# Towards comprehensive treatment of rare-earth scandate substrates, an NdScO<sub>3</sub> case study

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# 2 Abstract

NdScO<sub>3</sub> (NSO) is a rare-earth scandate suitable as a substrate application for films of other perovskites. BaTiO<sub>3</sub> (BTO), a well-known ferroelectric perovskite, is an interesting material for thin film deposition, as it gains almost no strain with NSO, which makes domain changes at that phase possible to be comprehended in detail. This study investigates different strategies for treating NSO substrates before deposition, relating the quality of their topmost surface with the characteristics of the films deposited on top by means of Pulsed Laser Deposition (PLD). A more in-depth exploration of the steps in the production of films considers all possible factors that contribute to a lack of reproducible epitaxial films, including the quality of the target materials for deposition and the PLD process itself, which rises to the suggestion of using Pulsed Laser Interval Deposition (PLID) to relax the surface between pulses.

# 3 Introduction

Perovskite materials have become more and more popular through the years due to their electronic, magnetic and physical properties. One of those properties, piezoelectricity is investigated for among others, energy harvesting from vibrations. Although the power output is low, these devices can be used to power low power systems, like watches, sensors or microelectrochemical systems, that only need  $\mu$ W or mW levels of power <sup>1,2</sup>. One perovskite material is barium titanate, BaTiO<sub>3</sub>. Its bulk piezoelectric and pyroelectric properties were described in 1962<sup>3</sup>. It's properties have been thoroughly investigated as a bulk crystal, but not as much as a thin film. As a thin film, materials develop new properties, due to not only a constraint in one dimension, the height is in the micrometer range, the small size also makes it easier to apply a constant strain to the material with a substrate. The piezoelectric response of thin film barium titanate has been investigated to be around 7mW/cm<sup>2</sup><sup>4</sup>. It also has domain transformations within certain phases of the material that haven't been investigated in depth yet, making it a prime candidate to analyse further. A common substrate for thin films is silicon, although its crystal structure is not compatible with perovskite materials. A perovskite substrate that is used often, is strontium titanate. Rare-earth (RE) scandates are a good suggestion as a substrate. They are also perovskite materials with a similar molecular size to BTO. Out of those, neodymium scandate, NdScO<sub>3</sub>, comes the closest with a molecular size that is the same of BTO. The catch is that NSO hasn't been used and investigated on as much as other RE scandates, like dysprosium scandate (DSO). This makes it a more difficult substrate to use, since procedures to epitaxially grow barium titanate on it have to be made up from scratch or adapted from different, more commonly used substrates like dysprosium scandate or strontium titanate.

# 3.1 Crystal representations with Bravais lattices, Miller indices and space groups

# 3.1.1 Bravais Lattices

To understand how a crystal is structured, it needs to be described in some way. This is done with Bravais lattices. There are 14 Bravais lattices that describe all different kinds of crystals. They are based on three vectors, a, b and c, for the three spatial dimensions and form together a quadrilateral polyhedron. The 14 lattices differ not only in angle and size between vectors, but also in placement of atoms within them. Bravais lattices are categorized with two variables: the centring type and the lattice system. The centring type describes the reference points within a lattice for atoms to lie in. Lattice systems are the shape of the lattice, described by the relative length of dimensions and angle between. There are four centring types and seven lattice systems that are categorized within the Bravais lattices. The four centring types are: primitive (P), base-centred (A, B or C), body-centred (I) and Face-centred (F). In primitive lattices, only the corners of the polyhedron are used for lattice points. Base-centred lattices have an additional point to P at the centre of one face and its parallel face of the polyhedron. Body-centred lattices have an additional point to P in the centre of the polyhedron. Face-centred lattices have an additional points to P in the centre of all faces of the polyhedron.

The lattice systems are from least to most symmetry: triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal and cubic. Triclinic lattices have different lengths for a, b and c and the angles between the vectors are all different. Monoclinic lattices have two vectors with the same length and two angles at 90°. Orthorhombic lattices have all vector lengths different, but all angles between them at 90°. Tetragonal lattices have two vectors with the same length and all angles at 90°. Rhombohedral vectors have the same length and angle, but not at 90°. Hexagonal lattices have 2 vectors share the same length, two angles are 90° and one is 120°. Hexagonal lattices can form a hexagon shape, which is where the name comes from. The last lattices are cubic. Their vectors are all at the same length and have a 90° angle between them. Together these can describe the bases of the crystal structure of all crystalline materials.

Bravais	Parameters	Simple (P)	Volume	Base	Face
lattice			centered (I)	centered (C)	centered (F)
Triclinic	$a_1  eq a_2  eq a_3 \ lpha_{12}  eq lpha_{23}  eq lpha_{31}$	Ш			
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$		j.		
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$		Į.		V.
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$		Į.		
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^{\circ}$	$\widehat{\mathbb{Q}}$			
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^{\circ}$		X		×.
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

Figure 1 All possible Bravais Lattices<sup>5</sup>.

# 3.1.2 Miller indices à, a, $\vec{a}_1$ (001) (100) (010) ₫ı (110) (101) (011) $\vec{a}_3$ (0T1) (T10) (T01) (111) (111) (T11) **a**. (11T) (102) (T02)

When a direction or a plane within a crystal lattice has to be noted, Miller indices are used. These are three positive or negative integers representing the reciprocal of the three vectors, h, k and l, representing the x, y and z axis enclosed by round brackets: (hkl). 1 is the whole length of the vector, 2 is half the length, 0 is an infinite length, etc. Negative numbers are written with a bar above them. Together they describe a plane within the crystal lattices. The set of all planes with the same integers is noted by curly brackets, {hkl}, and represents the symmetrical planes of all 8 possible positive and negative combinations: (h, k, l), (h, k, l), (h, k, l), (h, k, l), (h, k, l) & (h, k, l), (h, k, l).

A direction within a lattice is represented by the perpendicular direction of the plane (hkl) from the origin, noted with square brackets: [hkl]. For example, a (111) plane is a triangle within the lattice that touches three corners of that lattice a single unit away from the origin. The [111] vector will go from the origin perpendicularly through the plane. Just like planes, directions have sets. The sets of crystal directions is noted by angle brackets, <hkl>, and have the same symmetry requirements as the planes.

For hexagonal lattices the Miller indices are a bit different, there is a fourth integer, i, in between k and I: (hkil). h + k + I =0 is a requirement in this indication. This means that (110) becomes (1120). The first three integers provide information about the three directions in the hexagonal x y plane and the last integer indicates the z plane. This makes it easier to visualize the miller indices for hexagonal structures.

Figure 2 Examples for Miller indices.

#### 3.1.3 Space groups

Symmetry is very important in crystallography. The symmetry of a crystal structure can say a lot about the structure, so if all symmetry elements are found of a system, then the structure can be determined. Space groups group the symmetry elements of crystals in what kinds of symmetry they have. The elements consist of symmetry operations, point groups, and translational symmetry operations, space groups. With both the rule is that once an operation is performed, the new configuration has to be identical to the old.

The operations in point groups are: Reflection, rotation, inversion and improper rotation. Reflections, or mirror planes, inverse one dimension, while keeping the other dimensions the same. For example if there is a (100) mirror plane, then x will be mirrored, but y and z will stay the same:  $(x, y, z) \rightarrow (-x, y, z)$ . A rotation will have an axis in some direction around which the atoms will rotate. It's a full rotation divided by a number of parts. For example, a 4 fold rotation will rotate the crystal by 90°. Inversions will inverse the whole system from a certain inversion point. If the inversion is at the origin, then (x, y, z) will inverse into (-x, -y, -z). Improper rotations are a combination of a rotation axis and a perpendicular mirror plane.

The translational symmetry operations are: pure translation, glide plane and screw axis. Pure translations will translate an atom by a single lattice in a certain direction. A glide plane adds a mirror

plane to the translation. There are 5 different glide planes: a, b, c, n and d. A, b and c glide planes translate parallel to a given direction half a unit cell and mirror along that and the a, b or c direction. N glide planes are mirrored diagonally and d glide planes are translated a quarter of a unit cell and are also mirrored diagonally.

A screw axis adds a rotation axis to the translation, parallel to that translation. Screw axes are noted by a number with a subscripted number. The first number is the rotation axis and the subscripted number is that number divided by the first number of translation of the lattice. For example a  $3_1$ screw axis will rotate 180° and translate 1/3 of a unit cell parallel to the screw axis direction. There are a limited number of screw axes. The only possibilities are 2, 3, 4 & 6 and their translations are 1 to 1 less than the rotation axis, so for example for a 4 fold rotation axis, there are 3 screw axes:  $4_1$ ,  $4_2$ &  $4_3$ .

Combining all these operation results in 230 distinct space groups. These space groups are noted by 4 symbols. The first is the centring type. The other three are symmetry operations. These are glide planes, screw axes or a mirror plane, which is notated as an m.

#### 3.2 Materials

## 3.2.1 Perovskite metal oxides

The materials used in this project are perovskite metal oxides. Perovskite materials contain 3 elements with an ABX<sub>3</sub> chemical formula. A and B are cations with different sizes and X is an anion. Perovskite materials have numerous properties, like piezoelectric or thermoelectric, and applications, like photovoltaic devices. There are many options of cation and anions. These give a wide variety of possible combinations and materials. All materials used in this project have a perovskite structure. These are barium titanate, neodymium scandate and strontium ruthanate, SrRuO<sub>3</sub> (SRO).



Figure 3 Crystal structure of a perovskite material. The blue sphere is A, the black spheres are B and the red spheres are X.

# 3.2.2 Barium Titanate

Everhardt<sup>6</sup> investigated the structure of barium titanate (BaTiO<sub>3</sub>). It was discovered during the second world war as a material with a dielectric constant much higher than any other found at the time and is still the most widely used ferroelectric material.<sup>7</sup> Ba<sup>2+</sup>Ti<sup>4+</sup>O<sup>2-</sup><sub>3</sub> is a perovskite material with a tetragonal structure at room temperature. The unit cell parameters are a=b=3.992 Å and c=4.035 Å<sup>8</sup>. This perovskite material has a range of multiple phases in which piezoelectric domains form. The ca<sub>1</sub>/ca<sub>2</sub> phase (Figure 4) transitions from one to the other in a temperature range of 80°C to 25°C (Figure 5). Herein stripes can be seen with a piezo force microscope (PFM). When lowering the temperature, the stripes will go perpendicular to the original stripes until all stripes are shifted to the new domain. During the previous research, the formation of original stripes on the perpendicular stripes during cool down was observed to originate from other original stripes and propagate in between existing lines. The goal was to research this domain change in depth



Figure 4 Phase diagram of misfit strain versus temperature of  $BaTiO_3$ <sup>9</sup>. The graph shows the different phases dependent on temperature and misfit strain. The combination phases are portrayed below and all four contain two perpendicular facing domains that can occur, where the a/c and a<sub>1</sub>/a<sub>2</sub> are completely perpendicular and the aa\*/ca\* and ca<sub>1</sub>/ca<sub>2</sub> phases are slightly tilted versions of the other two respectively.



Figure 5 Temperature-dependent lateral PFM of BTO with 0 misfit strain. A) a/b domains at room temperature before measurement. B-f) Cooling down from the paraelectric phase at 200°C, starting at 70°C with 10°C interval. At 70°C the domain stripes are perpendicularly aligned and during cool down, the original stripes start to come back<sup>6</sup>.

