distributed randomly over the surface and the specular spot intensity drops down due to the large amount of unit cell high steps caused by the newly arrived atoms. The signal recovers quickly while atoms diffuse and form islands. In case of step-flow growth no islands are formed and the surface roughness does not change, resulting in a steady state RHEED signal. This intensity drop and recovery after each laser pulse is much more pronounced in step-flow growth. The RHEED recovery time is indicative of the adatom residence time  $\tau$  used in equation 1.1. Surface roughness can also be described in terms of step density. A rough surface has many steps compared to a smooth surface. A high step density corresponds to a rough surface and a low specular spot intensity.

#### 1.3.2 Termination conversion

During deposition the target material is converted into a plasma of individual atoms while only complete perovskite cells are expected to adsorb to the substrate surface. In case of  $SrRuO_3$ one of the species,  $RuO_x$ , is very volatile. It is easy to imagine if this volatile species is present at the topmost layer, it could evaporate. Rijnders et al. [14] have shown this indeed happens during growth of the first few layers of  $SrRuO_3$  on  $TiO_2$  terminated  $SrTiO_3(001)$ . During growth the surface termination switches from B-site  $TiO_2$  to A-site SrO. The time required to switch is twice the time required to create a single layer. When two complete cells or four half unit cells are expected to grow only three half-unit cells grow. This was registered using RHEED, the period of the first oscillation was twice the normal period. This behaviour is expected to be related to  $SrRuO_3$  and therefore is also expected for growth of  $SrRuO_3$  on  $ScO_2$  terminated  $DyScO_3$ . Therefore it could provide information about which termination nanowires prefer to grow on.

### 1.4 Crystal growth simulations

The kinetic model described in section 1.2.1 considers individual movement of unit cells on a crystal surface. These movements depicted in figure 1.3 can be simulated. A method for simulating growth during vapour deposition techniques is described in section 1.4.1. This model was used to simulate nanowire growth in this report. Only features which will be applied to these specific simulations will be discussed.

#### 1.4.1 Solid-on-Solid model

To simulate nanowire growth a Monte Carlo algorithm is applied to the kinetic theory described in section 1.2.1. Monte Carlo methods rely on repeated random sampling to study the behaviour of systems with many coupled degrees of freedom. This combination of Monte Carlo and kinetic theory is referred to as a Solid-On-Solid[15] (SOS) model. Perovskite unit cells are treated as single entities on a matrix grid of possible positions. Physically similar to the crystal positions on a crystal surface. The cells are allowed to diffuse according to kinetic theory. Only one cell moves at a time, selected by a random pick. The chance a cell is selected to move is proportional to the diffusion coefficient given by equation 1.2. After a cell has moved the next cell is selected to move. This selection process is repeated for as long as desired.

SOS assumes a  $n \times m$  grid of possible sites, each site is able to contain single unit cells stacked upon each other. Cells are only allowed to hop to neighbouring sites. In this report a SOS neighbour is defined by a simple square lattice. The hopping probabilities k is given by an Arrhenius type equation, like equation 1.2, more specifically given in equation 1.3 where  $k_0$  is the attempt frequency for hopping.

$$k = k_0 e^{\left(-\frac{E_D}{k_B T}\right)} \tag{1.3}$$

The diffusion energy  $E_D$  consists of several individual energy barriers.  $E_S$  is the of the energy barrier due to bonding with the substrate and  $E_N$  is the nearest-neighbour bond energy. The nearest neighbour bond energy is multiplied by the number of nearest-neighbour bonds n before being added to diffusion energy, as given by equation 1.4. The number of nearest-neighbours is calculated by comparing the height of one grid site with its four neighbours. In this SOS model ideal sticking of arriving atoms is assumed and no re-evaporation is allowed. Once a unit cell has arrived at the substrate it must diffuse 1.3(b) until it nucleates 1.3(c) or becomes incorporated below a new layer of arriving cells 1.3(f). Atomic processes desorption 1.3(f) and cluster diffusion or deposition 1.3(b), 1.3(g) are not considered for nanowire growth simulations.

$$E_D = E_S + n \cdot E_N \tag{1.4}$$

RHEED intensity oscillations can also be simulated using a SOS model. The step density can be calculated from the models matrix grid, using equation 1.5. A large step density corresponds to a rough surface and would be indicated by a low RHEED signal. The RHEED intensity evolution is proportional to 1 minus the normalized step density.

$$S = \frac{1}{n \times m} \sum_{i,j} |h_{i,j} - h_{i,j+1}| \cos \phi + |h_{i,j} - h_{i+1,j}| \sin \phi$$
(1.5)

To simulate RHEED monitored growth using a SOS model each laser pulse is simulated by a random deposition of a certain number of unit cells. After this pulse all hopping probabilities of each grid position in all four hopping directions are calculated and stored. The cells are allowed to diffuse for a certain amount of time or for a fixed number of simulation steps using the Monte Carlo method described in section 1.4.2. During diffusion surface morphology and step density evolutions are recorded. After diffusion a new random deposition of cells takes place. This process continues until the desired amount of cells are deposited.

#### 1.4.2 Monte Carlo

Unit cell or adatom diffusion is simulated by simply selecting one diffusion process or event. The chance an event is selected depends on its hopping rate. Events with a higher hopping rate have a higher hopping probability. An event is selected by calculating the total hopping probability Lby summing up all individual hopping rates for every grid site (i, j) and every hopping direction (x),  $L = \sum_{i,j} \sum_{x} k_x$ . A random number 0 < r < L is selected and the event corresponding to this random number is selected. This event selection process is drawn schematically in figure 1.7. An example grid is drawn as well, showing the periodic boundary conditions. Event selection is repeated millions of times during a simulation. The implementation of event selection is of great importance for minimizing simulation time. A binary chop algorithm is used[16] to select events. Binary chop divides all possible events drawn in figure 1.7 into two groups and calculates the total hopping rate of the first group  $L_1$ . It checks if the selected random number within the first group:  $r < L_1$ . If it is in the first group the process is repeated within the first group, if not it is repeated within the second group. Finally it will find a group consisting of only one event and the event is selected. To decrease simulation time, this binary chop from all possible events is divided into two parts, known as fast Monte Carlo [16]. All events are divided into groups. For instance the left quarter of the matrix grid is chosen as one group of events. First a group is selected by binary chop and secondly an event inside the group is selected. A more detailed description of this fast Monte Carlo method is given by Maksym [16].



Figure: 1.7: Example 5x5 grid indicating hopping directions up, down, left, right from gridsite(2,0). Periodic boundary conditions are used, depicted for hopping to the left. For each possible direction a rate  $k_x$  is calculated. All rates summed up and by picking a random number  $0 < r < \sum k_x$  an event is selected by means of a binary chop algorithm.

# Chapter 2

# Fabrication, characterization & simulation

This chapter contains an overview of the experimental conditions and equipment used to fabricate nanowires and study their properties. The final section of this chapter contains a detailed description of the modified SOS model used to simulate SrRuO<sub>3</sub> growth on DyScO<sub>3</sub>.

### **2.1** $DyScO_3$ substrate treatment

The DyScO<sub>3</sub> substrates used for this research were manufactured by CrysTec GmbH using a Czochralski process. This method results high crystallinity and low mosaicity compared to, for example commonly used  $SrTiO_3$  substrates.



Figure: 2.1: TM-AFM  $10 \times 10 \ \mu m$  images of a DyScO<sub>3</sub> substrate before and after annealing for 4 hours at 1000 °C on a low miscut substrate. Images (a) shows a low miscut sample before annealing. After annealing the steps order in straight lines (b), however unit cell high islands are still present at the surface.

The received substrates have been cleaned with acetone and ethyl-ethanol before being annealed at 1000 °C under oxygen flow for various periods of time, ranging from 30 minutes to 85 hours. Example as-received and annealed  $DyScO_3$  substrate TM-AFM images are depicted in figure 2.1. The as-received (a) image shows the substrates surface before annealing, the step edges are very rough. Image (b) shows a TM-AFM image of the same sample after annealing for 4 hours at 1000 °C. Due to the low miscut of this sample, resulting in a step width of 1000 nm, the annealed substrate still shows unit cell high islands on the terraces.<sup>1</sup>. Figure 2.2 shows typical AFM images of an atomically smooth  $DyScO_3$  surface without these islands or holes indicating unit cell high steps and a stepwidth of approximately 300 nm.



Figure: 2.2: TM-AFM  $2 \times 2 \ \mu m$  image with a sharp tip recorded at a scan speed of 1 Hz and a line profile averaged over 5 lines. RMS roughness is below 0.05 nm indicating an atomically smooth surface

Four hours annealed DyScO<sub>3</sub> substrates with a miscut angle above  $0.07^{\circ}$  show atomically smooth surfaces with unit cell high steps and straight step edges. Typical peak to peak surface roughness is below 0.2 nm. For SrTiO<sub>3</sub> it is assumed[17, 13] that sodium contamination at the surface is likely to cause this roughness. Since DyScO<sub>3</sub> has polar layers it seems even more likely to attract these contaminations. An example TM-AFM image recorded with a sharp tip is depicted in figure 2.2.

### 2.2 Pulsed Laser Deposition growth parameters

All films are grown using Pulsed Laser Deposition (PLD), described in section 1.3. A KrF excimer laser with a wavelength of 248 nm was used. Maximum pulse energy of the laser is 1000 mJ and minimal pulse duration 25 ns. The parameters used for growing SrRuO<sub>3</sub> on DyScO<sub>3</sub> are presented in table 2.1. Sc<sub>2</sub>O<sub>3</sub> and Dy<sub>2</sub>O<sub>3</sub> growth parameters are shown as well. Deposition from these targets on DyScO<sub>3</sub> substrates was done in order to manually create ScO<sub>2</sub> and DyO surface terminations.

