Novel phases in ferroelectric BaTiO3 thin films
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Chapter 3: SrRuO$_3$ thin film growth on a NdScO$_3$ substrate

Abstract

The substrate used for all the films in the thesis, NdScO$_3$, has an anisotropic lattice, so one in-plane lattice parameter is longer than the other one. The substrate was treated to obtain a single terminated surface. Afterwards the exceptionally difficult growth of SrRuO$_3$ thin films with a $\pm2\%$ strain mismatch was obtained as described in this chapter. These SrRuO$_3$ thin films were grown to provide a suitable electrode for subsequent electrical characterization of the ferroelectric material. The laser fluence was found to be the most crucial factor determining the quality of the films, which were grown as a combination of layer-by-layer and step bunching growth modes. The SrRuO$_3$ films, while fully strained to the substrate, were found to have relatively high resistivity for this metallic material and had a significantly larger lattice parameter compared to other SrRuO$_3$ found in the literature (on different substrates). These observations were attributed to a large number of defects and vacancies. However, the films were still metallic enough to be used as bottom electrodes for the growth of the next material layer. And next to that an interesting, large increase of the metal-to-insulator transition thickness was found for this large strain state from the commonly found 4 unit cells to 8 unit cells.
Chapter 3

3.1 Rare Earth Scandate substrates

The thin films in this thesis have been grown on NdScO$_3$ substrates, bought commercially from CrysTec GmbH. The single crystal substrates have been cut with dimensions of 5x5x0.5 mm. The unit cell parameters of NdScO$_3$ and several other of the rare earth scandate family (REScO$_3$) are given in Table 3.1. The scandates have an orthorhombic symmetry (Figure 3.1), out of which a pseudocubic perovskite unit cell can be constructed. In orthorhombic notations, the out-of-plane lattice parameter of the scandates used for the thin film growth is the [110] axis, and the in-plane lattice parameters are the [-110] and [002] axes. The angles between the [002] and <110> axes is exactly 90° which means that the in-plane lattice is orthogonal. The angle between the [110] and [-110] axes is 88.027°. The used pseudocubic lattice parameters for NdScO$_3$ are 4.014 Å for the out-of-plane and one of the in-plane directions ([110] and [-110]), and 4.002 Å for the other in-plane direction ([002]). So the substrate has anisotropic in-plane lattice parameters.$^1$

<table>
<thead>
<tr>
<th>Crystal</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>0.5(a$^2$ + b$^2$)$^{1/2}$ (Å)</th>
<th>0.5c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DyScO$_3$</td>
<td>5.440</td>
<td>5.717</td>
<td>7.903</td>
<td>3.946</td>
<td>3.952</td>
</tr>
<tr>
<td>TbScO$_3$</td>
<td>5.466</td>
<td>5.731</td>
<td>7.917</td>
<td>3.960</td>
<td>3.959</td>
</tr>
<tr>
<td>GdScO$_3$</td>
<td>5.480</td>
<td>5.746</td>
<td>7.932</td>
<td>3.970</td>
<td>3.966</td>
</tr>
<tr>
<td>SmScO$_3$</td>
<td>5.527</td>
<td>5.758</td>
<td>7.965</td>
<td>3.991</td>
<td>3.983</td>
</tr>
<tr>
<td>NdScO$_3$</td>
<td>5.575</td>
<td>5.776</td>
<td>8.003</td>
<td>4.014</td>
<td>4.002</td>
</tr>
</tbody>
</table>

Table 3.1 Taken from Ref.$^{1,2}$ Lattice parameters of REScO$_3$, with RE = Dy, Tb, Gd, Sm or Nd. The lattice parameters of both the orthorhombic unit cell (first three columns) and of the pseudocubic perovskite unit cell (last two columns) are given.

Of interest for the piezoelectric properties for thin films are the elastic constants of the substrate, which will largely determine the mechanical properties of the thin film/substrate system. For NdScO$_3$ they are given in Table 3.2, and compared with the piezoelectric material BaTiO$_3$. 