#### 3.2.3 Rare-Earth Scandates

Materials that are promising as a substrate for BTO are rare-earth (RE) scandates. The RE elements that work with scandate are Dy, Gd and Nd. Others are radioactive or not stable.



Figure 6 Lattice constants (Å) of various perovskite thin films and substrates<sup>10</sup>, going from 3.70 to 4.00 Å, with BTO on the right most. The top materials are thin films and the bottom are substrates. For the substrates, the RE-scandates are closer to BTO's lattice constant than LaAlO<sub>3</sub> or StTiO<sub>3</sub>, which are other common perovskite substrates. NSO is the closest of the RE-scandates and has the same lattice parameter as BTO.

#### 3.2.3.1 Neodymium Scandate

The substrate used to get 0 misfit strain should have the same lattice constant as BTO. From Figure 6, it can be seen that neodymium scandate (NdScO<sub>3</sub>, NSO) is a good candidate as a substrate for BTO with 0 misfit strain. NSO however is orthorhombic with a  $P_{nma}$  space group. In a (100) cut substrate, NSO would not be compatible, however when cut through the (110) direction, it looks pseudo cubic and almost perfectly matches the lattice constant of that of BTO. This orientation consists of layers of

 $NdO^+$  and  $ScO_2^-$ , which are polar. This polarity can intervene with experimental procedures, so it needs to be accounted for if unexpected results come forth.

Although close, substrates are never cut at exactly the angle that is wanted to receive a single layer on top of the material. There is always a slight error in the angle of this cut, called a miscut. The angle of the miscut determines how many layers of the crystal are cut through. The surface of the substrate then looks filled with jagged edges. When the crystal layers are straightened, the surface look like terraces of a mountain farm. A low miscut cuts through less layers than a higher miscut and therefore will have wider terraces than a high miscut.



Figure 7 Representation of the surface of a perovskite material. A)  $ABO_3$  unit cell with blue A a RE metal ion, yellow B a transition metal and white oxygen. B) A received substrate. The blue AO layers are on top of the yellow  $BO_2$  layers. The step height of the terraces are at ~2, 4 and 6 Å. C) A single terminated substrate after treatment where the  $BO_2$  layer is on top<sup>11</sup>.

#### 3.3 Diffusion

While stationary, individual molecules still move randomly in a liquid or gas, which is based on temperature. They amount of collisions makes the movement unorderly. This is called Brownian motion. When a dye is added to water, it's initial density of numbers is the highest at the source spot and will gradually dissipate through the liquid until the density of dye in water is equal through the whole container. Brownian motion explains the process, as the dye molecules will collide with the water and get displaced through the volume. This displacement is called diffusion. Diffusion is continuous and it's speed is dependent on the temperature. It does end when all chemicals are mixed together, but is unnoticeable after equilibrium is formed. Diffusion is also possible for solids, but restricted. Surface diffusion is one way of solid diffusion and is restricted to two dimensions. An adatom, which can be foreign or part of the material itself, needs a high enough temperature to get activated. This activation energy for diffusion,  $E_{a,diff}$ , can be expressed by the Arrhenius equation<sup>12</sup>:

$$D = D_0 e^{\frac{E_{a,diff}}{RT}}$$
3.1

Where D is the diffusion coefficient,  $D_0$  is the diffusion coefficient at infinite temperature and T the temperature in Kelvin. This Arrhenius equation gives the exponential relation between the temperature and diffusivity of a material on a surface. With the diffusion coefficient and diffusion

interval,  $\tau$ , diffusion over a mean distance, d, using a two-dimensional random walk expression can be calculated<sup>12</sup>:

$$d = \sqrt{D\tau}$$
 3.2

From here the relationship between distance and time can be easily seen as quadratic.

Bulk diffusion is also possible. In this case material can flow from the inside out of the surface. This occurs at higher temperatures than surface diffusion.

#### 3.4 Techniques and equipments

#### 3.4.1 Atomic force microscopy

Atomic force microscopy (AFM) is a form of scanning probe microscopy (SPM). In SPM a probe traces around the surface of a sample to define its topography. Because the movement of the probe is measured, the surface height can be measured precisely. AFM, like its name suggests, uses physical force of a needle on a cantilever to probe a surface. The cantilever is moved close to the surface, until the needle touches it, which bends the cantilever. Multiple variables can be measured from here. The force that the cantilever applies and the movement of the cantilever itself are some of them. To measure the movement of the cantilever, a laser is used. This laser is focused on the tip of the cantilever at an angle and reflects onto a photodiode<sup>13</sup>, see Figure 8. When the cantilever bends, the angle changes and the beam will hit a different spot of the photodiode. The size of the cantilever is in the scale of micrometers and the radius of the tip of the needle is in the nanometer scale. This setup can measure height differences in the scale of hundredths of nanometers, which makes it a great technique to analyse single lattice height differences in substrates. Measurements done in this thesis were from areas of 1 to 10 micrometers. This size is appropriate for NSO. The surface and terraces are well visible and can be measured for their height and width. Smaller and larger areas are possible to scan too. The two most used measuring methods are contact mode and tapping mode.



Figure 8 Schematic view of an AFM. A laserlight is deflected from the probing tip onto a photodetector to record its movement<sup>13</sup>.

The simplest method of scanning a sample is by dragging the needle along the surface of the sample and is therefore called contact mode. A piezoelectric device holding the tip to the machine can precisely move the tip up and down. By changing the height of the tip to adjust the force put on the substrate to be constant, the height can be measured of the surface.

Tapping the surface with a tip is also possible, by vibrating the tip. The tip will oscillate close to its resonant frequency by the piezoelectric element. When the vibrating tip comes close to a surface, its tapping frequency and amplitude will change slightly due to the force the tip and the surface apply to each other. These extra variables can give more information about the scanned surface. A phase map of the surface can be made, where the phase change is plotted instead of the height. Also the amplitude error can be plotted. The amplitude error shows shifts in amplitude of the tip, which occur when it reaches a change in height, like at the edge of a grain or unit cell.

A disadvantage of using a probe is that it can interfere with imaging the surface of a sample. When it is too big to fit in a well, only part of the well will be imaged and it will look like a small pit. The same can happen with a steep hill that is still narrow. The width of the tip can make it look a lot wider than that it is.

The speed of making a scan with an AFM is also a lot slower than other microscopes. Since a physical probe needs to be dragged along the surface, it takes a certain time to record a surface area, while a light microscope can receive the whole image relatively immediately. The scanning speed is dependent on the movement speed of the tip, the size of the scan and the number of lines that are scanned. More lines give a higher resolutions, but also lengthen the scanning time. Scanning speed also affects the resolution. Lowering the tip velocity gives the tip more time to distinguish small changes in the surface. This lower speed also affects the phase change and amplitude error, since with a lower scanning speed, the tip can adapt easier to big changes in the surface. Dragging the tip across a surface wears the tip. A blunt tip amplifies tip effect, distorts the image and

Dragging the tip across a surface wears the tip. A blunt tip amplifies tip effect, distorts the image and makes an all in all lower quality image. Regular replacement is required to keep sharp tips with workable precision

# 3.4.2 Piezo force microscopy

It's possible to test the piezo effect of a material with SPM. A piezo force microscope (PFM) works the same as an AFM, but can also polarize a sample. This way piezoelectric domains and their deformation directions can be found.

A piezoelectric material distorts when an electrical bias is applied to it. The direction of displacement is based on the direction of the electric bias and the shape of the material. Domains within a material can have differently orientated piezoelectric displacement. This property can be used to distinguish the domains within a grain, crystal or layer of a material.

A sample that is piezo electric, can deform slightly while the tip is probing and applying an alternating current bias to it. This deformation will bend the tip laterally and vertically (Figure 9)<sup>14</sup>. A requirement for PFM is that the material underneath the sample is conducting, so that a bias can be applied to the sample. Because NSO, the substrate necessary for BTO to be in the desired phase, has

a low conductivity, an electrode layer of SRO has to be deposited between NSO and BTO.



Figure 9 Piezoelectric response affecting PFM tip<sup>14</sup>. Besides height changes from the surface, the rotation and tilting can displace the tip when a bias is applied. In this picture the applied bias <u>distorts</u> the crystal and displaces the tip in one domain in the x direction and the other in the z direction.

#### 3.4.3 Scanning electron microscopy

Scanning electron microscopes, SEM, use an electron beam to visualize a sample. Electrons are used because their "wavelength" is much shorter than that of usable light in microscopes. This makes SEMs great for nanoscale microscopy. There are two methods of detecting electrons scattered from a sample: Secondary electron and backscatter electron detection. Images can be made in real time, making it much faster than AFM. It's also easier and faster to change spots and magnification of the sample. Drawbacks are that first of all the sample has to be conducting to emit electrons, otherwise the sample will just charge from the electrons that are bombarded onto it. If a sample that is non-conducting, like biological samples, is subject to the SEM, it can be coated with gold by gold sputtering, to get a conductive surface of the sample. Even with conducting materials, charging can still occur and the scanned surface will look darker than non-scanned surfaces. Also scans have to be done in low pressure, so that gas molecules don't interfere with the electron beam. Because atoms in the samples get bombarded with electrons, they can also emit x-rays from releasing their energy.

There are a couple of different types of electrons that can be captured by an SEM. When an electron from the beam hits a sample atom, an electron from that atom will be kicked out. That electron gets detected by the detector and an image can be made. This is called a secondary electron. The electrons from the beam can also be reflected from the sample, called backscatter electrons. A separate detector detects them. Heavier atoms scatter electrons stronger than light atoms, so this technique can be used to distinguish between different masses.

#### 3.4.3.1 Energy dispersive X-ray spectroscopy

If a lower orbiting electron gets knocked out of an atom by the electron beam, a higher electron can fall back to the unoccupied space and emit an x-ray from the switch. These orbital changes are characteristic per element and can thus be used in spectroscopy combined with the electron microscopy part. A beam can be focussed on single spots, lines of spots or whole surface areas of spots in a surface that's being scanned. The emitted x-rays are then detected by energy. The machine has a database of most of all elements and their electron shell energies to determine from which elements the x-rays come from. This is called energy dispersive x-ray spectroscopy (EDX). EDX is used to find the presence and relative abundance of elements in a sample. To be as accurate as possible and to make it easier for the machine to calculate which elements are in the scanned spot and at what percentage, the known elements in the sample have to be selected. As a result the machine can show the percentage and change of elements in a scanned area.