	SrRuO <sub>3</sub>	$Sc_2O_3$	$Dy_2O_3$	
Temperature (setpoint)	750	950	950	[°C]
Fluency	2.1	2.1	2.1	$[J/cm^2]$
Mask size	60	20	60	$[\mathrm{mm}^2]$
Laser repetition rate	1	1	1	[Hz]
Target substrate distance	50	50	50	[mm]
Pressure	0.3	0.01	0.01	[mbar]
Gas mixture $O_2/Ar$	50	100	100	$O_2[\%]$

Table 2.1: Pulsed Laser Deposition growth parameters

<sup>&</sup>lt;sup>1</sup>These unit cell deep holes or islands and their evolution during annealing is described in more detail for  $SrTiO_3$  substrates[13].

#### 2.3 Characterization equipment

Most films have been grown in the COMAT system. This system connects 4 UHV chambers with a central distribution chamber. It allows for samples to be transferred under UHV conditions from a PLD-RHEED system to a sputter chamber, a SPM chamber and a XPS/UPS chamber.

#### 2.3.1 Atomic Force Microscopy

In order to investigate the surface morphology of both substrates and films, several types of scanning probe techniques were used. For analysing substrates and films outside vacuum conditions, either the Veeco MultiMode SPM or the Veeco Dimension Icon AFM was used in air and at room temperature. Both can be operated in either Contact-Mode (CM) or Tapping-Mode (TM). For this work CM tips with a thickness of  $2 \pm 1 \ \mu m$ , a length of  $450 \pm 10 \ \mu m$  and a width of  $50 \pm 7.5 \ \mu m$  and TM tips with a thickness of  $4 \pm 1 \ \mu m$ , a length of  $125 \pm 10 \ \mu m$  and a width of  $30 \pm 7.5 \ \mu m$  were used. The force constants are  $0.02 - 0.72 \ N/m$  and  $10 - 130 \ N/m$  respectively and the TM-tips had a frequency of  $204 - 489 \ kHz$ . A third SPM system, Omicron MultiMode SPM, is connected via a UHV connection to the PLD chamber and is able to do CM, Non-Contact mode (NC) and STM in vacuum conditions.

Since  $DyScO_3$  substrates are insulating, AFM is the main tool to investigate surface morphology. Both CM and TM AFM have been used to study the substrates after annealing. The main difference between these modes of operation is the force regime in which the tip-sample interaction takes place.

For CM-AFM the tip is in contact with the surface and de tip deflection in the z direction is fed trough a feedback loop which effectively keeps tip height constant. The repulsive forces involved are in the nano Newton range. The tip can also show deflection in the xy-plane, the tip twists as a result of scanning it across the surface. Measuring this type of deflection is called lateral force microscopy or friction force microscopy. In case of scanning perovskite materials, both terminations can have a different tip-sample interaction strength which will give rise to lateral force contrast. Figure 3.2 shows an example CM-AFM image with a friction map.

For NC-AFM and TM-AFM an oscillating cantilever is brought into close contact with the substrate. A feedback loop is applied to either the amplitude of the oscillation or the frequency. Typical forces involved in NC-AFM are in the pico Newton range, for TM-AFM the forces involved are higher and approach the repulsive regime of CM-AFM. Both TM-AFM and NC-AFM allow for phase imaging. Phase imaging registers the phase shift in the measured signal compared to the drive signal. A phase shift can be induced by areas of different adhesion or different friction, thus providing information similar to lateral force microscopy.

#### 2.3.2 Microwave Impedance Microscopy

Microwave Impedance Microscopy[18] (MIM) is a technique based on AFM. A modulated microwave (1GHz) signal is applied to a specially fabricated AFM tip. This method provides an absolute measurement of the local dielectric properties. Both the real (MIM-R) and imaginary (MIM-C) components of the tip impedance are recorded. It can be operated CM-AFM and TM-AFM.

#### 2.3.3 X-Ray Photoelectron Spectroscopy & X-Ray Diffraction

X-Ray Photoelectron Spectroscopy (XPS) spectra for several samples were recorded using an Omicron EA125 Analyser and an Cu  $K\alpha_1$  x-ray source part of the COMAT system. X-Ray Diffraction (XRD) was used to measure substrate miscut prior to annealing and to check crystal quality. XRD was performed ex-situ on a Bruker D8 XRD.

#### 2.3.4 Nanomanipulator electrical measurements

In order to measure the transport properties of the nanowires, a Zyvex S100 nanomanipulator was combined with a Keithley 4200-SCS Semiconductor Characterization System. These measurements were performed during SEM imaging using a Jeol JSM-6490 SEM. This system allows for positioning probes onto features down to 100 nm in size.

#### 2.4 Nanowire growth simulations

A SOS model, described in section 1.4.1 was written in C++ programming language, using Microsoft Visual C++ 9.0 and compiled for windows 32bit platforms. C++ allows for easy implementation of well known classes and routines. Most of the classes used are part of the ROOT tool kit<sup>2</sup>.

#### 2.4.1 Simulation parameters

Using a SOS model many PLD growth modes and corresponding RHEED signals can be simulated. For example the RHEED intensity drop and recovery after each laser pulse is clearly visible in all simulations. Island growth and step-flow growth can be simulated by choosing the appropriate parameters. A transition from island shaped layer-by-layer growth to step-flow growth can be induced by either increasing the temperature or decreasing the stepwidth. The latter is used to verify the models behaviour, described in more detail in section 2.4.1. An overview of SOS parameters is shown in table 2.2.

SOS is just a model and results must be interpreted keeping in mind some effects might be caused by the model itself and are not related to any physical phenomena. For example, the grid size parallel to the step edges is reduced to decrease simulation times. Periodic boundary conditions are used to model adatoms traversing the grid boundary. On a vicinal substrate both sides of the grid perpendicular to the step direction have a different substrate height. A correction must be applied to compensate the height difference between both sides of the grid. In the direction parallel to the step edges the grid size is reduced, sometimes it is reduced below the diffusion length, thus limiting the diffusion length. Since the model is created for nanowire growth simulations, the exact behaviour in the direction parallel to the step edges, also parallel to the wires is not of interest. As a result of limiting the diffusion length on top of the wires by reducing the grid size, step density oscillations might be visible when growing step-flow like on top of nanowires.

Another intrinsic problem is caused by reducing the simulated environment to two dimensions. Only the topmost atom on every grid site is allowed to diffuse. Atoms are only allowed to sit on top of other atoms. No 3D overhang is allowed and only 2D growth modes can be simulated easily. In the case of nanowire growth which is 3D, adatoms can hop on and off islands without any influence of the height difference they must overcome. This was compensated for by a method described in section 2.4.2, basically introducing a barrier for hopping up a nanowire or island depending on the height difference.

Rijnders [19] determined the diffusivity of SrRuO<sub>3</sub> on SrO terminated SrRuO<sub>3</sub> and found a corresponding activation energy of  $1.0 \pm 0.2$  eV. The SOS settings used by Rijnders [19] were modified slightly for SrRuO<sub>3</sub> on DyScO<sub>3</sub> growth simulations. The temperature used for nanowire simulations is lowered to save simulation time<sup>3</sup>. This resulted in a step-flow to layer-by-layer

 $<sup>^{2}</sup>$ The ROOT system provides a set of Object-Oriented frameworks with all the functionality needed to handle and analyse large amounts of data in a very efficient way. Developed at CERN in the context of the NA49 experiment. URL: http://root.cern.ch/

 $<sup>^3</sup>A$  512  $\times$  128 simulation at 700  $^\circ \rm C$  required 1-2 weeks of simulation time, while at 300  $^\circ \rm C$  12 hours was sufficient.

	Rijnders [19]	Example	Nanowires	
Temperature	600	700	300	[°C]
Attempt frequency $k_0$	10	10	10	[THz]
Grid size $(n \times m)$	$490 \times 490$	$512 \times 128$	$512 \times 128$	[pixels]
$\mathrm{E}_S$	0.75	0.75	0.55 - 0.85	[eV]
$\mathbf{E}_N$	0.60	0.65	0.25	[eV]
Pulses per monolayer	20	30	30	[#]
Pulse repetition rate	2	4	4	[Hz]
Stepwidth	23-51	$23,\!152$	68,102	[nm]

Table 2.2: SOS model growth parameters

growth transition on top of the nanowires, but did not alter the formation of the nanowires since the diffusion length remained larger than the nanowire spacing.

#### Layer-by-Layer to step-flow growth transitions

Figure 2.6 shows SOS results for a layer-by-layer to step-flow growth mode transition as a result of changing the substrate miscut angle from  $0.15^{\circ}$  to  $1.00^{\circ}$ . Rijnders [19] showed this transition occurs using the following parameters:  $E_S = 0.75 \ eV$  and  $E_N = 0.60 \ eV$ . The parameters used for this example are depicted in table 2.2.

Figure 2.6a shows a layer-by-layer growth mode. Islands form and coalesce to form a new layer of material after deposition of 30 pulses. This is clearly visible in the corresponding step-density function depicted in figure 2.6c (light), which shows oscillations. 2.6b shows a step-flow-growth mode, no islands form and the step density in figure 2.6c (dark) remains constant<sup>4</sup>.

#### 2.4.2 Modified Solid-on-Solid model

Normally SOS models are used to simulate 2D growth modes, since most 3D growth modes are more easily described by thermodynamics. To simulate the formation of nanowires a 3Dlike growth mode must take place. To allow wired growth through diffusion, step-up diffusion must be allowed. In most SOS models step up diffusion is specifically prohibited. If step-up diffusion is prohibited or energetically unfavourable, step-flow growth will occur. Wire growth simulations thus require step-up diffusion to be energetically favourable. The difference between step-flow and step-up growth is schematically drawn in figure 2.3. In case it is energetically unfavourable to hop onto steps the film remains smooth (left). If adatoms hop up steps on the surface nanowires start to grow in heigth (right).