Figure 3.1 Taken from Ref.$^{[3]}$ Pseudocubic unit cell of one of the REScO$_3$ substrates, DyScO$_3$, which is representative for the whole REScO$_3$ family. The size of the rare earth ion is too small for an ideal perovskite, resulting in tilting of the ScO$_6$ octahedra, $a, a, a, c, +$ in Glazer’s notation$^{[3]}$.

Figure 3.2 Adapted from Ref.$^{[4]}$ Pseudocubic lattice parameters for several rare earth scandates and other common perovskites. The red and blue lines are the lattice parameters of pseudocubic NdScO$_3$, long (110) and short ([002]) axes, measured between 25 and 200 °C. The anisotropy between those two directions decreases at higher temperatures.
SrRuO$_3$ growth on a NdScO$_3$ substrate

<table>
<thead>
<tr>
<th>Material</th>
<th>C$_{11}$</th>
<th>C$_{12}$</th>
<th>C$_{13}$</th>
<th>C$_{22}$</th>
<th>C$_{23}$</th>
<th>C$_{33}$</th>
<th>C$_{44}$</th>
<th>C$_{55}$</th>
<th>C$_{66}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdScO$_3$ (GPa) [5]</td>
<td>307.9</td>
<td>307</td>
<td>281.5</td>
<td>107.8</td>
<td>89.5</td>
<td>81.2</td>
<td>146.7</td>
<td>129.7</td>
<td>130.3</td>
</tr>
<tr>
<td>BaTiO$_3$ (GPa) [6]</td>
<td>222-275</td>
<td>151-165</td>
<td>54.4-61.1</td>
<td>113-134</td>
<td>134-179</td>
<td>111-152</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2 Taken from Ref. [5,6] Elastic constants for bulk NdScO$_3$, where the indices refer to the orthorhombic unit cell, and for BaTiO$_3$, where the indices indicate the tetragonal unit cell.

The thermal expansion for some rare earth scandates and a few other commonly used perovskites is given in Figure 3.2. Thermal expansion is of high importance because it determines the mismatch strain for thin film growth at high temperatures. Low mismatch at the growth temperature makes epitaxial growth without defects easier. Next to that, it is preferable if the thermal expansion of the substrate and thin film is similar to prevent defects formation during cooldown.

### 3.2 Scandate substrate treatment

It is important to achieve a flat and single-terminated surface of the substrate to ensure smooth and homogeneous thin film growth. For SrTiO$_3$ substrates, a well-known procedure exists to achieve such surfaces that involves chemical etching by HF acids and annealing at high temperature [7]. In 2010 a similar method has been developed for REScO$_3$ substrates by Kleibeuker et al. [8].

Substrates are cut from single crystals under a small miscut angle $\alpha$. This miscut angle is introduced, not only by accident because it is impossible to have an exactly 0 ° miscut angle, but also deliberately to make it easier to work with the substrates afterwards. The step edges that result from the angle are nucleation centers for the thin film growth and the substrate treatment. The first step in the substrate treatment is to obtain straight step edges by a heating step in a furnace. Kleibeuker et al. [7] have been using a heat treatment at 1000 °C in an oxygen environment. The time is 4 hours if the miscut angle is larger than 0.1 °, but should be increased for smaller miscut angles.