#### 3.4.4 X-ray Diffraction

To find the structure of a crystalline material, x-rays can be used. X-rays have a small enough wavelength, that they can go in between the atoms of a crystal. When they approach a crystal at a certain angle, they can reflect back, due to the distance between the atoms acting as grating interfering with the x-rays. The pattern of dots that come from diffracting can then be used to calculate these distances. It is a reciprocal space map of the crystal. When diffraction is done on a single crystal, this map can be made in 2D, but with thin films or polycrystalline materials only a 1D map can be made. A cathode tube is used to make the x-rays. It is a vacuum tube that has an anode that shoots electrons to a cathode at a certain voltage. The emitted x-ray wavelength depends on the used voltage and the metal cathode. Copper is used in the x-ray diffraction, XRD, machines used in the experiments. The x-rays that the tube emits consist of bremsstrahlung and excitations characteristic per element. In the case of copper these are K<sub>a1</sub>, K<sub>a2</sub> and K<sub>β</sub> get filtered out and K<sub>a1</sub> is used for the diffraction and its wavelength is 1.5406 Å. K<sub>a2</sub> is not filtered out, due to its wavelength being close to that of K<sub>a1</sub>. Braggs law is used to calculate the crystal lattice and directions of the diffracted light through the crystal<sup>15</sup>:

$$n\lambda = 2dSin(\theta) \tag{3.3}$$

Here n is an integer,  $\lambda$  is the wavelength of the used x-rays, d is the length between two parallel crystal planes and  $\theta$  is the incident angle of the x-rays. In XRD, the angle between the x-ray gun and the receiving slit is used as a variable, which is 2 times the incident angle, 2 $\theta$ , and the response is the intensity collected by the photodiode on the other side. This intensity is best measured in counts per second (cps) to take measurement time into account. The intensity peaks recorded from the diffractometer can then be used to calculate the d value and from there which crystal direction the peak is on. This is performed with the following formula:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$
 3.4

a, b and c are the length of each side in the lattice and h, k and l are the Miller indices. It only applies with lattices where the sides are all 90° apart from each other. It can also be simplified if the structure is tetragonal, making a=b, and if it is cubic, making a=b=c, reducing the formula to:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
 3.5

This also makes it clearer that any multiple of (hkl) can be reduced with n:  $d = \frac{a}{\sqrt{(2h)^2 + (2k)^2 + (2l)^2}} = \frac{a}{2\sqrt{h^2 + k^2 + l^2}}$ . This and other tricks can be used to find both the Miller indices per angle and from that the dimensions of the lattices. The found Miller indices can give information about the Bravais lattice. Some lattices have excluded Miller indices, since the reflections are forbidden. It can also be seen in the diffraction pattern if the lattices are orthorhombic, tetragonal or cubic. Cubic structures have the same length in all 3 directions, so (100), (010) and (001) are all the same, while for orthorhombic systems they give different peaks.

#### 3.4.4.1 Thin Film X-ray Diffraction

For thin films on substrates there is a separate XRD machine. It can move the substrate in all six axes and scan the substrate at a high range of angles. Since it can move in all directions, the highest possible intensity can be found before making a scan. A drawback is that the x-rays will penetrate the thin film and substrate from only the cut direction. If the thin film is single crystalline, then that direction won't show up in the diffraction pattern. This can also be an advantage, since less peaks will show up and the calculations can be simpler if the incident direction is known.

#### 3.4.4.2 Powder X-ray Diffraction

When an XRD pattern is made for powders a different machine is used. In this machine only the scan angle can be changed. Powders contain multiple crystals, so there is no perfect direction for the machine to scan. To be certain that an average direction is taken of the powder, it can be rotated perpendicularly to the scanning axis while a scan is being made. The rotation speed can be changed. Although this is an easier method of obtaining an XRD pattern of a sample, the peaks are broader than that of thin films, due to slightly differently angled grains of crystals within the pellet.

# 3.4.4.3 X-ray reflectivity

Pure reflection of x-rays can also be used to gain information about thin films. X-ray reflectivity (XRR) uses the same thin film machine as thin film XRD, but at low angles from ~0 to 7 degrees. At these angles the x-rays reflect from the sample, while partially penetrating it. The interferences introduced by the sample tell about the thickness and density of the thin films in the samples. Oscillations within the signal are related to the thickness of the films. The highest intensity of the reflection is related to the density of the film.

# 3.4.5 Pulsed Laser Deposition

The technique used to get a layer of (B)SRO and BTO on NSO was pulsed laser deposition. It vaporizes target material with a high powered laser inside of a vacuum chamber with a tightly controlled environment. PLD was popularized after an Y-Ba-Cu-O compound with high T<sub>c</sub> superconductivity was discovered<sup>16</sup> and is used in many thin film deposition techniques requiring specific oxygen levels and epitaxial growth. First a laser pulses on a target material. This material heats up rapidly, becoming a plasma and blows out of the target, see Figure 10. It then hits a substrate, gets adsorbed and forms a new layer on top of the substrate. Multiple pulses are needed to form a layer on the substrate and it is possible to deposit multiple layers on top of each other. A vacuum is necessary for this process, to keep the plasma from interacting with other molecules or particles before depositing on the substrate. The temperature of the chamber can also be changed to manipulate the growth of new layers. Due to the relaxation of deposited material, if the deposition rate is too high, islands may form instead of an epitaxial layer. Introducing an interval into the process gives time for the deposited material to relax on the surface and grow layer by layer. This is called pulsed laser interval deposition<sup>17</sup>.



Figure 10 Inside a PLD chamber. A plasma of target material is blown onto a substrate<sup>18</sup>.

#### 3.4.6 Reflection high-energy electron diffraction

During the deposition of material in the PLD, electron diffraction can be used to measure the progress of deposition. Reflection high-energy electron diffraction (RHEED) gives information about the surface of a substrate. In this research two properties of RHEED were used: The pattern itself and the intensity change during deposition. The pattern gives information about the topology. The intensity change during deposition is due to growth of layers on top of the substrate. Like XRD, RHEED shines a beam at an angle on a sample, which gets diffracted and recorded by a phosphor screen, which is shielded from ablated PLD material. The electron beam in RHEED comes from an electron gun and gets focused on the sample at a glancing angle. The shorter this angle, the less the material is penetrated and more signal comes from the surface. The beam splits in lines and describes the reciprocal space of the surface, see Figure 11. In the reciprocal space the crystallinity and roughness among others can be determined. The pressure of the PLD chamber is an important contributor in RHEED noise. Electrons in high pressure collide easily with gas particles and a combination of elastic and inelastic scattering<sup>19</sup>, defocussing the electron beam. The difference between 10<sup>-5</sup> and 50 Pa of pressure can completely remove Kikuchi lines<sup>20</sup>, which are formed from electrons diffracting along a certain crystal direction. For many processes a relatively high pressure of O<sub>2</sub> has to be present during PLD, so that oxygen vacancies won't occur. Fortunately a method has been found to reduce the scattering of electrons at higher pressure vacuums, by adding an extension tube. In general the beam has a distance of 500 mm between the source and the substrate, while the distance between the substrate and the phosphor is around 50 mm. With an extension tube, that contains a vacuum of a pressure below 10<sup>-4</sup> Pa, the distance can be reduced to 50 mm. This makes it more feasible to do RHEED measurements at pressures like 1 Pa<sup>21</sup>.

During growth of a layer on a substrate with PLD, these lines and spots can change intensity in an oscillating pattern.<sup>22,23</sup> First there is a maximum intensity, since all electrons diffract from a flat substrate. Then a new layer gets formed and some of the electrons diffract at a slightly different angle due to the islands being a bit higher. When a layer is at 50% of its growth, half of the surface is of a different height and the intensity is at its minimum. The intensity goes up now that "holes" are being filled up and when the layer is finished, the intensity is at its local maximum, which is slightly lower than that of the first maximum. If the intensity of RHEED spots is recorded during deposition,

the number of deposited layers, i.e. number of crystal lattices, can be counted and the thickness of the layer can be calculated.



Figure 11 a) PLD setup with electron beam and RHEED screen. While material is being ablated by the laser from the target onto a substrate, an electron beam is emitting electrons perpendicularly to the substrate and the electrons are captured by the RHEED screen. B) RHEED patterns forming from electrons diffracting from the surface of the sample<sup>24</sup>.



Figure 12 RHEED oscillations during monitoring of PLD growth. A & b show the interference occurring when electrons diffract from multiple layers. C shows the progression of growth of a single layer during deposition, with d showing the corresponding RHEED intensity at that point. When  $\vartheta$ =0.5, the intensity is the lowest due to maximum interference<sup>22</sup>.

#### 3.4.7 Other equipment

For annealing a tube furnace was used. This is a small furnace that consists of a glass tube and heating elements around it. The tube is attached to an oxygen inlet to generate a high oxygen pressure environment during annealing, which can be used to remedy oxygen vacancies formed

during annealing. The used tube furnace can go to around 1200°C. The heating speed and time can also be selected.

# 3.5 Determining termination

All AFM images were made with a Bruker AFM in standard tapping mode. Scan rate was at 1Hz with a resolution of 512 lines per scan and aspect ratio 1:1. The scales used were 5µm and 1µm. These were chosen to view a manageable amount of terraces, 10-60 dependent on the cut-angle, and more detailed terraces themselves respectively. z sensor, amplitude error and the phase trace and retrace were recorded. Dependent on the quality of the recorded image, around 3 spots would be scanned: around the middle, near the edge of the substrate and some arbitrary random spot. In these spots a 5µm image was first made and if the image was of good quality, a 1 µm image was made inside the window. The images were saved as "NAME SUBSTRATENAME TREATMENT DATE IMAGENUMBER.spm". They were processed through an SPM visualization and analysis program called Gwyddion. More information about the procedure can be found in the appendix.

# 4 Experimental

# 4.1 Materials

NSO substrates of 5x5x0.5 cm were used with 5 different miscut windows: 0.03-0.04°, 0.05-0.07°, 0.07-0.1° & 0.18-0.21°, manufactured by CrysTec. These miscuts have a window of their miscut, as there is a range of terrace widths within the surface of the substrates, calculated by XRD.

In total only 13 substrates were used. Some of them were reused for multiple experiments. Table 1 summarizes all used substrates with their batch number and miscut. Although the different miscuts made it possible to analyse the effect of miscut on the annealing and deposition, this wasn't the reason that multiple miscuts were used. Each batch had substrates with two arbitrary miscuts.

Sample	batch	miscut (°)
A1	1	0.07-0.1
B5	1	0.07-0.1
C3	1	0.05-0.07
C6	1	0.05-0.07
ba2A1	2	0.07-0.1
ba2A2	2	0.07-0.1
ba2D1	2	0.18-0.21
ba2D2	2	0.18-0.21
ba2D3	2	0.18-0.21
ba3A1	3	0.03-0.04
ba3A2	3	0.03-0.04
ba3A3	3	0.03-0.04
ba3D1	3	0.18-0.21

Table 1 Used NSO substrates, batches they were from and miscut of each substrate

A single and polycrystalline BTO, one polycrystalline SRO and one polycrystalline BSRO target were used for deposition on NSO. The BTO targets were bought, while the BSRO target was produced by the group. The most used target, the single crystal BTO target, was already heavily used previously.

# 4.2 Method

# 4.2.1 DyScO<sub>3</sub> treatment

The first method was made by Everhardt during his work on NSO. He derived it from a standard RE scandate preparation made by Kleibeuker.<sup>11</sup>

- Cleaning (dust removal): sonicate 10 min. in acetone and 10 min. in ethanol (EtOH) (abs.)
- Thermal annealing: 45 min./ 900°C/ 4-6 h 18 L/h (300cc/min.)  $O_2$ -flow
- Chemical etching:
  - 4h sonication in 12M NaOH
  - 30min. sonication in 1M NaOH
  - 3x washing in deionized water (DI)
  - 1x washing in EtOH
    - Complete these steps without drying the surface

In the first step dust is removed to make sure no material gets burned onto the substrate surface during annealing. 900°C is high enough to burn dust off, but it's better to make sure none is on the surface that could interfere with annealing.