#### Mixed termination anisotropy

In order to grown nanowires the substrates mixed termination must make it energetically favourable to hop up steps. Therefore mixed termination is simulated by creating ordered areas of different diffusion barrier  $E_S^A$  and  $E_S^B$  while keeping the nearest neighbour interaction term constant. An higher  $E_S$  value decreases the hopping rate, this lowers the diffusivity. The first layer of adatom always replicates the ordered areas if diffusion length is large enough for adatoms to reach the area with the highest  $E_S$  value. The second layer of cells must overcome an addition nearest neighbour bond to jump up the first layer. To allow for nanowires to grow in height on areas where  $E_S = E_S^B$  and not in width equation 2.1 should hold. If the difference between both sides of equation 2.1 is small, the growth rate plays a role as well. If a new pulse of

<sup>&</sup>lt;sup>4</sup>The variations in the step density function for step-flow growth are caused by the finite simulation grid and boundary effects. Steps leave and appear on the simulation grid, causing minor changes in the step density.



Figure: 2.3: Step flow vs step up diffusion indicating that after completion of one layer of adatoms on top of B-site terminated areas either step-flow growth (left) or step-up growth (right) can occur. The balance between both depends of the difference in hopping barrier for both situations, given in equation 2.1.

material is applied before the previous adatoms have reached areas with a high hopping barrier, these new adatoms could hinder the previous adatoms from reaching these areas, by providing extra nearest neighbour bonds.

$$E_S^A + E_N < E_S^B \tag{2.1}$$

#### Hetroepitaxy anisotropy

The model simulates  $SrRuO_3$  growth on  $DyScO_3$ . The hopping barrier for hetroepitaxy:  $SrRuO_3$  on  $DyScO_3$  is expected to be different than the barrier for homoepitaxy  $SrRuO_3$  on  $SrRuO_3$ . This can be introduced by chancing the  $E_S$  value after growth of one cell[20]. Figure 2.4 gives an example of such hetroepitaxy. In this example the hopping barrier is lowered locally from 0.75 eV to 0.45 eV. This induces a transition from layer-by-layer to step-flow growth after completion of the first monolayer which is clearly visible in the calculated step density values. The nanowires are simulated by creating an area with a low  $E_S^A$  value and a high  $E_S^B$  value. The  $E_S^A$  area has a high diffusivity and cells prefer to stick at areas with  $E_S^B$ . The difference between  $E_S^B$  and the films  $E_S$  value are assumed to be small. Different types of nearest neighbour interactions[20] are not studied in this report, most neighbours are  $SrRuO_3$  except for the substrate step edges.

#### Step-up barrier

Cells are allowed to hop onto steps, islands and wires independent of the height difference. Without mixed termination anisotropy such a jump would be unfavourable anyway, since a nearest neighbour bond must be broken to make the jump. This neighbour is not regained after the jump. Also a additional Ehrlich-Schwoebel barrier positive or negative [21] could be included. This could prevent or enhance the chance of an atoms stepping down a step. Since wire growth due to mixed termination anisotropy is studied no additional Erhlich-Schwoebel barrier is added, which could drastically alter the growth behaviour.

Diffusion along the nanowire or island sides is no different from diffusion along the surface, gravity does not play a role in this force regime. Physically an atom stepping up a nanowire



Figure: 2.4: Simulated increased diffusivity indicated by a change from oscillating RHEED to steady-state RHEED after completion of the  $1^{th}$  layer. The change is induced by a lowering of the energy barrier  $E_S$  by 0.3 eV at example SOS condition shown in table 2.2.

should hop up the side of the nanowire step by step. To incorporate this into the model an additional barrier is added depending on the number of steps required to hop onto a nanowire. This barrier scales with the wire height and is given by equation 2.2. This equation holds only for  $h_n > h$  where h is the original atom height and  $h_n$  the height of the neighbour the cell is jumping towards. Equation 1.4 gains an additional term:  $E_D = E_S + n \cdot E_N + E_{add}$ .

$$E_{add} = E_B(h_n - h) \tag{2.2}$$

#### 2.4.3 Nanowire growth model

Mixed termination anisotropy, hetroepitaxy and an additional step-up barrier described above are added to the standard SOS model to simulate wire growth. A-site and B-site choice is arbitrary in the model. The energy barrier for diffusion related to the surface interaction at Asite termination is chosen relatively low,  $E_S^A=0.55 \text{ eV}$  to force adatoms on A-site to step-flow at the selected temperature. The surface related energy barrier on B-site is chosen to be  $E_S^B=0.85$ eV. The adatom-adatom surface interaction hopping barrier is chosen slightly lower,  $E_S=0.75$ eV. A nearest-neighbour interaction energy of  $E_N=0.25 \text{ eV}$  is used. The step-up barrier increases with height  $E_B=0.01 \text{ eV/cell}$ . An overview of the important energy barriers is depicted in figure 2.5. The choice of these parameters is based on the settings proposed by Rijnders [19] and Molecular Beam Epitaxy (MBE) parameters used by Vvedensky et al. [22]<sup>5</sup>.



Figure: 2.5: Overview of typical 2D SOS energy barriers

<sup>&</sup>lt;sup>5</sup>Parameters used by Vvedensky et al. [22]:  $k_0=10^{13}$  Hz,  $E_S=1.3$  eV,  $E_N=0.25$  eV and a temperature between 0 and 500 °C.



(s) Corresponding simulated RHEED oscillations

Figure: 2.6: Step-flow to layer-by-layer growth transition for two miscut angles using example growth parameters depicted in table 2.2. Images correspond to deposition of 1, 15, 30, 45, 60, 75, 90, 105 and 120 pulses from top to bottom.

# Chapter 3

# Experimental results

This chapter gives an overview of all experiments relevant for discussion in chapter 4. First all physical experiments, such as PLD growth and AFM measurements are shown and explained. Finally the SOS model results are listed and clarified.

### 3.1 Acquiring mixed terminated $DyScO_3$

The first step for growing nanowires is substrate treatment. Since the wires are expected to grow on one of the DyScO<sub>3</sub> chemical terminations, this treatment is a crucial step for growing nanowires. The mixed termination ratio was determined using lateral force microscopy. It was not always straightforward to record such a lateral force/friction contrast. Several factors make it difficult to detect mixed termination. The quality of the AFM tip and the alignment of the AFM laser should be optimized. Since optimization is just a matter of time and effort, the actual difficulty might be surface contaminations. For SrTiO<sub>3</sub> sodium and water contaminations are known to disturb the AFM measurement [13],[17]. DyScO<sub>3</sub> has polar layers and different surface termination might be more sensitive to different kinds of contaminations. These contaminations could equalize the surface friction contrast. Contaminations are easily obtained by human perspiration on beakers or tweezers. The contaminations are difficult to clean chemically. Above  $500 \,^{\circ}$ C in vacuum these contaminations sublimate[17] and thus should not influence the SrRuO<sub>3</sub> growth, but might make recording a friction contrast more difficult.

The vicinal mixed terminated substrates theoretically allow for three different kinds of ordering. These different kinds of stacking are depicted in figure 3.1. Option (a) results from continuous half unit cell high steps, resulting in an alternating friction contrast (inset). Option (b) depicts half unit cell steps down followed by full unit cells step down. This stacking would result in a doubled period of the friction contrast. Stacking option (c) shows half unit cell steps up followed by 1.5 unit cell steps down, resulting in friction contrast similar to staking (a).

The influence of the anneal time on the mixed termination ratio was measured by annealing three samples for different periods of time, 30 minutes, 4 hours and 8 hours at 1000 °C. The substrates were prepared as described in section 2.1. After annealing the surface morphology was checked using CM-AFM. The AFM height and friction force images are depicted in figure 3.2. The samples were cut from the same 10x10mm, 0.1 °miscut substrate. The miscut direction and stepwidth varied slightly over the substrates surface. In general the steps run parallel to a bulk crystal edge. The series shows an straightening of the step edges between 30 minutes to 4 hours of annealing. The 8 hours sample shows little or no mixed termination. The friction contrast around the step edge of the 8 hours sample is likely to be caused mainly by the step edge and not by mixed termination. The inverted colour of the friction map of sample (c) is caused by scanning across the substrate in an other direction compared to the first two friction maps. For the 30 minutes and the 4 hours sample, the friction force image overlaps perfectly



Figure: 3.1: Possible mixed termination stacking variations. Dark boxes correspond to A-site termination, white boxes to B-site termination. Square insets show schematic phase or friction contrast resulting from the corresponding stacking. Option (c) is usually measured. A phase or friction contrast for option (b) has never been recorded.

with the height image. Although it is difficult to find half unit cell, 0.2 nm steps in the height profile, a clear contrast in the height images is visible. This contrast area indicates a lower lying area before the step upwards. This indicates 1.5 unit cell steps up followed by 0.5 unit cell steps down on each terrace, staking option figure 3.1 (c).

Height and phase TM-AFM images of three different samples which were annealed for 4 hours as well, show mixed termination in two cases and possible single termination in one case. The images are depicted in figure 3.3. Sample (a) and (g) have a comparable stepwidth (130 vs. 160 nm, while sample (d) has a large stepwidth (600 nm). Sample (a) and (d) show mixed termination while sample (g) does not. Treatment of all samples was similar, except that sample (g) was cleaned and annealed separately from samples (a) and (d).