For some substrates the step edges were not yet visible before the heat treatment (Figure 3.3a). Following the heat treatment of Kleibeuker et al. [8] at 1000 °C resulted in straight step edges (Figure 3.3b), but the procedure was not fully reliable and particles on the surface of the substrates could often be found, either distributed randomly (Figure 3.3c) or mostly along the step edges (Figure 3.3d). These particles are not reported in previously mentioned literature, and can either originate from loose particles from the thermocouple which in this laboratory is only a few millimeters from the sample, or from off-calibrated furnaces: too large temperatures can create a large diffusion of the material, and some grains from the sample, or particles from the side of the sample, could migrate towards the surface. Then the temperature was reduced in several steps to 900 °C to prevent the generation of those particles. The occasions in which particles were found decreased with each temperature, but only at 900 °C they were practically never found anymore. The lower diffusivity that is paired with the decreased amount of particles also has a drawback because it means that the step edges are locally no longer straight (Figure 3.3e). Longer annealing times (Figure 3.3f) to give more diffusion did not yield more straight step edges.

The second step in the substrate treatment is a chemical treatment to selectively remove one of the two possible terminations. REScO$_3$ substrates are built up of alternating REO and ScO$_2$ layers. A single termination can be achieved if the reactivity for one of those two layers with some reactant is larger than for the other layer. While acidic solutions will not produce such selectivity, NaOH reacts faster with REO than with ScO$_2$, and it will form the soluble compound RE(OH)$_3$ [8]. Since all rare earth elements are chemically similar, this selective etching will be possible for all REScO$_3$ substrates. The overall reactivity of this etchant is quite low, so it will have to react for long times. The recipe by Kleibeuker et al. [8] requires 1 hour of etching, but here 4 hours was used to ensure single termination. Such long etching times could be used without destroying the surface since the
etching with this solution does not produce any holes in the surface.

The determination of double termination can be quite difficult in an AFM system. Sometimes it is obvious (Figure 3.4a-d) that there is double termination from the fact that there are 2 Å unit cell steps (a full perovskite unit cell is ~4 Å) and that the phase contrast in those two areas is different. But when the double termination forms small islands, smaller than the AFM cantilever resolution, it will not show up in the phase image as a different chemical surface and it will not be possible to tell if the substrate is or is not single terminated.[9] Alternatively, step edges themselves (Figure 3.4e-g) will always appear to be double terminated due to different adhesive forces when scanning down from a step edge or up onto a step edge. The step edges will show up as lines in the phase image with an enhanced or decreased phase, which should be of equal magnitude. Double termination sitting on the step edges, which is a common place for those type of defects to sit on because step edges break the homogeneity, will show up as unequal magnitudes in the phase image.

The last steps of the substrate treatment are the cleaning steps. The dissolved RE(OH)$_3$ must be washed away while they stay in solution, since otherwise they will deposit as solid particles on
SrRuO\textsubscript{3} growth on a NdScO\textsubscript{3} substrate

the surface of the substrate which are not easy to remove afterwards. For this task, after the chemical etching in a (nearly saturated) 12 M NaOH solution, the substrate was brought to a 1 M NaOH solution (for at least 30 minutes) to prevent too fast precipitation of the RE(OH)\textsubscript{3} solution on the substrate. Afterwards, it was washed three times in deionized water and once in ethanol. It was then blown dry with dried nitrogen in one smooth and fast blow to prevent the solution from slowly drying out on the surface of the substrate. The nitrogen stream blows any remaining solution to the side of the substrate where it might still precipitate into particles, but that gives less problems for later thin films since the sides or the substrates are less used anyways. It is important during this whole process to always keep the substrate wet from the top side, because otherwise the instant precipitation of particles is still possible.

If the heating step had directly created particles on the surface of the substrate, it was found that there is no method to get rid of those particles afterwards, apart from a repolishing of the surface. If the temperature of the furnace was higher than 900 °C, it was occasionally found that particles would appear after the chemical treatment, even if the chemical treatment was done correctly and the particles were not there after the heat treatment. Those particles could also not be removed by any other method than repolishing. If on the other hand particles appeared after the chemical treatment while the correct procedures for the full substrate treatment were followed, then those particles could be removed afterwards by redoing the full substrate treatment procedure. It means that those particles, which are most likely to be RE(OH)\textsubscript{3} precipitates, are different in nature from the particles that came from the heat treatment. So even if a chemical treatment has failed, the full substrate treatment can be tried many more times afterwards without repolishing.