An extra step was added if particles were present on the surface. It was scrubbed with lens tissue and reannealed at a low temperature to remove particles formed on the substrates.

- Surface scrubbing: scrub lightly with a fingertip lens tissue wetted with ethanol over the surface of the substrate in a circular motion for about 30 seconds.
- If there are still numerous particles on the surface after etching and scrubbing:
  - 3x 30 min. sonication in EtOH
  - Thermal annealing 40 min./ 400°C/ 20 min. 12L/h (200 cc/min.) O<sub>2</sub>-flow

# 4.2.2 PLD of BTO on NSO

The deposition was done by Cynthia Quinteros. One or more substrates were loaded in the PLD chamber with a BTO and BSRO target inside.

[PLD treatment]

BSRO was first deposited, followed by BTO. During heating of the system and deposition, RHEED was done to follow the deposition of the layers.

# 4.2.3 Improving method

Due to perceived difference in needed etching and annealing time between different miscuts of NSO, these were tweaked a bit and experimented upon.

# 4.2.4 Analysing targets

The quality of the targets was thought to might have an impact on the deposition. XRD and SEM analyses were made to assert the quality of the targets. 3 targets were used: A single crystalline BTO target, a polycrystalline BTO target and a polycrystalline BSRO target.

# 4.2.5 Designing new method

While focussing on annealing, time and temperature were tweaked to gain desired results of straight single terminated terraces. It was found that with higher miscuts, less time (1-2h) was needed for annealing. Etching was also regarded to be more problematic than helping, so it was left out in later experiments, leaving only the cleaning and thermal annealing step.

# 5 Results

# 5.1 Substrate Preparations

The first step was preparing the substrate onto which the film will be deposited on. This step was adapted by Everhardt<sup>6</sup> for NSO from the DSO preparation of Kleibeuker<sup>11</sup>. The NSO substrates had a miscut of 0.03-0.04°, 0.05-0.07°, 0.07-0.1° and 0.18-0.21°, respectively. These came in 3 different batches containing substrates of 2 miscuts each. Every step was recorded by AFM imaging to view the quality of the terraces, the termination and any contamination such as particles.

5.1.1 -Learning procedure (from DSO)



Figure 13 AFM images of first full treatment of a 0.05-0.07° miscut NSO substrate. The scale bar of A is applicable to B and C to D. A) NSO as received. Terraces are hardly visible. B) NSO substrate after 8 hours of annealing at 900°C. Terraces are visible, but not straight and filled with islands and holes. C) After etching for 2 hours in 12M NaOH. Particles have formed on the surface. The substrate is also by eye visibly dirty, as seen on the top right image. The shadow is from the AFM tip and around 2mm wide. D) After reannealing at 500°C to remove particles. It still looks the same as B.

The first experiment was a full procedure performed on a 0.05-0.07° miscut substrate. The substrate was placed in a tube furnace with a steady 18 L/h O2 flow, lying down on a ceramic container. It was warmed up to 900°C for 45 minutes, followed by annealing for 4 hours. Afterwards it was gradually cooled down to room temperature, which took 2-4 hours. AFM images of the topography of the surface show a gradual diffusion of surface atoms straightening the terraces in order to lower the surface area into an equilibrium state. Islands and holes were present, while the edges were not

straight. Annealing a second time under same conditions to continue diffusion did not improve the straightness of the edges, see Figure 13 B, and the substrate was etched to continue the procedure.

The substrate was submerged in a 12 M NaOH solution containing beaker and sonicated for 2 hours, after which it was transferred to a beaker containing 1 M NaOH and sonicated for 30 minutes, not to let the etched material settle on the substrate. The substrate was then rinsed 3 times with deionized water and 1 time with ethanol, after which it got dried by a nitrogen gun. Figure 13 C shows the results of this step. Etched material did settle down on the surface and was clearly visible with the eye. Scrubbing the surface with an ethanol wetted lens tissue for roughly 30 seconds in circular motion did remove some material, but it was still visible through the camera of the AFM (Figure 13 C smaller picture). Scanning a relatively clean area did not prevent finding particles. These were between 50 and 100 nm in diameter. The substrate was reannealed at 500°C for 20 minutes with 12 L/h O2 flow. This temperature was high enough to remove particles, but low enough that surface diffusion did not occur. The substrate looked the same as before etching (Figure 13 D), making the 500°C step successful, but the whole procedure unsuccessful.



Figure 14 AFM images (height) of 2 different NSO substrates with a miscut of 0.18-0.21°. The left was annealed for 4 times, going from 1 to 4 hours with 1 hour interval. The right was annealed the same number of times from 10 to 4 hours with 2 hours interval. In total the left was annealed for 10 hours and the right for 28 hours. Terraces were already straight after 1 hour of annealing and reannealing did not reset the surface. Particles started to show up from 3 hours of total annealing. For the right substrate, it looks like particles showed up at the second procedure, but after the first one particles were visible and the images were scanned around them.

The annealing time has been found to influence the termination of DSO substrates<sup>25</sup>. To investigate if NSO is influenced similarly, two substrates with miscut of 0.18-0.21° were annealed for different durations: 1, 2, 3 and 4 hours for the first substrate and 10, 8, 6 and 4 hours for the second substrate (Figure 14 left and right respectively). These durations and orders were chosen under the assumption that reannealing a substrate would reset the surface. By having 4 hours of annealing for both substrates as the last treatment, they should look similar. This experiment showed that the terraces were not straightening, regardless of the time per annealing step. For the 1, 2, 3 & 4h annealed substrate (Figure 14 left), the surface was already fairly straight after one hour of annealing. Particles started to show up after the third annealing with in total 6 hours annealed. For the third and fourth

annealing it is visible that the particles were inhibiting the straightening of the terraces. The terraces were flowing around the particles on the surface.

The 10, 8, 6 & 4h annealed substrate (Figure 14 right) already looked finished after 10 hours of annealing. Particles were visible with just the camera of the AFM, but were avoidable. One particle is visible in the picture of the second annealing, after a total time of 18 hours of annealing. Even though it was annealed for a total of 24 hours at the third annealing session, the substrate was looking better than the third annealing session with a total annealing time of 6 hours of the other substrate. Particles were not everywhere and the terraces were still straight. The last annealing brought particles to the surface, destroying the step-terrace morphology. It looked much like the left substrate at the last step. In total the two substrates were annealed for 10 and 24 hours, respectively.

#### 5.2 Diffusion of terraces



Figure 15 AFM images of diffusion of NSO substrates from untreated to almost straight terrace edges from left to right. The first four pictures (A-D) were of substrates with a miscut of 0.03-0.04°. The last picture, E, used a 0.18-0.21° miscut substrate. These pictures are all windows of the same size cut from pictures with the same parameters. As received, A, the terraces can be visible. There is not a well-defined edge and the layers are sporadically spread out. B) When the substrate is at a high enough temperature for the surface to diffuse, the layers clump together, forming holes and islands. From this step the terraces are clearly visible. C) During diffusion, holes will move out of and islands will combine with the terraces. The edge of the terraces is also clearly visible. D) All holes are removed and all islands are combined. The edge is still undulating from formation. E) The terraces are finished and the edges are mostly straight.

During the research, many pictures of different stages diffusion of the substrate terraces were made. This made it possible to make an assumption to how terraces form from the rough cut surface. Terraces are possible to be found before any treatment has been done. This is more prominent with low miscut substrates, as the terraces are wider. High miscut substrates will mostly look like noise, as the terraces are so small. ( $\pm 1 \mu m$  wide at 0.03-0.04° and  $\pm 0.5 \mu m$  at 0.18-0.21°). In Figure 15 A, three terraces and holes of a fourth are visible of an untreated substrate with a 0.03-0.04° miscut. The edges of the terraces are rough and sporadic. After 2 hours of annealing at 900°C, the surface has had enough time to combine into terraces with well-defined edges. There still are parts of material that haven't combined with the terrace and holes in the terrace that aren't removed from the terrace. Figure 15 C is a substrate annealed for 14 hours. All holes have been removed, some islands are still present. [It is assumed that this process happens due to surface tension of the material. It wants to interact as little with the air as possible. Removing holes and islands, reduces the vertical surface area and straightening the edges reduces the length of the edge of the terrace, therefore

again reducing surface tension. Figure 15 D is a different area of the same collection of AFM images and is further progressed. All islands are removed, but the edge is still undulating from the removal and combination. Figure 15 E is the closest to being straight. It is a 0.18-0.21° miscut substrate annealed for only 2 hours.



5.2.1 Annealing temperature

Figure 16 AFM images of 2 NSO substrates with a 0.07-0.1° miscut annealed at 1000°C for 1 hour. Substrate A looks decently straightened. There is a clear line at the edge in the phase trace and retrace, but there is no contrast, indicating possible double termination. Substrate B looks not only double terminated from the phase trace and retrace, but also from the height. The image isn't sharp and the edges are less straight than A. There's also a particle in the middle of the image.

Everhardt stated that annealing at 1000°C would diffuse material from the bulk to the top, resulting in particles on the surface. This was tested on two substrates with a 0.07-0.1° miscut. They were annealed for 1 hour and did not have as many particles on the surface as expected, but did have some remarkable results. Figure 16 shows the height and phase trace and retrace of the two substrates, named A and B. A was just slightly wavy and looked fairly straight. There wasn't phase contrast, but the phase changes did only occur at the edge of the terraces. This might mean that the substrate is double terminated, but can also be an artifact of the AFM tip. Substrate B looked a lot different. It not only had a particle in the middle, but also was far better defined as double terminated. From the height image, it was noticeable that the terrace edges were waving more than A and that there were height differences on the terrace itself. There was also no contrast in the phase, but more importantly, there were two different phases that had roughly the same surface area and weren't defined by just the terrace edge. This is a good indication of double termination, since the tip of the AFM is interacting with two different surfaces and therefore the phase changes on not the tip changing height, but environment. Unfortunately Figure 16 B wasn't sharp, due to some issues during recording. This meant that recording the step height wasn't possible.



Figure 17 AFM image of two NSO substrates that were annealed for 2 hours at 900°C at same scale.. The top substrate has a miscut of 0.18-0.21°. The bottom substrate has a miscut of 0.03-0.04°. The height (Z sensor), phase trace and retrace are shown at the same scale. Both substrates have contrasting phases. The height, and phase images are a continuation of the same image.

Annealing results varied widely between substrates. The high amount of different miscuts made it hard to find the best annealing time for a substrate to finish diffusing. This was most prominent with the highest miscut received, 0.18-0.21°. After one hour of annealing, the substrate looked similar to substrates of lower miscuts that had to be annealed for 4-6 hours. Comparing the highest miscut with the lowest was the best option to show what the effect of the miscut was to annealing the substrates. These two miscuts were 0.18-0.21° and 0.03-0.04°. The first notable difference was the terrace size between the two substrates. At the high miscut, the terrace width is 70 to 100 nm, while the lowest miscut has a terrace width of 500 to 600 nm. This has to influence the amount of necessary annealing. In Figure 17 two substrates are shown. The top with the highest and the bottom

with the lowest miscut. They were both annealed for 2 hours at 900°C and the images are at the same scale. The top substrate is mostly straight and has narrow terraces. The bottom substrate has much wider terraces and contains islands and holes. On the phase side, these two substrates do have contrasting phase. This is clearly visible on the top substrate, which has brighter lines on the edges during phase trace and darker during phase retrace, indicating a jump of the tip from one layer to the other up and down. Although it is harder to see, this is also the case for the low miscut substrate. Both lighter and darker lines are visible in the trace and retrace. This is due to the tip tracing both up and down terraces from the islands and holes on the surface.