The height image of sample (a) shows almost perfectly flat terraces with unit cell 0.4 nm high steps, while a strong phase contrast is recorded simultaneously. The height image does show vague features centred on the terrace which correspond to the phase image. If any half unit cell steps had to be appointed to these features it seems to be more likely to be 0.2 nm up instead of the expected 0.2 nm down. Figure 3.1 (b) gives a schematic representation of a such a 0.2 nm up, 0.4 nm up stacking and the corresponding friction pattern. This does not match the measured phase pattern and thus can not be the case. Stacking option (a) matches the measured phase image, but does not match the 0.4 nm steps. Possibly the AFM friction forces influence the height measurement and the real stacking is still option (c). Sample (d) clearly shows that both the straightening of the step edges and the ordering of the mixed terminated areas is not completed yet, due to the low miscut.

Substrates have also been annealed for 12, 16, 48 and 86 hours (not shown). For most different anneal times at least one mixed terminated substrate was found during this research. Many substrates did not show mixed termination, but seemed to be single terminated. Even though they had a similar miscut and were treated simultaneously.

## 3.2 PLD growth of SrRuO<sub>3</sub> on DyScO<sub>3</sub>

 $SrRuO_3$  was grown by PLD using the experimental conditions described in section 2.2. For every sample RHEED images before growth, after growth and the intensity oscillations of the specular spot were recorded. This section shows some typical examples of the RHEED signal before, during and after growth. Generally the evolution of the pattern shape was similar for all samples. The specular spot intensity oscillations did differ slightly. Images shown bellow are indicative of all grown films, nanowires, islands and smooth films.



Figure: 3.2: Contact-AFM  $1 \times 1 \ \mu m$  height and friction images for various anneal times. Anneal process done at 1000 °C under oxygen flow. Height images (a,d) indicate 0.6 nm high steps preceded by 0.2nm steps near the centre of the terrace, resulting in an average height difference on one terrace of 0.4 nm. Part of the terraces show a different friction force (b,e) related to the 0.2 nm height difference, these samples are mixed terminated. Images (g,h) show no clear mixed termination. Height and friction profiles (c,f,i) are averaged over 4 scan lines. The linescan position is indicated in the corresponding height images.

#### 3.2.1 RHEED before, during and after growth

Figure 3.4 (a),(c),(e) show images before growth for three different 2D crystal directions. The directions refer to a square representation of the surface. The direction are determined by the relative angles between successive RHEED patters during rotation of the sample. This leaves several options for the exact crystal direction. Assuming square symmetry these directions are similar and are referred to by (10), (12) and (11). The angle between (10) and (12) is  $26.5^{\circ}$  and the angle between (12) and (11) is  $18.5^{\circ}$ . The angles between (01)-(21) and (21)-(11) are  $26.5^{\circ}$  and  $18.5^{\circ}$  as well. Images (b),(d),(f) correspond to the same directions on the same sample after growth of SrRuO<sub>3</sub>. Before and after growth, all directions show a clear 2D RHEED



Figure: 3.3: TM-AFM  $(2 \times 2 \ \mu m, 6 \times 6 \ \mu m, 2 \times 2 \ \mu m)$  height and phase images for various samples all annealed for 4 hours. Sample (a) and (g) had a similar miscut but only (a) shows mixed termination. Low miscut sample (d) shows clear mixed termination, but due to the low miscut the steps and mixed terminated areas are not straight. Profiles (c,f,i) are averaged over 4 scan lines.

pattern including Kikuchi lines[23]. However after growth more spots are visible, indicating a 3D component to the surface morphology, normally related to island growth. These 3D spots are relatively strong after growth in the (10)-direction.

During growth the RHEED signal usually drops down within 30 seconds after starting the deposition. It rises again, sometimes showing a maximum after 60-70 seconds. A typical RHEED oscillation is shown in figure 3.5(g). RHEED images for various deposition times (a)-(f) are shown as well. A weak maximum around 30 seconds is also quite common. After 60 seconds a transition from layer-by-layer growth to a steady-state RHEED signal occurs. After each pulse the RHEED intensity drops sharply and recovers quickly. More RHEED oscillations are shown in figure 3.13.

The growth rate of  $SrRuO_3$  on  $DyScO_3$  is difficult to determine from the RHEED signal, since no consistent oscillations were recorded. However when depositing  $SrRuO_3$  on  $DyScO_3$ at a lower oxygen background pressure (0.01 mbar) stable oscillations are recorded, depicted in



Figure: 3.4: RHEED images before and after nanowire growth (SrRuO<sub>3</sub> on DyScO<sub>3</sub>) for three different crystal directions. RHEED during growth for the same sample is depicted in figure 3.5. Images recorded at room temperature in vacuum.

appendix B.3, figure B.4. These oscillations show 27 pulses are required for each monolayer of  $SrRuO_3$ . This roughly matches the first oscillation sometimes registered at higher pressure, 30 seconds. For estimating the amount of  $SrRuO_3$  on  $DyScO_3$  during PLD 30 pulses per monolayer will be used.

#### Surface morphology after growth

After growth on substrates shown in figure 3.2, STM image were recorded under vacuum conditions. The resulting STM images are depicted in figure 3.6. The  $SrRuO_3$  film morphology clearly mimics the original substrate mixed termination. The lines are discussed in more detail in section 3.2.2. Figure 3.6(e) shows a relatively smooth film with only unit cell high steps. The original stepwidth is still visible as well. The top-left corner shows a measurement artefact.

#### 3.2.2 Nanowire growth

Table 3.1 gives an overview of the substrate and growth parameters which resulted in nanowire growth and the corresponding wire properties. The substrates which resulted in line patterned growth generally had a similar miscut. Lines were grown for three different deposition times, 3, 4 and 5 minutes. The volume of the resulting wires scales with the deposition time. A maximum wire height of 8 nm was found.

The sample depicted in figure 3.7 shows nanowires after growth of 3 minutes, 180 pulses. At a growth rate of 30 pulses per monolayer this corresponds to approximately 6 layers of  $SrRuO_3$ 



Figure: 3.5: RHEED images during growth aligned to the (12)-direction, typical for SrRuO<sub>3</sub> on DyScO<sub>3</sub> nanowire growth. During the first 30 seconds the RHEED intensity drops (b). After 60 seconds (c) the DyScO<sub>3</sub> spots disappear and SrRuO<sub>3</sub> spots appear and the growth mode changes from more layer-by-layer like to a steady-state growth mode (g). After 60 seconds the RHEED signal remains constant (d),(e),(f). Image were recorded at deposition conditions.

Stepwidth [nm]	Anneal time [h]	Pulses	Wire height [nm]	Wire width [nm]
185	4	300	8	70
185	1/2	300	7	80
250	86	180	6	100
100	12	240	6	90
$160^{*}$	4	180	4	50
$1000^{*}$	1/2	180	3	50

Table 3.1: Nanowire samples. \* Samples grown in a different PLD. Last sample did not show straight nanowires, due to the low miscut and short anneal.

if it would grow flat. The lines have an average height of 6 nm, 15 layers and cover 45%<sup>1</sup> of the surface. The ammount of material deposited rougly matches the ammount of material in the

<sup>&</sup>lt;sup>1</sup>Area estimated using NC-AFM image 3.7 by aplying a threshold value to height. A threshold value equal to the average height value was used, this visually matches the line patterns (3.7(c)).



Figure: 3.6: In-situ  $1 \times 1 \ \mu m$  STM images after 5 minutes of SrRuO<sub>3</sub> growth for various DyScO<sub>3</sub> anneal times. Substrates correspond to AFM images depicted in figure 3.2. Line profiles (b,d,f) are averaged over 4 scan lines.

lines  $45\% \times 15 = 6.75$ . This is very rough estimate, but it shows it is likely that no material is evaporated from the surface.

Figure 3.7d shows a height profile averaged over 4 scan lines. Original substrate stepwidth is clearly visible. The lines run directly next to or on top of the original step edge. Smaller lines are higher, thus the amount of material in one line remains constant. This also indicates no material is evaporated from the surface during deposition.

Image 3.7b shows deep wells in the nanowires. The wells are as deep as the lines are high. These deep wells are expected to be related to defects the original mixed termination. This is not confirmed. Occasionally and island grows in between the nanowires, four islands are visible in image 3.7a. The islands have similar dimensions to the lines and the pair of islands in the lower left corner shows an island spacing comparable to the wire spacing. Indicating the wire spacing could be closely related to the diffusion length of  $SrRuO_3$  on  $DyScO_3$ .



Figure: 3.7: TM-AFM  $(5 \times 5 \ \mu m, 1 \times 1 \ \mu m, 5 \times 5 \ \mu m)$  images of nanowires of SrRuO<sub>3</sub> on DyScO<sub>3</sub> after 3 minutes of SrRuO<sub>3</sub> deposition. Image (a) and (b) show height images and image (c) shows an overlay covering areas higher than the average height value of image (a). Image (d) shows a line profile averaged over 4 scan lines. The linescan corresponds to the line indicated in image (b). Typical nanowire properties are indicated as well(d). The original substrates steps are still visible after nanowire growth.

#### 3.2.3 Island growth

Instead of wires, some samples showed islands after growth. The height and width of these islands are comparable to the height and width of line patterns. An overview of island properties for various samples is given in table 3.1 and two samples with islands are depicted in figure 3.8.

Stepwidth [nm]	Anneal time [h]	Pulses	Island height [nm]	Island size [nm]	Coverage
222	4	360	8	50-90	70%
170	1/2	240	4.5	30-100	56%
282	15	240	5	30-80	52%

Table 3.2: Properties of samples with island. Islands are usually asymmetrically shaped and sizes distributed inhomogeneously.

The dimensions of the islands scales similar to the dimensions of wires, although their variation in width is much larger. The inter-island distance is smaller and the coverage generally slightly higher for islands compared to lines.



Figure: 3.8: NC-AFM  $(1.5 \times 1.5 \ \mu m, 2 \times 2 \ \mu m)$  images islands after SrRuO<sub>3</sub> growth of 4 (a) and 6 (b) minutes indicating island growth.