3.3 SrRuO\textsubscript{3} thin film growth using Pulsed Laser Deposition

The perovskite material SrRuO\textsubscript{3} has mainly attracted attention because it is one of the few metallic perovskite materials, even though also some additional interest is found in its the ferromagnetic properties, chemical stability or physical structure and domains.\textsuperscript{[10]} Perovskite materials are a large class of materials with many different properties while having similar lattice constants. That makes those materials an ideal system for the epitaxial growth of strained thin films and multilayers. SrRuO\textsubscript{3} plays an important role in this strain engineering by providing an epitaxial electrode layer on which other perovskites can grow, while retaining their intended strain state.

While for most purposes it is assumed that the SrRuO\textsubscript{3} bottom electrode layer does not have any additional structural influence on the next perovskite layer, this is not generally true. Next to strain, perovskite systems can also easily adopt octahedron rotations.\textsuperscript{[13]} SrRuO\textsubscript{3} has in bulk a tilt mode (in Glazer notation of a’a’c’), but it can also adopt other tilts depending on its epitaxial relationship with the substrate. Sometimes those tilts can also be relaxed within some unit cells.\textsuperscript{[11–14]} Another important property of SrRuO\textsubscript{3} films is that the B-site RuO\textsubscript{2} is extremely volatile and it is impossible to have RuO\textsubscript{2} as the termination layer. If SrRuO\textsubscript{3} is grown on SrTiO\textsubscript{3} or REScO\textsubscript{3} substrates, which after chemical treatment are B-site terminated, the film will first grow 1.5 unit cells to change the termination to A-site SrO.\textsuperscript{[15]} This change in termination layer is generally propagated throughout the next perovskite layers and can have pronounced influence on the domain states\textsuperscript{[16]}, the direction of the polarization\textsuperscript{[17]} or the appearance or no appearance of a 2D electron gas on the interface between LaAlO\textsubscript{3} and SrTiO\textsubscript{3}.\textsuperscript{[18]}

Here for the first time the epitaxial growth of SrRuO\textsubscript{3} (lattice parameter 3.93 Å\textsuperscript{[9]} \textsuperscript{[9]} thin films on a NdScO\textsubscript{3} (lattice parameter ~4.01 Å) substrate, which has a tensile misfit strain of +2%, are reported. While it is not impossible for perovskite oxides to grow under such large misfit strain\textsuperscript{[19,20]}, it is still a large mismatch which will result in difficult growth. One set of parameters for Pulsed Laser Deposition growth that lead to fully strained, flat, epitaxial SrRuO\textsubscript{3} thin films have been found after many attempts with different growth parameters. Those parameters have been found to not only work for NdScO\textsubscript{3} substrates, but also for other REScO\textsubscript{3} substrates (GdScO\textsubscript{3}, TbScO\textsubscript{3}, DyScO\textsubscript{3}) and
SrTiO\(_3\). A detailed discussion of these growth parameters is given in the following:

- The required fluence is determined to be in between 1.35 to 1.50 J/cm\(^2\). This is a large range due to the uncertainty of determining this parameter, due to inexact determination of the losses from the window and the spotsize on the target. But it is of exceptionally high importance that the used fluence is correct within 0.5 %. If the fluence deviates more than 0.5 %, it will be absolutely impossible to obtain good, flat growth. Obtaining the exactly right fluence is what makes the growth of SrRuO\(_3\) on NdScO\(_3\) very difficult and it will take many experimental iterations until the right fluence is found. For substrates with lower misfit strain, the fluence range that allows the proper growth of SrRuO\(_3\) is larger, so it is recommended for new setups to first start growing SrRuO\(_3\) with these parameters on other REScO\(_3\) substrates before trying NdScO\(_3\) to get a rough idea of what the right fluence should be.