These results show that the annealing time is dependent on the width of the terraces and therefore the miscut of the substrates. It is also apparent that to get single terminated substrates, annealing time is not required to be 4-6 hours, since it's possible for the lowest and the highest miscut to get the correct termination at 2 hours of annealing.



Figure 18 2 hour annealed substrate of 0.18-0.21° miscut with two different scans. Although the measured terrace heights are averaged at 3.5Å and both are from the same collection of scans, the scans have contradicting phase contrast. A has a clear contrast between the phase during the trace and retrace of the tip. The phase trace and retrace of B are identical.

Phase contrast and step heights 5.2.3

From the start of the experiments, it was hard to find a good relation between phase contrast and step height. Although it's relatively easy to see if there is contrast in the phase trace and retrace, the polarity of the substrate and speed of the tip was problematic. These two variables made it possible for single terminated substrates to show no contrast in phase trace and retrace. For all substrates that were measured, they looked single terminated. From the AFM and analysis software (Gwyddion) the lowest recorded step height didn't go below 3 Å for the substrates annealed after the procedure was completely understood. For the first couple of substrates some terraces with 2 Å step heights was recorded, but these were not measured and treated as well as later substrates. In fact, etching the substrates would not just form particles on the surface of the substrates, but also make it more difficult to find single termination in the substrates. Contact mode was considered as an alternative to tapping mode for AFM imaging, which was quickly abandoned due to a lack of knowledge in the technique.

5.2.4 Particle formation and an effect



Figure 19 AFM image of a 0.18-0.21° miscut substrate annealed for a total of 38 hours in 5 sessions. The edges are generally more crooked than wavy, except for ~0.5 um around the ~1 um particle, where the terraces are mostly straight, but bending toward the particle. On the top right is an image of the camera. Large particles are visible and scattered all over the surface.

After annealing the same substrate as Figure 14 B for a last time for 10 hours, the AFM showed some strange anomalies from the previous treatments. Particles were more visible on the surface and even with the naked eye. Figure 19 contains one of these visible particles. It has a diameter of about 1  $\mu$ m

and what looks like an extra radius of  $1 \mu m$  of differently terminated terraces around it. A smaller single particle is lying on the top left and gives the possibility to easily compare the difference between the large particle and the previously seen particles scattered around the surface. Since the image is focused on the terraces, the large particle is oversaturated, but some shapes are still visible around particle. It is possible that this is a cluster of smaller particles like the one of the top left. The terraces around the large particles have a different shape to the terraces at the rest of the image. They are smoother and form around the large particle, while the rest of the terraces are more crooked.



Figure 20 Visualization of the orthorhombic NSO. Sc is purple, Nd is orange and O is red. A red (001) plane is projected through the ScO layer and a parallel green plane going through the NdO2 layer. The blue and green planes are the (110) planes for the layers respectively. The perovskite structure can be made by using the Sc atoms as corners of a pseudocubic structure. A) An overview of the whole structure. B) The structure perpendicular to the c axis, showing the (110) planes from the front.

NSO has an orthorhombic lattice structure, but to get the perovskite, the lattice has to change. By rotating the structure 45° and halving the c axis, the perovskite structure is visible. The transformations for the axes are:

$$a, b \rightarrow \frac{1}{2}\sqrt{a^2 + b^2}$$
  
 $c \rightarrow \frac{c}{2}$ 

The resulting lattice is close to 4Å in all sides, but the c axis is slightly larger, making the structure pseudocubic.

The (001) and (110) planes are shown in Figure 20. They are similar as they cut through the same type of layers, but the structure is pseudocubic and not as symmetrical as a standard perovskite [figure perovskite] structure. This makes it important to know if there is a difference in length between the (001) and (110) layers. The layers have been calculated to be 1.998Å for the (110)

planes and 2.0018Å for the (001) planes. This difference is less than 0.2%. In Figure 20 B the front view of the (110) plane is visible. The Sc atoms are aligned, but the Nd center atoms are slightly shifted from their neighbors. It was the question if this would affect the distance between terraces, but can be neglected, as each step is still ~2Å. Although not necessarily confirmed, the information of CrysTec can be trusted that all substrates are cut through the (110) plane. It might be possible that some substrates have been cut through the (001) plane, but the difference is negligible.



Figure 21 powder XRD images of the measured crystalline and ceramic BTO target, together with the calculated powder XRD peaks for BTO. All peaks are shown linearly, except for the <111> and <002> peaks, which are shown on a logarithmic scale to accommodate to low intensity peaks. The ceramic and crystalline <00l> peaks were a bit shifted for the ceramic target compared to the single crystal. Except for 2 very low intensity peaks at 40.5° and 41°, The single crystal target only had <00l> peaks, while the ceramic target had all possible peaks. These peaks were also shifted by 0.5° for all peaks, suggesting that the ceramic substrate was misaligned during diffraction.

The single crystal BTO target was showing signs of age. There was a visible crack going through the crystal. During PLD the surface would first be ablated for clean material to emerge. To make sure that the target wasn't too contaminated and that the ceramic BTO target was a suitable alternative, a powder xrd scan was done on the two targets. In Figure 21 top a linear image of the XRD can be seen. The single crystal target only shows peaks for the <00I> family of diffraction directions, while the ceramic target has all possible diffractions. A note on the ceramic target is that all peaks are shifted by 0.5°. This could be that the dimensions were slightly off from the calculated peaks of Figure 21 bottom, but this shift was constant throughout the whole scan from the <001> peaks to the <113> peaks. Misalignment through the preparation of the powder XRD scan is a better explanation for this shift. The scan was also plotted logarithmically. For the ceramic target, no additional peaks were found, but the single crystal target did have some peaks show up. Most new peaks were between 30 and 45°, with others around 20, 65 and 80°. This can be caused by a couple of factors. The first is some material recrystallizing on the surface, showing different diffraction angles of BTO outside of the <001> family. The second factor is different material being deposited onto the surface during any process.



5.3.3 SEM images of BTO

Figure 22 SEM backscatter images of the single crystal BTO target. Multiple spots were analyzed at different magnifications. A) top right corner with one major crack and multiple small vertical cracks with even distance between each other. B) Edge of ablated material. The cracks from A are easier visible and are perpendicular to the ablation edge. C) Zoomed in ablated edge at a different spot. D) A spot with a lot of contrast. The area is not looking smooth like most of A or B.

The BTO single crystal target surface was analyzed by SEM. Since it had been used for multiple PLD procedures before, it had a visible crack and might be damaged so much that material couldn't be ablated correctly from the target anymore. The crack is shown in A. The picture also shows small cracks vertically aligned to the target with a fairly consistent width between each crack. A bit down of A the edge of the ablated material is shown in B. The cracks from A are more visible and there is a clear distinct edge between where the material is ablated and is still clean. The cracks look like they

are introduced from stress occurring during high heating of the surface by the IR laser during ablation. C is a different spot of the target and the ablated edge. This image also contains vertical cracks like in A and B. It looks like a layer of material on top of new material that was behind ablated BTO. Noticeable are also the vertical waves on the top layer. Lastly a spot was chosen that looked polycrystalline or amorphous. This was investigated more in depth with EDS.





Lsec: 50.0 411 Cnts 0.970 keV Det: Octane Super

#### **eZAF Smart Quant Results**

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
OK	13.68	44.37	725.80	9.61	0.0439	1.3836	0.2318	1.0000
SiK	1.41	2.61	234.76	9.26	0.0103	1.2628	0.5774	1.0065
SrL	5.29	3.14	432.96	6 <mark>.0</mark> 3	0.0368	0.9499	0.7302	1.0015
BaL	51.56	19.48	1575.77	3.15	0.4446	0.8412	1.0270	0.9981
TiK	28.06	30.41	2539.44	2.81	0.3044	1.0905	0.9627	1.0333

Figure 23 EDS of a single crystal BTO target. Chosen elements for fitting were: O, Si, Sr, Ba and Ti. These were for BaTiO<sub>3</sub> and possible contaminants silicon and SrRuO<sub>3</sub>. The Sr peak is at the same spot as an Si peak, which might offset the abundance at the EDS spot.

During the SEM imaging it was also possible to do EDS. A spot was chosen that looked particularly amorphous and contaminated, see Fig. Since The BTO target was in the PLD chamber with an SRO target, it was expected that if there were some contaminants that Sr would be one of them. RuO<sub>2</sub> is a volatile compound, so Ru is unlikely to be detectable on BTO. Si was also chosen as a possible contaminant, as it is used often as a substrate. From the EDS scan a trace amount of Sr and Si was found. The Sr peak did combine with an Si peak, making it possible that the percentage that was fitted for the graph wasn't completely correct. It did prove that there are contaminants on the target at the moment of recording.

#### 5.4 Growth conditions



Figure 24 RHEED recording of BSRO deposition onto an NSO substrate.. Oscillations from deposition are visible during the BSRO deposition from 1 to 6.5 minutes. The top right shows the recorded areas of the RHEED image. The blue and green spot showed the highest amplitudes during deposition.

During PLD RHEED images were recorded to investigate the progress of the surface. In Figure 24 The intensity if 5 spots in a RHEED image recorded are shown. Both the deposition of BSRO on NSO (A) and BTO on BSRO (B) were recorded. Oscillations for BSRO deposition are visible from just before 1 minute to 6.5 minutes into recording. In total 21 oscillations were counted for spot D and E and slightly visible for C and H, indicating that about 21 layers of BSRO were deposited on NSO. The oscillations started off rough, started regulating at 1.5 minutes and had a regular amplitude around the 3 minute mark. The lattice parameters of BSRO are about 4Å, so a height of 21\*4 = 84Å is expected. The deposition of BTO didn't look as smooth. No oscillations were done on the sample and lamellae were cut from it to analyse the layer heights in a scanning tunnelling electron microscope. The width was measured as ~10 nm for BSRO and 140 nm for BTO. 10 nm is 4 layers of BSRO more than counted. This can be because of a miscount or because the last 4 layers weren't deposited epitaxially anymore.

#### 5.4.2 XRR of deposited and clean substrate

XRR were performed on a number of scandates and again when material was deposited on them. Fig. Shows a graph of the XRR of one NSO substrate without BSRO and BTO and with the two layers from 0 to 3.5°. Counterintuitively, the oscillations were visible in the undeposited substrate, while there were no oscillations in the deposited substrate. This made it impossible to do height or density calculations on the layers, reaffirming that these layers were not grown epitaxially.



Figure 25 X-ray reflectivity image of a substrate, blue, and a deposited substrate, yellow. Remarkable are the oscillations on the substrate without any layers of different material on top and the retraction of the highest intensity peak going from 0.6° to 0.3°.