#### 3.2.4 Combined growth patterns

The nanowire sample discussed in the previous section already showed a few islands in between the lines. While most of the time the growth ends up in either lines or islands, a combined pattern is also possible, depicted in figure 3.9. Before deposition this sample showed areas with clear mixed termination, figure 3.9a and areas which showed almost no mixed termination, figure 3.9c. The miscut direction and stepwidth varied locally on the substrate surface. This resulted in lines on certain areas (i) and islands (j) on other areas, but mainly a combination of both (e-h).

This combined growth mode could provide information about the mechanism responsible for growing wires. The lines are separated spatially stronger than the islands. Around wires a depletion zone is visible, indicating the lines act as sinks in an Oswald ripening process. The lines grow at the expense of the smaller islands. However not all islands are influenced by the lines, only the islands closest to the lines. The distance the adatoms travel before nucleation can be estimated using these images. The distance is related to the diffusion barrier used for simulations. Figure 3.9e shows single islands between nanowires. The wire spacing is 240 nm, indicating a diffusion distance of 120 nm. Using an attempt frequency for hopping of 10 THz this results in an activation energy of  $E_A \approx 1.3 eV$  using equation 1.2. Rijnders [19] has found an activation energy of  $1.0 \pm 0.2 eV$  for SrRuO<sub>3</sub> on SrTiO<sub>3</sub>.

#### 3.2.5 Initial growth

To study the initial growth of  $SrRuO_3$  on  $DyScO_3$  mixed terminations, a short deposition was performed on a mixed terminated substrate. 30 Pulses were deposited using normal deposition conditions, table 2.1. Substrate CM-AFM images are depicted in figure 3.10a,b and TM-AFM images of the film are shown in figure 3.10d,e. The height image and substrate profile 3.10c show clear mixed termination before deposition. After growth the entire surface is covered with material and small islands grow everywhere. The height image and profile after growth show regions of high islands and regions with lower islands. The ratio between these regions is comparable to the mixed termination ratio of the substrate. The  $SrRuO_3$  film initially mimics the substrates mixed termination. Phase contrast is no longer visible after growth, this could indicate single termination after  $SrRuO_3$  growth. This seem likely when considering that Ru is highly volatile. Alternatively NC-AFM is less sensitive to  $SrRuO_3$  surface terminations compared to  $DyScO_3$  surface terminations.



Figure: 3.9: CM-AFM images before deposition (a-d) of SrRuO<sub>3</sub> and NC-AFM images after growth. All images are made on the same sample. (a,b,c,d,e,h)  $3\times 3$   $\mu m$ . (f,g)  $2\times 2 \ \mu m$ . (i)  $1.5\times 1.5 \ \mu m$ . (j)  $2.4\times 2.4 \ \mu m$ .

### **3.3** DyScO<sub>3</sub> termination control

Nanowire and island growth depends strongly on different growth behaviour of  $SrRuO_3$  on both  $DyScO_3$  terminations. To test this different growth behaviour  $SrRuO_3$  was grown on  $DyScO_3$  with an additional layer of  $ScO_2$  and on  $DyScO_3$  with an additional layer of DyO.



Figure: 3.10: CM-AFM  $1 \times 1 \mu m$  images of a mixed terminated DyScO<sub>3</sub> substrate (a),(b) and TM-AFM images (d),(e) after growth of 30 pulses SrRuO<sub>3</sub>. Profiles (c),(f) are averaged over 4 scan lines.

#### **3.3.1** SrRuO<sub>3</sub> growth on $ScO_2$

 $ScO_2$  was grown on DyScO<sub>3</sub> from a Sc<sub>2</sub>O<sub>3</sub> target using the parameters displayed in table 2.1. The growth rate of ScO<sub>2</sub> was around 32 seconds per monolayer. An example RHEED oscillation is shown in figure B.1a. Exploratory experiments showed that for up to 3 layers of ScO<sub>2</sub> the RHEED remained 2D. After the third layer 3D spots appeared. AFM images of a single ScO<sub>2</sub> layer showed a smooth film, without any phase or friction contrast, depicted in appendix B, figure B.1a,b. Directly after growing a single layer of ScO<sub>2</sub>, 240 pulses of SrRuO<sub>3</sub> were deposited at normal SrRuO<sub>3</sub> PLD parameters. The resulting NC-AFM images are shown in figure 3.11. The film showed island growth. The phase image shows a contrast between the islands and lower areas. The corresponding RHEED intensity oscillation is depicted in figure 3.13. The general shape of this oscillation is common for SrRuO<sub>3</sub> growth. The substrate used for growth of ScO<sub>2</sub> followed by SrRuO<sub>3</sub> had stepwidth of 170 nm.



Figure: 3.11: TM-AFM  $1 \times 1 \ \mu m$  images after SrRuO<sub>3</sub> growth on ScO<sub>2</sub> (a) height, (b) phase.

#### 3.3.2 SrRuO<sub>3</sub> growth on DyO

Similarly to  $ScO_2$ , DyO was grown on DyScO<sub>3</sub> using the parameters displayed in table 2.1 from a Dy<sub>2</sub>O<sub>3</sub> target. To growth rate is approximately 30 pulses per monolayer. After growth of 2 layers of DyO the RHEED pattern completely disappears indicating no single crystal or epitaxial film was grown. Likely caused by the large lattice mismatch between Dy<sub>2</sub>O<sub>3</sub> and DyScO<sub>3</sub>. After growth of a single monolayer of DyO, NC-AFM images still indicated a smooth film, almost similar to the DyScO<sub>3</sub> substrate, depicted in appendix B figure B.2a,b. A RHEED intensity example for DyO growth is depicted in figure B.2e.



Figure: 3.12: TM-AFM images after SrRuO<sub>3</sub> growth on DyOİmage (a) shows a height image, (b) a phase image. Image (d) shows a zoom of the height image. An auto correlation map is plotted in figure (c), indicating ordered islands. (a-c)  $6 \times 6 \ \mu m$ , (d)  $0.5 \times 0.5 \ \mu m$ .

240 pulses of  $SrRuO_3$  were added to this layer of DyO on a substrate with a stepwidth of 200 nm. The RHEED intensity oscillation is shown in figure 3.13. The general shape of this oscillation is common for  $SrRuO_3$  growth. However the time-scale differs slightly from the growth of  $SrRuO_3$  on  $ScO_2$ . When comparing the RHEED oscillation for growth of  $SrRuO_3$  on DyO or  $ScO_2$  in figure 3.5g:  $ScO_2$  matches normal  $SrRuO_3$  growth closest. NC-AFM images of the  $SrRuO_3$  film on DyO show islands, depicted in figure 3.12a,b,d. The islands are clearly elongated in one direction. Phase image (b) shows a contrast between the islands and lower areas, indicating the lower areas are likely to be a different material or termination. An autocorrelation function of the height image is shown in figure 3.12c. This auto-correlation function shows a striped pattern. The stripes are separated roughly by 200 nm, the original substrate stepwidth.



Figure: 3.13: RHEED intensity oscillations for SrRuO<sub>3</sub> growth on DyScO<sub>3</sub> with either one layer of DyO (black), ScO<sub>2</sub> (light grey) sandwiched between both layers. For comparison also a normal oscillation is shown. (grey)

### **3.4** SrRuO<sub>3</sub> film properties

#### 3.4.1 SEM imaging & electrical measurements

Scanning Electron Microscope (SEM) image of a sample depicted were recorded, depicted in figure 3.7. Two zoom levels of this sample are depicted in figure 3.14(a)(b). Image 3.14a shows long-range ordered nanowires up to at least  $25 \ \mu m$ . Nanoprobe IV curves were recorded<sup>2</sup>. The IV curves do not give any quantitative information. Figure 3.14e shows a voltage response which is likely due to contact resistance. Both the current running trough the upper and lower probe tip were recorded and are plotted on different axis. Figure 3.14f shows no voltage response. Mind the different range between figures (e) and (f). In figure 3.14c wires light in the SEM image up during the voltage measurements. This indicates current is flowing through the lines which is registered by the SEM. Such effects were not registered when the probes were positioned perpendicular to the nanowire direction. Several attempts to measure electrical properties by contacting the surface via gold contacts failed. Either the films were insulating or the measurements failed.

#### 3.4.2 Conductivity mapping

At Stanford, Microwave impedance microscopy scans were made on a nanowire sample. The results are depicted in figure 3.15. The MIM images shows a strong contrast related to the nanowires. The MIM tip dimensions matched the nanowire spacing. The tip probably did not reach the bottom of the valleys between the nanowires resulting in resulting in a non uniform MIM-C signal around the nanowires.

#### 3.4.3 X-Ray spectroscopy

XPS data of several films were recorded. Spectra of the Ru 3d band provide more information about electron correlation in the  $SrRuO_3$  film[24]. The appearance of an additional screened peak indicates the transition from insulating to metallic films. This is not studied in this report. Example XPS data are included in appendix B.3.

### 3.5 Model results

A selection of simulations results is depicted and interpreted in this section. All simulations were done using the nanowire simulation parameters in table 2.2, variations in parameters are explicitly mentioned.

<sup>&</sup>lt;sup>2</sup>Measurements performed by Peter de Veen.



Figure: 3.14: SEM images of SrRuO<sub>3</sub> nanowires indicating long-range order (a),(b) and IV curves (e),(f) recorded for directions parallel the lines (c) and perpendicular to the lines (d). During voltage sweep the nanowires light up (c) indicating a response to the measurement. No transport is measured perpendicular to the nanowires. Dark square areas image (d) caused by contaminations due to scanning areas with the SEM.