# 6 Discussion

# 6.1 Difficulties in determining double and single termination from AFM

Double and single termination can be seen in two ways on the AFM. The first is with the phase trace and retrace. The phase of the image will show irregularities in the surface of the sample. When the tip of the AFM goes up a terrace, it will have a slight delay between moving the tip up and it experiencing the surface getting higher. This change will slightly alter the frequency of the vibration of the tip. The opposite should also happen when the tip goes down a terrace, since it has more room instead of less room to vibrate. This means that a single terminated substrate will have distinct lines at the edges of the terraces and should be the opposite change with the trace compared to the retrace, like Figure 17 and Figure 18 A. Double terminated substrates should look identically in the trace and retrace of the phase. This is because the environment can also change the phase of the tip. NSO is polar<sup>10</sup>, which means that the tip will be disturbed by the change of  $SCO_2^-$  to NdO<sup>+</sup> and vice versa. This change is not different between phase trace and retrace, since it's still going from one layer to another, instead of going up and down a terrace. Double terminated substrates should therefore have identical phase trace and retrace. This however is not completely true. If the tip is moving fast enough, then the transition from each terrace is not different any more with going up and down, so an identical phase trace and retrace image could still be single terminated. The terrace step height is a different option. Single terminated substrates should have a step height of 4Å, completing a whole unit cell. Half a unit cell or 1 and a half, 2 and 6 Å respectively, would then mean double termination. This however has been proven to be unclear, since no resulting step height has been exactly 4 or 2 Å. They are mostly in between, which makes it hard to determine exactly what the termination is. Additional Table 1 shows the step height for the last procedure of all

substrates. These heights are all between 3.5 and 4.7Å. That is a maximum difference of 17.5%, which could be attributed to how it was recorded and through noise from the image. The heights however are all far closer to 4Å than 2Å. If double termination occurs in these substrates, it can only be at the step edge and would only be seen as part of the full step.

## 6.1 Necessity of etching

Wet etching is used in many preparations of perovskite substrates<sup>26</sup>. It is used to remove unwanted sublayers from the surface and make it single terminated. In the case of NSO, this was difficult. The double termination can occur all around the surface. It can form like islands and holes, as a whole terrace in itself, or a miniscule sub step before the next terrace. From the start of first treatment of the first substrate, it was clear that etching resulted in the forming of particles on top of the substrate. These particles come from the hydroxide that gets formed when the dissolved NaOH reacts with the NdO<sup>+</sup> and ScO<sub>2</sub><sup>-</sup> layers into Nd(OH)<sub>n</sub> and Sc(OH)<sub>m</sub>. These two hydroxides should then have dissolve into the water that is constantly agitated by the sonication bath<sup>27</sup>. This was not the case and gave a lot of trouble to the substrates. Scrubbing the substrates with lens tissue did remove the particles a bit and reannealing also helped, but once particles were on the surface, they were extremely difficult to remove every single one of them. This started the idea that etching was maybe not the best option for NSO. From just annealing the substrate, the terraces already looked single terminated and didn't need help from etching. This is opposing the procedures that state the necessity, but from conversations with other groups that treat other perovskite substrates, they don't etch or even anneal the substrate and let the heating of the PLD chamber be enough.

#### 6.2 Importance of annealing

#### 6.2.1 Straightness of terraces

From the results of all substrates, it was apparent that the edges of the substrates moved from a wavy state when received to straight edges after enough annealing, dependent on the miscut. It was very noticeable that the terraces behaved diffusively and wanted to minimize surface energy by minimizing the terrace edge length. The following function<sup>10,28–31</sup> explains the free surface energy,  $\gamma$ :

$$\gamma(\theta, T) = \gamma^{0}(T) + \beta(T) \left(\frac{\tan\theta}{h}\right) + g(T) \left(\frac{\tan\theta}{h}\right)^{3}$$
6.1

In here T is the temperature,  $\theta$  is the cut-angle, h is the step height, tan  $\theta$ /h is the terrace width.  $\gamma^0(T)$  is the free energy of the surface tension of the terraces.  $\beta(T)$  is the free energy for a single step. The last part is based on the terrace interaction and is inversely proportional to the square of the terrace width. This function is contradictory to the results of the experiment. It was stated that the miscut should be lower than 0.1°, to obtain single unit cell steps<sup>10</sup>, but miscuts of up to 0.18-0.21° were used and they still had a step height of one unit cell. This function is also more based on the width of the substrates and not necessarily the formation of the step-edge.

To get the annealing time, the two equations 3.1 and 3.2 give a good approximation. Since these equations are mostly for single adatoms moving multiple Ångströms in distance and the annealing time being very arbitrary, this is not a completely quantitative way of calculating  $E_{a,diff}$ ,  $D_0$  and the annealing time for each miscut, but it does give a relation between them. First of all, the diffusion coefficient should be calculated from the two-dimensional random walk expression,  $D = d^2/\tau$ . d is a bit hard to define, as the starting point and end point for all surface material is not exact, but if the width of a substrate terrace contains the extremes of the diffusion material and the middle the

endpoint, then d can be described as half the terrace width. Calculating from the results of two samples annealed at 900°C and 1000°C for 1 hour, the results are:

Sample	Miscut (°)	Temperature (K)	terrace width (m)	d (m)	Expected annealing time (s)	D (m²/s)
ba2D1	0.18-0.21	1173.15	1.18E-07	5.88E-08	7200	4.80E-19
ba2A2	0.07-0.1	1273.15	2.70E-07	1.35E-07	7200	2.52E-18

Table 2 calculations of diffusion coefficient from two different samples.

With these two diffusion coefficients at their respective temperature, the activation energy of diffusion is  $E_{a,diff} = 206.23 \text{ kJ mol}^{-1}$  and  $D_0 = 7.30*10^{-10} \text{ m}^2\text{s}^{-1}$ . These two constants are not exact, but function as an approximate value to the true value, usable to calculate the annealing time for other substrates.

Miscut	Mean	terrace width (m)	d	Annealing time r	nin. And max. (h)
0.18-0.21	0.195	1.18E-07	5.88E-08	1	2
0.07-0.1	0.085	2.70E-07	1.35E-07	5.26	10.53
0.05-0.07	0.06	3.82E-07	1.91E-07	10.56	21.13
0.03-0.04	0.035	6.55E-07	3.27E-07	31.04	62.08

Table 3 Annealing time calculated for each miscut based on 1 to 2 hours for 0.18-0.21°.

The annealing time window in the calculations of Table 3 Annealing time calculated for each miscut based on 1 to 2 hours for 0.18-0.21°. look close to the experimental results. The annealing windows are large with lower miscuts, which is seen experimentally with the substrates too.

Figure 15 shows the progress in the substrates from as received to straight edged terraces. This is a mix of different substrates, but this process works in every one of them, just at different speeds. In Figure 15 A the terraces are already visible. The jaggedness of the edges make them as wide as the terrace itself, but the surface energy can only be reduced when the surface can diffuse and come together. Figure 15 B is after the substrate has had enough time to form clearly visible terraces, but not with straight edges. The same occurs in Figure 13. The visible islands and holes are formed during drift. The islands were part of the terrace that got together, but didn't attach to the bulk terrace. The holes formed when two "peninsulas" attach to each other. One "peninsula" can attach its end to the rest of a substrate as well to form holes. The parts with holes will try to remove them by thinning out the terrace between the hole and the outside of the terrace, until it opens, which is visible in Figure 15 C. At the stage of Figure 15 D, all holes are removed and islands are connected to the terrace. The substrate is now still a bit wavy, but will straighten more until it finally gets to Figure 15 E. At this point the terraces are almost as straight as possible. Diffusion is still happening, but unnoticeable.

#### 6.2.2 Occurrence of half lattices

It was regarded at the start of the project that etching was a necessity. From annealing alone however, the substrates looked single terminated though. This and the problem of particles forming during etching, made annealing more important than thought before. The only questions left for annealing was: Are the apparent single terminated terraces really all single terminated and if so, is there still a bit of an in between layer at the edge? This layer can be below or above the terrace and can inhibit epitaxial growth. These were not found and hopefully were not hidden due to their small size of ~10nm. Double termination can sometimes be seen easily. Figure 16 B is the clearest example of this. Although the image is blurry, a darker, lower, terrace can be seen on each terrace. The phase also clearly shows two distinctly different kinds of terrace, suggesting that the tip senses a different environment. A different example is Figure 19. By following the terraces around the particle for 3  $\mu$ m, new terraces are seen in between the others. Half terraces that form underneath the terrace at the edge of the next terrace haven't been found. If measured, the AFM should note a 1.5 lattice change, but the rise has never been more than 5 Å. Another reason that these holes might not occur is that they increase surface energy and diffusion will reduce that, fixing these holes. That is less possible for half terraces, which still do increase surface energy, but can't easily be fixed with just surface diffusion.

#### 6.2.3 Dependence on miscut

Due to the large amount of different miscuts used, the relation between them and annealing was easy to find. This was the clearest with the lowest and highest miscut. The highest miscut (0.18-0.21°) needed only a maximum of 2 hours of annealing to become straight and single terminated. The lowest miscut (0.03-0.04°) on the other hand took 10-14 hours and still wasn't straight. This was thanks to the terrace width of the substrates. For the lowest miscut (0.03-0.04°), a measured terrace width was 0.5  $\mu$ m and calculated with the expected terrace height of 4 Å it was 0.65  $\mu$ m. The 0.18-0.21° miscut had a terrace width of 0.12  $\mu$ m both calculated and measured from one substrate. This is a difference of 1:5.6. That's a huge difference when surface diffusion is involved. That's a 5.6 times increase in the free energy and a 5.6<sup>3</sup> ≈ 175 times increase in the terrace interaction. Although the free surface energy ,  $\gamma$ , does not directly give the necessary annealing time, it does show the significance of miscuts and their surface energy affecting surface diffusion. In a follow up study the factors of  $\gamma$ :  $\gamma^0(T)$ ,  $\beta(T)$  & g(T) might be found and calculated to get a necessary needed time for diffusion.

# 6.2.4 Possibility of reannealing

While at first it was thought that annealing a substrate a second, or third time, would reset the annealing process, later experiments showed that they only added up to each other. Although etching and annealing are different from each other, once particles are introduced onto the substrate, annealing does not remove all of them. When they are sitting on the substrate, the terraces will also form around them and will not get straight.

Annealing is possible to do in multiple steps. The surface can diffuse at a high enough temperature. Below that, it freezes until it's at a high enough temperature again. This means that a substrate can be reannealed, but not that what has been done can be reverted by just annealing again. It is however important to mention that the amount of particles on the surface may increase after every application. Figure 14 is an example of more particles appearing regardless of the annealing time. Both substrates look similar after 4 times of annealing, while having a wide difference in total annealing time. That's why it's recommended to reanneal as little as possible.

# 6.2.5 Formation of particles on the surface during annealing

During the process of annealing, over time particles would form on the surface. This would happen after at least 4 hours of annealing at 900°C and already after 1 hour at 1000°C. These particles differed from size. Their size ranged from 100nm to 1µm and were similar to the particles forming during etching. They weren't analysed, so it can only be guessed what they were. The first suggestion is that they were dust, but annealing at 500°C after etching and annealing at 900°C and 1000°C should burn off any organic material. Residue left from a different sample could be another possibility. There was a case of silver paste contaminating the furnace tube. This was only a problem for around a week and particles should have deposited on the surface immediately during annealing, but most substrates annealed at 900°C didn't have particles on them when annealed for 1-3 hours. Oxygen vacancies can also be a cause of particles forming. In one experiment, the O<sub>2</sub> valve wasn't turned on and after annealing the substrate was filled with particles. This complies with the oxygen vacancy explanation, since there wasn't a high enough flow of O<sub>2</sub> to reduce the release of O<sub>2</sub> out of the substrate during annealing. The last possibility is that due to the higher temperature, the free energy is so high, that material can flow out of the bulk of the material and collect at the surface of the substrate.

In Figure 19 a particle of ~1 $\mu$ m is seen that has a 1 $\mu$ m radius terraces around it that are straighter than the rest of the terraces in the image. This was of a substrate that was annealed 5 times at 900°C and for 38 hours in total. After each treatment more particles appeared, but after the last treatment that was 10 hours long, the density was lower than before, but the particles were so big that they were even visible from just the camera of the AFM (top right of Figure 19). This particle might be a cluster of smaller particles that was growing. The straightness of the terraces around it is also interesting. It must have some influence on the terraces, that could be stealing material from those terraces or protecting them from something else.

#### 6.3 PLD factors



6.3.1 PLD pulse time compared to terrace length

Figure 26 Morphological phase diagram from PLD of Zhang group<sup>26</sup>.



Figure 27 Morphological phase diagram in our PLD calculated by C. Quinteros. The brown dot is the condition the PLD is in.

The growth of BTO on NSO was in all cases not epitaxial. This was first attributed to the preparation of the substrate, but PLD conditions are of course important to consider as well. Hong et al. described that the epitaxial growth of a material on a substrate is within a window of the terrace width (L) and deposition flux (F). Figure 26 shows their calculations at 700°C, where there is a step bunching, step flow and island formation region. To get epitaxial growth, the terrace width and deposition flux should fall in this step flow window. Figure 27 was made by Quinteros. She calculated the conditions our PLD was in and noted with a brown dot where we were. It is in the step bunching

region, making it obvious why there is no epitaxial growth. Changing the PLD parameters to the step flow region, could help relieve these problems that appeared.

# 6.3.2 Used targets

Three targets were used: a single crystalline BTO target, a polycrystalline BSRO target and a polycrystalline SRO target. There was also an option to use a multi crystalline BTO target, but that one wasn't used. Because the deposition wasn't epitaxial, it was thought that it might have been the case that the BTO target was defective. From the SEM it was noticeable that this target was heavily damaged. It was filled with cracks and from EDX had traces of Sr and Ru containing particles. The target was still usable and not the main cause of the deposition problems. The polycrystalline BTO target was therefore and for the thought that a single crystalline target would deposit better, not used.

# 7 Conclusion

Due to difficulties of deposition of BTO on NSO, no analyses could be made of the domain changing properties of BTO in its zero strain phase. The preparation steps of NSO were therefore investigated more in depth. Through the experiments it turned out that etching gave negligible results for providing single terminated terraces and that annealing was far more important. Furthermore, etching gave rise to particles that deposited onto the surface.

The miscut of a substrate determines the annealing duration quadratically. This duration needed to be as low as possible to diminish the probability of bulk surface interaction and particle formation on the surface. The highest miscut substrates (0.18-0.21°) gave the best results. Their short terraces made annealing quick (1 hour at 900°C) and clean and are most suited for deposited material to attach to and grow epitaxially. In the end, although not proven, the PLD parameters were off and caused the non-epitaxial growth of both the BSRO and the BTO layer. PLID could be another solution to relax the surface and gain epitaxial growth.

# 8 References

- 1. Vullers, R. J. M., van Schaijk, R., Doms, I., van Hoof, C. & Mertens, R. Micropower energy harvesting. *Solid-State Electronics* **53**, 684–693 (2009).
- 2. Hajati, A. & Kim, S. G. Ultra-wide bandwidth piezoelectric energy harvesting. *Applied Physics Letters* **99**, 083105 (2011).
- 3. Cook, W. R., Berlincourt, D. A. & Scholz, F. J. Thermal Expansion and Pyroelectricity in Lead Titanate Zirconate and Barium Titanate. *Journal of Applied Physics* **34**, 1392–1398 (1963).
- 4. Park, K. il *et al.* Piezoelectric BaTiO3 thin film nanogenerator on plastic substrates. *Nano Letters* **10**, 4939–4943 (2010).
- 5. File:Miller Indices Felix Kling.svg Wikimedia Commons. https://commons.wikimedia.org/wiki/File:Miller\_Indices\_Felix\_Kling.svg#filelinks.
- 6. Everhardt, A. Novel phases in ferroelectric BaTiO3 thin films: Enhanced piezoelectricity and low hysteresis. 104 (2017).
- 7. Randall, C. A., Newnham, R. E. & Cross, L. E. *History of the First Ferroelectric Oxide, BaTiO 3*.
- Kwei, G. H., Lawson, A. C., Billinge, S. J. L. & Cheong, S.-W. Structures of the Ferroelectric Phases of Barium Titanate. J. Phys. Chem vol. 97 https://pubs.acs.org/sharingguidelines (1993).
- 9. Everhardt, A. S., Matzen, S., Domingo, N., Catalan, G. & Noheda, B. Ferroelectric Domain Structures in Low-Strain BaTiO3. *Advanced Electronic Materials* **2**, (2016).
- 10. Biswas, A., Yang, C. H., Ramesh, R. & Jeong, Y. H. Atomically flat single terminated oxide substrate surfaces. *Progress in Surface Science* **92**, 117–141 (2017).
- 11. Kleibeuker, J. E. *et al.* Atomically defined rare-earth scandate crystal surfaces. *Advanced Functional Materials* **20**, 3490–3496 (2010).
- 12. Atkins, P. & de Paula, J. *Physical chemistry*. (2014).
- 13. Butt, H. J., Cappella, B. & Kappl, M. Force measurements with the atomic force microscope: Technique, interpretation and applications. *Surface Science Reports* vol. 59 1–152 (2005).
- 14. Kalinin, S. v. *et al.* Vector piezoresponse force microscopy. *Microscopy and Microanalysis* **12**, 206–220 (2006).
- 15. Stanjek, H. & Häusler, W. Basics of X-ray Diffraction. Hyperfine Interactions vol. 154 (2004).
- 16. Wu, M. K. *et al.* Superconductivity at 93 K in a new mixed-phase Yb-Ba-Cu-O compound system at ambient pressure. *Physical Review Letters* **58**, 908–910 (1987).
- 17. Koster, G., Rijnders, G. J. H. M., Blank, D. H. A. & Rogalla, H. Imposed layer-by-layer growth by pulsed laser interval deposition. *Applied Physics Letters* **74**, 3729–3731 (1999).
- File:Pulsed Laser Deposition in Action.jpg Wikimedia Commons. https://commons.wikimedia.org/wiki/File:Pulsed\_Laser\_Deposition\_in\_Action.jpg.
- 19. García, G., Blanco, F. & Williart, A. Cross-sections for electron scattering by O 2 at intermediate and high energies, 0.1-10 keV. *Chemical Physics Letters* **335**, 227–233 (2001).

- 20. Rijnders, G. & Blank, D. H. A. Real-Time Growth Monitoring by High-Pressure Rheed During Pulsed Laser Deposition. *Thin Films and Heterostructures for Oxide Electronics* 355–384 (2005) doi:10.1007/0-387-26089-7\_12.
- 21. Karl, H. & Stritzker, B. Reflection high-energy electron diffraction oscillations modulated by laser-pulse deposited YBa2Cu3O7-x. *Physical Review Letters* **69**, 2939–2942 (1992).
- 22. Hasegawa, S. Reflection High-Energy Electron Diffraction. in *Characterization of Materials* 1– 14 (John Wiley & Sons, Inc., 2012). doi:10.1002/0471266965.com139.
- 23. Neave, J. H., Joyce, B. A., Dobson, P. J. & Norton, N. Dynamics of film growth of GaAs by MBE from Rheed observations. *Applied Physics A Solids and Surfaces* **31**, 1–8 (1983).
- 24. Kuiper, B. *Size effects in epitaxial oxide thin films*. *PhD Thesis* (2014). doi:10.3990/1.9789036536097.
- 25. Dirsyte, R. *et al.* Thermal-induced change in surface termination of DyScO3(110). *Surface Science* **604**, (2010).
- 26. Hong, W. *et al.* Persistent step-flow growth of strained films on vicinal substrates. *Physical Review Letters* **95**, 095501 (2005).
- 27. Koster, G., Kropman, B. L., Rijnders, G. J. H. M., Blank, D. H. A. & Rogalla, H. Quasi-ideal strontium titanate crystal surfaces through formation of strontium hydroxide. *Applied Physics Letters* **73**, 2920–2922 (1998).
- 28. Williams, E. D. Surface steps and surface morphology: understanding macroscopic phenomena from atomic observations. *Surface Science* **299–300**, 502–524 (1994).
- 29. Gyu Bong Cho, Kamada, Y. & Yamamoto, M. Studies of self-organized steps and terraces in inclined SrTiO3 (001) substrate by atomic force microscopy. *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers* **40**, 4666–4671 (2001).
- 30. Krug, J., Tonchev, V., Stoyanov, S. & Pimpinelli, A. Scaling properties of step bunches induced by sublimation and related mechanisms. *Physical Review B Condensed Matter and Materials Physics* **71**, 045412 (2005).
- 31. Pimpinelli, A., Tonchev, V., Videcoq, A. & Vladimirova, M. Scaling and universality of selforganized patterns on unstable vicinal surfaces. *Physical Review Letters* **88**, 2061031–2061034 (2002).

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# 10 Appendix

10.1 Abbreviation	าร	
Barium titanate	BaTiO₃	BTO
Neodymium scandate	NaScO₃	NSO
Dysprosium scandate	DyScO₃	DSO
Strontium titanate	SrTiO₃	STO
Strontium ruthanate	SrRuO₃	SRO
Barium strontium ruthanate	Ba <sub>x</sub> Sr <sub>1-x</sub> RuO <sub>3</sub>	BSRO
Rare-earth		RE
Deionized water		DI
Ethanol	$C_2H_6O$	EtOH
Atomic force microscope		AFM
Scanning probe microscope		SPM
Piezo force microscope		PFM
Scanning electron microscope		SEM
Energy Dispersive x-ray spectr	oscopy	EDX
X-ray diffraction		XRD
X-ray reflectivity		XRR
Reflection high-energy electro	n diffraction	RHEED
Primitive		Р
Base-centred (A, B or C)		A, B or C
Body-centred		I
Face-centred		F

# 10.2 AFM image procedures

For visualization and analysis the free SPM visualization and analysis program Gwyddion was used. When opened, the .spm file contains all recorded images of the AFM scan in their raw form. The raw images have to be edited to be easily visible. First the color, giving height data, can be changed. The standard colors of the image are black and white, going from the lowest to the highest number of the recorded variable. This can be changed to a number of palettes. The one used in the images shown in here is Gwyddion.net, which transitions from black to white with red, orange and yellow in between. This palette makes the height of AFM images easier to see.