#### 3.5.1 Nanowire growth

Two nanowire surface morphology evolutions are depicted in figure 3.16 for different values of  $E_B$ . Parameters used for this nanowire simulation were:  $E_S^A = 0.55 \ eV$ ;  $E_S^B = 0.85 \ eV$ ;  $E_S = 0.75 \ eV$ ;  $E_N = 0.25 \ eV$ ;  $T = 573 \ K$  and stepwidth = 68 nm. Figure 3.16a shows two different regions of surface diffusion barrier  $E_S$ , dark areas indicate a low  $E_S$  value, a high diffusivity. Morphology evolutions (left) and (right) indicate wire growth for  $E_B = 0.01 \ eV/cell$ and  $E_B = 0.025 \ eV/cell$  respectively.

The first layer grows step-flow on A-site areas, no islands grow on the A-site area. The



Figure: 3.15: AFM (a),(c) and MIM-C (b)(d) images on two nanowire samples. Sample A also depicted in figure 3.6c. Both images show a MIM contrast related to the nanowires

materials reaches the B-site areas by step-flow across the A-site areas and sticks as soon as it reaches a B-site area. This is visible around near the boundaries of the B-site areas, most material initially sticks at the B-site boundary. Material arrives on both sides of the B-site terminated areas. For the first layer,  $E_B$  does not yet play a role. After completion of the first layer of material on the B-site area, the value of  $E_S$  changes from  $E_S^B = 0.85$  to  $E_S = 0.75$ . This enhanced diffusion is indicated by larger islands on top of the first layer of the nanowire, compare image row 1 with row 5 for example, but it does not play any major role. If no  $E_B$ value is used,  $E_B = 0$ , the wires will continue to grow, exactly matching the original mixed termination (not shown). It is not realistic to allow adatoms to jump up high wires or islands in one single step, so an  $E_{add}$  barrier is added. Such a barrier for two different  $E_B$  values as discussed in section 2.4.2. A higher  $E_B$  value results in wider and lower nanowires. Changing  $E_B$  with respect to the stepwidth and mixed termination ratio provides a method to tune the simulated wire properties to match experimental data.

#### 3.5.2 Island and smooth growth

The nanowires simulations were also run without substrate mixed termination on both single A-site and single B-site termination. The results are depicted in figure 3.17, (left) A-site termination, (right) B-site termination. Simulation was run with the same parameters as for nanowire growth depicted in figure 3.16(left). On the A-site, high diffusivity termination high islands of  $SrRuO_3$  grow. The first layer of small  $SrRuO_3$  islands act as sink sites for newly arriving  $SrRuO_3$  cells, similar to B-site termination and larger islands form on the surface. The  $SrRuO_3$  island prevent step-flow growth mode. In case of B-site termination the difference between substrate and  $SrRuO_3$  is much smaller and normal layer-by-layer growth occurs. This smooth growth is measured during PLD as well[11] when the substrates are chemically treated.

#### 3.5.3 Combined growth

On substrates with a lower miscut, a combined island and wire growth mode was simulated using the SOS model. Parameters used were the same as for nanowire sample 3.16(left), only the stepwidth was increased to 102 nm. These results match experimental observations of islands growing in between the nanowires. Low miscut results are depicted in figure 3.18.



(a) Mixed termination



Figure: 3.16: Nanowire SOS simulation results for two different  $E_B$  values. Image (a) indicates to the original substrate  $E_S$  values, dark areas correspond to a low  $E_S$  value, high diffusivity, A-site termination. Left series done using  $E_B = 0.01 \ eV/cell$ , right series using  $E_B = 0.025 \ eV/cell$ . The series show a different evolution of the nanowires width and height. Images from top to bottom correspond to deposition of 1,15,30,45,60,75,90,105,120,135 pulses.



Figure: 3.17: Simulation results for single terminated A-site and B-site substrates,  $E_B = 0.01 \ eV$ . Indicating island growth on A-site termination and a smooth film is grown on B-site termination. Images from top to bottom correspond to deposition of 1,15,30,45,60,75,90,105,120,135,150 pulses.



(a) Mixed termination



Figure: 3.18: SOS simulation on a sample with a stepwidth of 102 nm and  $E_B = 0.01 \ eV$ . Image (a) indicates to the original substrate  $E_S$  values, dark areas correspond to a low  $E_S$  value, high diffusivity, A-site termination. Islands grow on the A-site terrace wile a nanowire grows on the B-site terrace. Images from top-left to bottom-right correspond to deposition of 1,15,30,45,60,75,90,105,120,135,150,165 pulses.

# Chapter 4

# Discussion: model versus experiments

In this chapter the experimental data will be discussed, mainly in relationship with the simulation results. First  $DyScO_3$  substrate influences are discussed. Secondly the proposed physical mechanism governing wire growth is discussed by comparing PLD grown films and simulations. Finally the validity of the model is discussed.

### 4.1 The $DyScO_3$ surface

Annealed DyScO<sub>3</sub> substrates show ordered areas of both DyO and ScO<sub>2</sub> surface terminations. After sufficiently long annealing the mixed terminated regions line up along a step edge. The minimum anneal time required to acquire line shaped areas of mixed termination is equal to the time required to create straight step edges. AFM friction or phase images show a contrast related to the surface termination usually accompanied by a height contrast. Figure 3.1c shows the the stacking of mixed terminated areas deduced from AFM height images. On a mixed terminated substrate each terrace consists of a 0.6 nm (1.5 u.c.) step up and a 0.2 nm (0.5 u.c.) step down. No clear relation between anneal time and the amount of mixed termination was found. Preliminary anneal experiments indicated mixed termination disappeared after long annealing, however two 86 hours annealed substrates still showed clear mixed termination. Moreover mixed termination was detected for substrates annealed for various anneal times. The surface stoichiometry seems to change continuously during annealing. The exact ratio between DyO and ScO<sub>2</sub> at the surface is expected to depend on the mixed termination ratio prior to annealing combined with the substrates terrace width and the anneal time.

### 4.2 SrRuO<sub>3</sub> nanowire growth

AFM and RHEED data show that during PLD growth SrRuO<sub>3</sub> mimics the DyScO<sub>3</sub> substrate mixed termination areas. SrRuO<sub>3</sub> nucleates preferentially on one surface termination. No material is evaporated during growth, as the height of the wires scales with the mixed termination ratio. In other words the volume of the nanowires is equal to volume expected from the RHEED signal. Material deposited between the lines diffuses until it nucleates on a nanowire. The nanowires grow in height and width simultaneously. This kinetic balance is studied successfully using a SOS model. The SOS models assumes difference of  $\Delta E_S = 0.3 \ eV$  between both diffusion barriers. Compared to the nearest neighbour bond energy of  $E_N = 0.25 \ eV$  it is preferential to hop onto the areas with the highest  $E_S$  value, even if this hop crosses a step in the substrate. Next to this difference in diffusion barriers the diffusion length of adatoms on A-site areas must be larger than the step width in order to grow nanowires. Otherwise islands grow in between the nanowires, similar to PLD grown nanowires.

#### Preferred termination

The model requires a difference in diffusivity for both surface terminations. The termination which has the lowest diffusivity will act as a sink site for adatoms to nucleate, this is the preferred termination for nanowire growth. SrRuO<sub>3</sub> also grows selectively on SrTiO<sub>3</sub> mixed terminations [25], where it is assumed to grow on TiO<sub>2</sub> termination. This is supported by SrRuO<sub>3</sub> growth on chemically treated SrTiO<sub>3</sub> substrate [10] resulting in TiO<sub>2</sub> termination. If not all SrO is chemically etched, deep trenches remain present after growth of SrRuO<sub>3</sub>, related to the SrO terminated areas. If growth on TiO<sub>2</sub> is driven by selective growth of SrRuO<sub>3</sub> on B-site terminated crystals, the same preference is expected for growth on DyScO<sub>3</sub>.

#### Termination conversion & initial growth

Using similar SrRuO<sub>3</sub> PLD parameters on SrTiO<sub>3</sub> substrates, a termination conversion in registered in the RHEED signal, described in section 1.3.2. This same conversion is measured when growing on  $DyScO_3$ , indicating a large area of the surface is  $ScO_2$  terminated and the nanowires grow on this termination. Sometimes a weak oscillation is recorded with a maximum after 30 seconds, for example depicted in figure 3.5g. This maximum could be related to the degree of mixed termination. The A-site area of the substrate would be growing 1 full mono-layer in 30 seconds while the remaining B-site area would require more time to switch termination before completing the first mono-layer. This does not provide conclusive evidence about the preferred termination, since this extra oscillation did not show systematically. The model assumes no material grows on A-site termination, so this explanation does not match the model. Two more phenomena can explain the 30 seconds maximum. In the first place, if  $SrRuO_3$  only grows on  $ScO_2$  which covers 50% of the surface and no material evaporates: the number of pulses required to create a smooth layer is expected to be half the number of pulses required for 100% ScO<sub>2</sub> termination. This decreased first oscillation length was not registered systematically. However this change in oscillation period does give an explantion for the irregular lenght of the measured first oscillation, for example between  $SrRuO_3$  growth on deposited  $ScO_2$  and DyO this first oscillation differed by 15 seconds, figure 3.13. Secondly, during termination conversion an intermediate smooth layer could form, not as smooth as a for full oscillation, but still show up in the RHEED signal. The exact origin of the 30 seconds maximum remains unknown.

AFM images made after growth of 30 seconds of deposition, figure 3.10, shows material clearly grows more quickly on one termination, even before a termination conversion has occurred. These possible stacking variations are depicted schematically in figure 4.1 assuming substrate stacking 3.1c. Initial growth shows 0.8-1.2 nm heigh steps after 30 seconds of deposition. Only option (d) is able to explain these high features after 30 seconds. The termination on top of the 0.6 nm step is expected to be the preferred termination. The double period of the first RHEED oscillation indicates this termination is  $ScO_2$ .