Raw AFM data can be messy due to microscopic changes in the environment during a scan. Most of that is negated by enclosing the machine in a soundproof, shielded and shockproof box. Still, small changes in height can occur during a scan. With the "Level data by mean plane subtraction" tool, which levels the data by subtracting its average height, the surface of the sample can be straightened.

During recording artifacts will show up from the needle not exactly being in the same environment as the last made line. These are corrected by the "align rows using various methods" tool. This tool has

8 methods that can be used to align the rows. The most consistent method was a polynomial with 5 degrees and left the least streaks in the images. This method however has difficulties when particles are on the image with a size much higher than that of the low roughness of the substrate itself. For these images the method "Median of difference" is used, which works better, since it doesn't leave shadows like the polynomial method. The last method that was used, was "Matching", which was similarly as good as "Median of differences".



Figure 28: different row alignment methods of Figure 19. A has no rows aligned. There are noticeable streaks between each row recorded by the tip. B) Aligned by median of differences. Most of the streaks are gone and there is a slight inverse shadow horizontally along the particle. C) Aligned by matching. Streaks are similarly removed as with median of differences. There is however a large artifact from the particle. Streaks coming from the particle are overexaggerated compared to the rest of the substrate. D) Aligned by removing a polynomial background of 5 degrees. Streaks from the needle are almost invisible. The large particle did leave a big artifact streak. The smaller particle on the left side of the image also shows a darker artifact. Because B is least affected by the large particle, median of difference was used for Figure 19.

Now that the image is visible, it can still be improved by changing the color range. This range was good with the raw image, but the improvements done also made the differences in the variable smaller. In the tool "Stretch color range to part of data" a minimum and maximum value can be

assigned to be represented with the colors. Anything outside that will be the same color as the maximum or minimum. Using this tool a specific height range within an image . This was mostly done when larger particles on the surface made the range too high to see the details of the surface. With the corrected image, the surface height can be measured. First the terraces should be levelled, to accurately define the step height of each terrace. The tools "Level data to make facets point upward" and "Level data by fitting a plane through three points" can do this. The first one does it automatically, but can be used multiple times to straighten the terraces even more. With the second tool an area is designated by three spots and the software will correct the image to get that area straight. Changing the color pallet to one with a high amount, like "Rainbow 1", helps finding if the terraces are straight. If each terrace has its own color, or at least shade, then the terraces are straight and level to the image. To find the height of each terrace, a line can be drawn with the tool "Extract profiles along arbitrary lines". It will put out a graph with the heights at each point of the line. The thickness of the line can be set from 1 to 128 pixels, visualized by perpendicular lines on the end of the drawn line. These thickness lines can be used to set the drawn line as perpendicular to the terraces as possible, to get well defined height jumps. Then the thickness can be reduced until the desired thickness that doesn't averages out the line too much, but also isn't unusably messy, is found. Further improvements can be done with the "Improve Direction" button, which orientates the line to get the best defined height that the software considers. After everything is applied, a line profile is generated that can be saved.







Figure 29 Processed AFM image through Gwyddion. A) Straightened AFM image with a drawn line to calculate the step height of the terraces. B) 3D representation of the AFM image. The length and width are in microns, while the height is in manometers to illustrate the terraces. C) Height plot from A. Each line is a terrace determined by Gwyddion and are all at a same height difference. The lines are slightly declining, indicating that the image was close to being flat.

There are a couple of ways to try to find the height of the terraces. The one used is the tool "Fit Terraces". The terraces aren't defined well enough that Gwyddion can assign the terraces itself, but there's also an option to manually select the terraces "Select region manually". The beginning and end of a terrace within the graph can then be picked. Gwyddion then calculates a single polynomial line based on the slope of all terraces (which should be close to 0) and puts this line on each terrace, making it as close to the slope of the terraces as possible (see Figure 29). The height of each terrace and other information about the polynomial fitting are then saved. By subtracting the height of a previous terrace from the height of the next terrace, the step height can be found. The average height or a histogram can then be made to find the step height of the whole substrate.

# 10.3 Additional pictures and tables

The substrates were named after the slot they were in inside the box for each batch. These boxes had a 5x5 grid with A-E for the rows and 1-6 for the columns. For the two batches of substrates after the first batch, the batch number was added to not confuse different A1 samples with each other. A1 is of batch 1, ba2A1 is of batch 2 and ba3A1 is of batch 3. In Additional Table 1 all measured procedures are given. This includes the miscut of the substrates, the procedures done on the substrate chronologically per substrate, the step height of the terraces and visual information.

Sample	batch	miscut (°)	step height after last treatment (m)	total annealing time (h)	total etching time (h)
C3	1	0.05-0.07	3.547E-10	14	4
A1	1	0.07-0.1	3.9E-10	4	0
B5	1	0.07-0.1	3.581E-10	4	0
C6	1	0.05-0.07	3.501E-10	4	8
ba2A1	2	0.07-0.1		1	4
ba2A2	2	0.07-0.1		1	6
ba2D1	2	0.18-0.21		21	0
ba2D2	2	0.18-0.21	3.67E-10	38	0
ba2D3	2	0.18-0.21	3.95176E-10	1	0
ba3A1	3	0.03-0.04	3.65E-10	14	0
ba3A2	3	0.03-0.04	3.92E-10	14	0
ba3A3	3	0.03-0.04	4.61126E-10	10	0
ba3D1	3	0.18-0.21	3.85323E-10	2	0

Additional Table 1 Summary of all used substrates. The step heights that are empty are of substrates that had too many particles on the surface to determine it, either from annealing or etching. The total annealing time was that of all procedures added up, just like the etching time.

ba2A1	ba2A1	ba2A1	<b>C</b> 6	C6	<b>C</b> 6	C6	C6	B5	B5	A1	A1	A1	ß	C3	G	ß	ß	ß	C3	Samo
0.07-0.1	0.07-0.1	0.07-0.1	0.05-0.07	0.05-0.07	0.05-0.07	0.05-0.07	0.05-0.07	0.07-0.1	0.07-0.1	0.07-0.1	0.07-0.1	0.07-0.1	0.05-0.07	0.05-0.07	0.05-0.07	0.05-0.07	0.05-0.07	0.05-0.07	0.05-0.07	niscur es
4	1	0	2	2	1		•	1	•	1	4	0	2	2	2	1	1		0	
1h 1000°C	1h 1000°C		4h	4h	4h	4h		4h	yes	4h	4h	yes	4h	4h	4h	6+4h	6+4h	6h		anne al
4h			4h		4h								4h	4h		4h				e4 64
yes			yes		yes			yes			yes		Yes	yes		yes				scrut
										yes			yes							SOD°C
3.979E-10	2.747E-10		3.501E-10	3.16E-10	3.55767E-10	2.345E-10			3.581E-10	3.9E-10	6.18E-10	4.002E-10	3.547E-10		2.332E-10	3.378E-10	3.28E-10	3.896E-10		step height (h)
no	no		no	no		no		yes*					no		no					Ahase .
					0		0								0	60	30			CONTRAST Mat. Lerr
no particles	one particle		no particles	one particle	no particles	one particle		some small particles	no particles	Less coated with the small particles	coated with extremely small particles and some bigger		some small particles		no particles	no particles	coated with extremely small particles	no particles		Rerence enere derricles
				5.00E-07		5.00E-07		2.00E-08		2.00E-08	2.00E-08		2.50E-08				2.50E-08			Particle c
Wavy	Mostly straight with long continuous islands on the	Jagged, but visible	Mostly straight	Mostly straight	Wavy with some holes	Mostly straight	Jagged, but visible	Mostly straight with a lot of islands	Mostly straight	Mostly straight	Mostly straight	Mostly straight with some holes	Mostly straight with some holes		Two distinct different kind of terrace	Better again	Less holes and islands than previous, straighter	Holes and islands, not straight	Jagged, but visible	step ette

Additional Table 2 Extended summary on procedures of all substrates.

ba2D3	ba2D3	ba2D2	ba2D2	ba2D2	ba2D2	ba2D2	ba2D2	ba2D1		ba2D1	ba2D1	ba2D1	ba2D1	ba2D1	ba2D1	ba2A2	ba2A2	ba2A2	ba2A2	ba2A1
0.18-0.21	0.18-0.21	0.18-0.21	0.18-0.21	0.18-0.21	0.18-0.21	0.18-0.21	0.18-0.21	0.18-0.21		0.18-0.21	0.18-0.21	0.18-0.21	0.18-0.21	0.18-0.21	0.18-0.21	0.07-0.1	0.07-0.1	0.07-0.1	0.07-0.1	0.07-0.1
1	0	ъ	4	ω	2	Ц	0	6		ъ	4	ω	2	1	0	1	1	1	0	1
1h		10h	4h	6h	8h	10h		10h		1h	4h	Зh	2h	1h		1h 1000°C	1h 1000°C	1h 1000°C		1h 1000°C
																6h	6h			4h
																	yes			
										yes						yes				yes
3.95176E-10		3.67E-10	4.05056E-10	5.7761E-10	3.82488E-10	3.84555E-10					3.5145E-10	3.988E-10	3.93E-10	5.6421E-10				3.734E-10		
yes and no		yes*	yes	yes	no	yes						yes	yes and no	yes and no		yes		no		
10		0	10	10	30	10						30	10	10				25		
		big particles	yes	visible with the camera	visible with the camera	visible with the camera		particles	Combination of small and bigger	filled with small particles	filled with small particles	filled with small particles				filled with small particles	filled with small particles	no particles		Filled with both small and very small particles
		7.00E-07	7.00E-08							2.00E-07	2.00E-07	1.50E-07				8.00E-08	8.00E-08			1.00E-09
wavy	barely visible terraces	jagged and straight around particles	wavy and stuck around the particles	more wavy	mostly straight	mostly straight	barely visible terraces	particles	wavy and stuck around the	wavy and stuck around the particles	wavy and stuck around the particles	wavy and stuck around the particles	mostly straight	mostly straight	No visible terraces	Holes and islands, not straight	lightly wavy, but mostly straight	lightly wavy, but mostly straight		Wavy

Additional Table 3 continuation of Additional Table 2

ba3A1	0.03-0.04	0						n	naybe visible
11004		-	104	 2 225-10	yes and	10		٧	vavy, but also containing island
DACPO	0.03-0.04	F	TOIL	3.23E-10	no	40		a	ind holes
ba3A1	0.03-0.04	2	4h	3.65E-10	yes	06		-	loles and islands, not straight
ba3A2	0.03-0.04	0						L	agged, but visible
ba3A2	0.03-0.04	1	2h	3.43803E-10	yes			H	loles and islands, not straight
ba3A2	0.03-0.04	2	12h	3.92E-10	no	70		-	loles and islands, not straight
ba3A3	0.03-0.04	0						j	agged, but visible
ba3A3	0.03-0.04	1	Oh					1	he same as received
ba3A3	0.03-0.04	2	10h 1000°C	4.61126E-10	no	40	visible with the camera	~	ery straight
ba3D1	0.18-0.2	0						п	othing visible
ba3D1	0.18-0.2	1	2h	3.85323E-10	yes	20		S	lightly wavy

Additional Table 4 continuation of Additional Table 3