#### Controlled surface termination analysis

Deposition of  $ScO_2$  and DyO layers on a DyScO<sub>3</sub> substrate before  $SrRuO_3$  film growth results in different RHEED signals. These RHEED intensity oscillations during growth of  $SrRuO_3$  on top of these single oxide layers are depicted in figure 3.13. Both show a long first layer completion time. Likely not the entire surface was covered with DyO after  $Dy_2O_3$  deposition, leaving the remaining  $ScO_2$  to act as sink sites for the anisotropic growth depicted in figure 3.12. The growth of  $SrRuO_3$  on  $ScO_2$  terminated  $DyScO_3$  by deposition of  $Sc_2O_3$  resulted in island growth. This



Figure: 4.1: Possible detailed stacking options after growth of SrRuO<sub>3</sub> on mixed terminated DyScO<sub>3</sub> after 60 seconds of deposition, assuming substrate stacking option 3.1c. If no selective growth occurs and termination conversion takes place on the lowest terrace areas (a) or on the highest terrace areas (b) and assuming selective growth of SrRuO<sub>3</sub> on ScO<sub>2</sub> terminated areas: on the lowest terrace areas (c) or on the highest terrace areas (d).

does not match the idea that nanowires grow coherently on  $ScO_2$  termination. Coherent growth is expected for single termination after chemical treatment, most likely  $ScO_2[11]$ . Possibly the deposition of a single  $ScO_2$  layer from the  $Sc_2O_3$  target failed.

#### Comparison with other types of anomalous growth

Wire patterned growth of  $SrRuO_3$  on  $LaAlO_3$  is explained by a stress relaxation due to the relatively high lattice mismatch between  $SrRuO_3$  and  $LaAlO_3[26]$ . Rippled patterned island form on the substrate. Island grow on the ripples while inter ripple regions remain uncovered. After growth of 5 nm these island coalesce to form rippled wire structures. This mechanism is very different from the model proposed in this report, it does not involve mixed termination. The wires resulting from  $SrRuO_3$  growth on  $LaAlO_3$  are not as well defined as  $SrRuO_3$  wires on  $DyScO_3$ . The wire spacing is small and the height varied greatly.

 $SrRuO_3$  wired patterns were grown on  $SrTiO_3$  surface terminations[25], similar to  $DyScO_3$ surface terminations. The growth of these wires is attributed to a difference in adatom sticking coefficient. The resulting wires are almost as wide as the original terraces, separated by small trenches. These  $SrRuO_3$  wires do not show the same long range spatial order and separation as  $SrRuO_3$  wires on  $DyScO_3$ . Other types of anisotropic growth for metals instead of complex oxides originate from preferred nucleation at step edges[27, 7] or form by self-organized growth on strain-relief patterns caused by dislocations[28]. These mechanisms do not involve mixed surface terminations.

#### 4.3 Physical mechanism

The SOS model explained in section 2.4.3 matches the results in chapter 3 qualitatively. A mixed terminated substrate results in nanowires assuming DyO termination to have a high diffusivity compared to  $ScO_2$  termination and  $SrRuO_3$  covered areas, figure 3.16. Nanowire formation is a result of mixed terminated areas which have a different diffusivity. By incorporating a step-up barrier related to the height of the wires the evolution of the wires width and height matches the measured evolution. The wires grow in width and height simultaneously in both the model and the experiments. The model shows that as the wires grow in height the chance of new cells

reaching the top of the wire decreases and the wires start growing in width more quickly. Islands occasionally grow in between the nanowires. This island growth is simulated by increasing the stepwidth while keeping the other SOS parameters constant. The diffusion length  $l_D$  of the SrRuO<sub>3</sub> cells on DyO termination becomes smaller than the nanowire spacing. This resulting in SrRuO<sub>3</sub> island in between the lines. Since the diffusion coefficient of SrRuO<sub>3</sub> on these SrRuO<sub>3</sub> island is also low compared to SrRuO<sub>3</sub> on DyO, these islands grow in height similar to the mixed terminated ScO<sub>2</sub> areas.

This diffusion length limit does not explain the combined growth patters measured on a substrate which showed a large local variation in miscut angle and stepwidth, figure 3.9. This sample's wires and islands give rise to an an alternative explanation for island growth. Island growth could also be caused by areas of  $ScO_2$  which remain on the substrate after annealing. Annealing is a diffusion driven process, just like PLD growth. Islands of  $ScO_2$  are most likely to be found on the centres of step terraces if they did not reach a step edge during annealing. However these island were never recorded except for this one sample which showed many features. If the annealed substrates do not show friction or phase contrast on the terraces, the islands in between nanowires are expected to be caused by diffusion during  $SrRuO_3$  growth and not by islands of  $ScO_2$  termination.

If single terminated substrates are simulated using the same parameters, the results also show a qualitative match with the measurements. A simulation of DyO termination results in island growth similar to some PLD results. The model thus implies island growth occurs on substrates which do not have  $ScO_2$  sinks. Simulation on  $ScO_2$  termination result in smooth films. According to the SOS model chemically treated single terminated substrates[11] resulting in smooth  $SrRuO_3$  films after PLD growth are  $ScO_2$  single terminated.

### 4.4 Model validity

The model nanowires are in good qualitative agreement with the PLD grown nanowires. The model requires a difference in the substrate diffusion barrier of 0.3 eV (section 2.4.3). This 0.3 eV difference is large enough to change step-flow growth into layer-by-layer growth (2.4.1). Such a transition is measured for growth of SrRuO<sub>3</sub> on SrTiO<sub>3</sub> after completion of the first layer[14]. The SOS  $E_S$  parameter varied from 0.75 eV to 1.3 eV for various applications[19, 20, 22] and  $E_N$  varied between 0.25 eV and 0.65 eV. The chosen parameters are within this range. Except for the substrate diffusion barrier on DyO, this  $E_S^B$  was chosen slightly lower to enhance diffusivity. The chosen parameters are mostly within established ranges. In order to get a quantitative match, the model should be used at higher temperatures and for lower miscut samples. This lower miscut requires simulation of larger areas. These large areas combined with the higher temperatures increase simulation time drastically.

#### Step up barrier

Basic SOS models<sup>[8]</sup> do not allow atoms to hop onto steps or islands, either by explicitly prohibiting this hop or because it is energetically unfavourable. It is not realistic to allow atoms to hop directly onto multiple unit cell high nanowires. The modified SOS models corrects for this by adding an additional barrier for cells hopping onto a nanowire. The barrier scales with the height difference an adatom must overcome to hop onto a higher area. Without this barrier the simulation only provides information on the initial growth of the first few layers. The barrier was tuned to acquire a qualitative match between simulation and measurements.

# Chapter 5

# **Conclusions & Recommendations**

The surface mixed termination ratio of  $DyScO_3(110)$  substrates can be tuned by annealing for different periods of time. The exact mixed termination ratio depends on the anneal time, substrates miscut angle and an unknown additional factor, possibly the post-anneal mixed termination ratio. During annealing the surface stoichiometry changes continuously, it is not possible to achieve single termination by long annealing. The best method for acquiring mixed termination suitable for nanowire growth is to anneal at least 2 hours at 1000 °C to straighten the step edges on pre-selected vicinal substrates, miscut angle  $\approx 0.1^{\circ}$ . Annealing for 4 hours resulted in the highest number of ordered mixed terminated substrates.

AFM analyses after growth indicates  $SrRuO_3$  mimics the original  $DyScO_3(110)$  chemical terminations during PLD. According the the measured termination conversion RHEED signal, the nanowires grow selectively on  $ScO_2$  termination. Typical nanowires show a height of 6 nm, width of 80 nm and are separated by 100 nm. When the nanowire spacing is increased, islands grow in between the wires. Growth on substrates which did not show mixed termination usually resulted in island growth.

The SrRuO<sub>3</sub> nanowires, islands and smooth films were simulated using a Solid-on-Solid model by assuming high diffusivity on DyO terminated areas compared to both ScO<sub>2</sub> terminated areas and the SrRuO<sub>3</sub> covered areas. By adding an additional hopping barrier which increases linearly with the nanowire or island height, the wire width and height evolution during growth was simulated successfully. The same model was adopted to explain island growth on DyO single terminated films and smooth film growth on ScO<sub>2</sub> single terminated substrates. By changing substrate stepwidth or the additional hopping barrier, the height and width evolution during simulations can be modified. Simulation resulting in nanowire growth were performed with a surface diffusion barrier of 0.55 eV on DyO terminated areas, 0.85 eV on ScO<sub>2</sub> terminated areas and a nearest-neighbour bond energy of 0.25 eV. The additional hopping barrier matched the experimental data when chosen around 0.01 eV per unit cell high step.

 $SrRuO_3$  conducting nanowires physical properties show a clear contrast with respect to the insulating  $DyScO_3$  substrates using MIM. The nanowires show an anisotropic responds to twopoint electrical measurements when the probes are aligned either parallel or perpendicular with respect to the nanowires.

#### Recommendations

The  $DyScO_3$  substrate mixed termination is currently acquired by a method which does not guarantee mixed termination. More control on the mixed termination ratio provides more control over the nanowire dimensions and quality. During the final stages of this master's thesis a method for acquiring single terminated substrates was developed[11]. These single terminated substrates could be used as a starting point for creating mixed terminated substrates with a controllable amount of both chemical terminations. For example by annealing single terminated substrates for various periods of time. More knowledge about the  $DyScO_3$  substrate will most likely lead to even more well defined nanowires.

The current simulation parameters are based on previously performed  $SrRuO_3$  hetroepitaxy measurements and MBE simulations. A large difference between DyO and ScO<sub>2</sub> surface diffusivity is assumed in the SOS model. Actual measurements of the diffusivity of  $SrRuO_3$  on both terminations will provide quantitative information on the diffusivity difference. For instance by measuring the RHEED recovery time as a function of temperature. This requires a large dataset and requires to be able to precisely control the surface termination. This could be done by studying single oxide,  $Sc_2O_3$ ,  $Dy_2O_3$  deposition in more detail and/or use of chemical treatment.

Only initial transport measurements were attempted during this research which indicated  $SrRuO_3$  nanowire properties differ from bulk properties,  $SrRuO_3$  nanowires seem to have a higher resistivity compared to bulk  $SrRuO_3$ . The physical properties of the nanowires are of high interest for their possible applications. These properties should be determined more precisely.  $SrRuO_3$  shows a metal insulator transition on  $SrTiO_3$  substrates as a function of film thickness[2]. This transition is expected to be different on  $DyScO_3$  substrates due to the tensile instead of compressive strain on  $DyScO_3$  with respect to  $SrTiO_3$ . This transition might occur in the nanowires as well and could provide more information about the mechanism behind the transition. Initial XPS data depicted in appendix B.3 indicate the  $SrRuO_3$  nanowires differ from thick  $SrRuO_3$  films on  $DyScO_3$  with respect to their transport properties. Conductive AFM on the nanowires could provide more information about the electrical properties as well.

PLD growth parameters were mostly kept constant during this research. Variations resulted in interesting growth behaviour depicted in appendix B.3. Changes in PLD conditions could be used to control nanowire dimensions.

 $SrRuO_3$  is sensitive to different surface terminations during growth, possibly due to it's high diffusivity or the highly volatile Ru species. It is interesting to study why  $SrRuO_3$  is sensitive to mixed termination and why this termination difference gives rise to a difference in diffusivity. There might also be other materials that show selective growth behaviour and have different functional properties. Possibly several materials can be combined to grow structured films with embedded patterns.

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Bouwe Kuiper - oktober 2009

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# Appendix A SOS Model code

Adding the full C++ SOS code to this report does not add to a better understanding of the model. Some of the most important pieces of code with respect to the actual SOS part are included in this appendix.  $^{1}$ 

### Binary chop

```
// D: start event
// U: numof events
int Grid::binary_chop(double * events, int D, int U)
{
        double R = 0; double Rh = 0; double rs, Rhlast;
        int h;
         //Calculate total R
        for (int i=D; i<U; i++) { R = R + events [i]; }
         //Generate a random number [0,R]
        rs = r \rightarrow Uniform(0,R);
        //If D = +1 the index is found
         while (U-D!=1) {
                 //Center index rounded down
                 h = D + (U - D) / 2;
                 {\rm Rhlast}\ =\ {\rm Rh};
                 //Calculate Rh upto halfway point
                 for (int i=D; i < h; i++) { Rh = Rh + events [i]; }
                 //First half reset Rh and store new limits
                 if(rs < Rh) \{ D = D; U = h; Rh = Rhlast; \}
                 //Second half save Rh and store new limits
                 else { D = h; U = U; Rh = Rh; }
        ktot = R;
        return D;
}
```

# Deposition

```
void Grid::Deposit(int atoms)
{
    for (int i=0;i<atoms;i++) {
        int n = int(floor(r->Uniform(0,H)));
        int m = int(floor(r->Uniform(0,W)));
        site[n*W+m].atom_add();
    }
```

<sup>&</sup>lt;sup>1</sup>The full code is available at request by electronic mail: b.kuiper@alumnus.utwente.nl.

# Counting the number of neighbours

```
int GridSite::neighbours (int level)
{
        int nns = 0;
        int corr = 0;
        //Up
        if (site [nn[0]]. height >=(level-corr)) nns++;
        //Down
        if(site[nn[1]].height >=(level-corr)) nns++;
        if(col==0) { corr = offset - site[nn[2]].offset; }
        else { corr = 0; }
        //Correct for offset height differences
        //Left
        if(site[nn[2]].height >=(level-corr)) nns++;
        if (col=H-1) { corr = offset - site [nn[3]].offset; }
        else { corr = 0; }
        //Correct for offset height differences
        //Right
        if(site[nn[3]].height >=(level-corr)) nns++;
        return nns;
}
```

# Rate calculation

```
double GridSite::rate(int evt) {
    double Et = EsS;
    if(height==offset+1) { Et = EsS - Es; }
    if(height<=offset) { return 0; }
    else{
        int cord = nn[evt];
        double E = Et+neighbours(height)*En;
        return k0*exp(-E/Kb/T);
    }
}</pre>
```

### Step density calculation

```
double GridSite::density(double phi) {
    double s1 = fabs(double(height-site[nn[0]].height));
    double s2 = fabs(double(height-site[nn[3]].height));
    double temp = (double)s1*cos(phi)+(double)s2*sin(phi);
    return temp;
}
```

# Height barrier

```
int GridSite::get_hbar(int evt, int levO) {
    int levN = site[nn[evt]].height;
    if(levN<=levO) {return 0;}
    else {
        return levN-levO;
    }
}</pre>
```

}

# Appendix B

# Additional results

In this chapter some additional results are given and discussed briefly. They provide complementary data or show interesting behaviour. This interesting behaviour could could be studied in more detail in the future.

## **B.1** Sc<sub>2</sub>O<sub>3</sub> on DyScO<sub>3</sub> growth

A ScO<sub>2</sub> single monolayer was deposited on DyScO<sub>3</sub> using a Sc<sub>2</sub>O<sub>3</sub> target. The corresponding RHEED and NC-AFM data are depicted in figure B.1. The RHEED intensity oscillations indicate slightly more than one monolayer was deposited, the maximum at 30 seconds was overshot by 12 pulses. The resulting film showed atomically flat terraces, but some deep holes. The origin of these deep holes is unknown. The RHEED spots remained clearly 2D even showing Kikuchi lines after growth under vacuum conditions. Growth parameters are depicted in table 2.1.

### **B.2** $Dy_2O_3$ on $DyScO_3$ growth

A DyO single monolayer was deposited on  $DyScO_3$  from a  $Dy_2O_3$  target. TM-AFM images of the resulting film depicted in figure B.2a,b show atomically flat terraces and a strong phase contrast. The phase contrast shows random areas of different phase. The RHEED intensity oscillations (e) indate a single monolayer plus one additional pulse was deposited. The RHEED signal (c),(d) remained fully 2D during and after deposition. Growth parameters are depicted in table 2.1.

### B.3 X-Ray spectroscopy data

For future comparison some XPS data are added. An overview of a thick  $SrRuO_3$  film is depicted in figure B.3a. A zoom in around the Ru and Sr levels is depicted in figure B.3b for both a thick  $SrRuO_3$  film resulting from 30 minutes of deposition and a 10 ML thick  $SrRuO_3$  film are shown. They differ only slightly in the Ru 3d3/2 peak around 284 eV, a shoulder appears for the nanowire  $SrRuO_3$  sample. This shoulder or two-peak structure could be related to the degree of electron correlation[24] and could be utilized to distinguish between insulating and metallic films. This shoulder or additional screened peak indicates a weak electron correlation and a more metallic film compared to samples that do not show this screened peak. This would indicate the thin film is more metallic than the thick  $SrRuO_3$  film. This measurement was not repeated and only performed on one sample. It interesting to study this in more detail.



Figure: B.1: Sc<sub>2</sub>O<sub>3</sub> on DyScO<sub>3</sub> growth, RHEED image before growth (c), after growth (d) and the corresponding RHEED intensity oscillation (e). NC-AFM images recorded after deposition show atomically flat terraces with unexplained deep holes.

Data from figure B.3b is scaled by first matching the low binding energy count rates and secondly by matching the high binding energy count rates. The nanowire peaks are shifted with respect to the thick film peaks by compensating the measured shift in oxygen peaks.

### **B.4** Tuning SrRuO<sub>3</sub> termination sensitivity

An SrRuO<sub>3</sub> film was grown on DyScO<sub>3</sub> using a background pressure of 0.01 mbar instead of 0.3 mbar. The RHEED oscillation period remained within 27-30 pulses per layer, depicted in figure B.4e. No double initial oscillation was detected although the second maximum at 60 seconds is slightly higher compared to the maximum at 30 seconds. The resulting film had a smooth surface, depicted in figure B.4a,b. The DyScO<sub>3</sub> substrate was cut from a larger substrate. Deposition under normal PLD conditions on an other substrate cut from the same piece resulted in wire growth. This could indicate that the sensitivity on mixed termination diffusivity difference can be tuned using the background pressure during deposition. Optimizing the pressure might result in more well defined lines. However by changing the background pressure also the SrRuO<sub>3</sub> film properties are changed. It seems interesting to investigate this in more detail.

### **B.5** Island shape control

 $SrRuO_3$  films have also been grown using a lower fluency resulting in a much slower growth rate. This resulted in square shaped islands on two occasions, depicted in figure B.5. The low growth rate could force the islands to grow in the kinetic limit. If adatoms not confined and are highly mobile the resulting film shows a minimisation of the number of kinks by creating straight step



Figure: B.2: Dy<sub>2</sub>O<sub>3</sub> on DyScO<sub>3</sub> growth. TM-AFM images (a),(b) indicate an atomically smooth film and a random phase contrast after growth. The RHEED signal (e) indicates the deposition of a single monolayer while the RHEED pattern remained fully 2D.

edges, thus resulting in square islands. This matches most SOS simulation results shown in this report, which are also kinetically limited.

The fluency could be tuned to grow square islands. Which might be interesting for studying dimension reduction phenomena and their effect on film properties. More measurements are required to prove this hypotheses, but it seems reasonable from these preliminary results.



Figure: B.3: XPS spectra. (a) overview spectrum (b) Detailed Ru, Sr spectrum 255-305 eV.



Figure: B.4: SrRuO<sub>3</sub> growth at a background pressure of 0.01 mbar showing stable RHEED oscillations (e) and a 2D film (c),(d) resulting in a smooth film (a),(b).



Figure: B.5: SrRuO<sub>3</sub> square islands on a DyScO<sub>3</sub> substrate grown at a slow growth rate. On two different samples, A and B.