- The spot size on the target should be 2.30 - 2.64 mm\(^2\) (the error is due to inexact determination of the spot size). This determines the amount of material for each pulse. It should be no more than 10% off or it will not grow good films.

- The growth temperature is about 700 °C and small variations of 20 °C are not a problem. Much higher temperatures will give problems with the volatility of Ru, but much lower temperatures will give less homogeneous crystallization.

- The oxygen pressure is about 0.1 mbar. It has some freedom to change, but should be no more than 0.03 mbar off. This oxygen pressure is for a target-substrate distance of 50 mm, which can also be varied by (at least) 5 mm and still give good growth.

- The frequency of the pulsed laser should be between 3 and 5 Hz. Lower frequencies do not work well in combination with these other parameters.

- Sample size should not be much larger than 5x5 mm. If the sample gets larger, the edges will not grow with exactly the same quality and will introduce more defects (seen in resistivity measurements).

- The cooling rate after growth should be at most 5 °C/min, since preliminary studies found that a cooling rate of 10 °C/min gave far lower quality films.

The SrRuO\(_3\) growth for optimal parameters has been followed by RHEED in Figure 3.5a-d. There are two large RHEED oscillations in the first growth phase of the deposition, followed by a transition into small amplitude RHEED oscillations. Stopping the deposition after that first growth phase shows that the step edges have hardly changed shape and they have only a small roughening. So the SrRuO\(_3\) thin film follows the step edges nearly perfectly with good layer-by-layer growth. If the deposition is stopped in the second phase of the growth, the AFM image shows rougher edges, typical for step-bunching mode growth\(^{[21]}\), and small islands, because the deposition was stopped halfway filling the next layer. It can be concluded from this surface and the damped RHEED oscillations that the growth mode has a transition from pure layer-by-layer growth within the first growth phase towards a mixture of layer-by-layer growth and step-bunching modes for the remaining growth. A similar transition from layer-by-layer to step-flow growth modes has been observed before for SrRuO\(_3\) thin film growth after the termination conversion from B-site to A-site and is associated to an increase of surface diffusivity for the arriving atoms.\(^{[15]}\)

Figure 3.5e shows the RHEED pattern of another film grown with slightly less optimal fluence. The oscillations from the layer-by-layer growth are damped out completely after the first growth phase and only a step-bunching-like growth mode is observed from the RHEED. The step edges in the AFM image Figure 3.5f, however, are similar to those previously observed in the combined layer-by-layer growth and step-bunching modes. So only the RHEED signal can be used to distinguish between optimal and slightly less-than-optimal fluence by showing a small change in layer-by-layer growth mode. The less optimal fluence changes the flux (amount of atoms arriving per time unit), which will have influences on the growth mode. Larger flux should give more layer-by-layer character\(^{[21]}\), so it should be possible to get RHEED oscillations by increasing the fluence slightly. The fluence cannot be increased to a too large value, otherwise it will give rise to three-dimensional growth.
3.4 Structure and conductivity thickness dependence of SrRuO$_3$ thin films on NdScO$_3$

The structural and physical properties of SrRuO$_3$ films are studied under moderate (1 %, grown on GdScO$_3$) and large (2 %, grown on NdScO$_3$) tensile strain in order to understand the influence of tensile strain on SrRuO$_3$. The role of lattice rotations will be ignored here as they are expected to be similar for both strain states.

Figure 3.6 shows that the SrRuO$_3$ thin films remain epitaxial and fully strained up to at least 20 nm even at this large strain state on NdScO$_3$. The structure found for SrRuO$_3$ thin films in literature is orthorhombic for compressive strained films for all thicknesses, while for tensile strain it is found to be tetragonal at large thickness and monoclinic at smaller thickness (the transition is typically at 10-15 nm). The 20 nm thick SrRuO$_3$ films discussed here are, in line with the reports, of tetragonal symmetry. Upon decreasing the film thickness it gets progressively hard to determine the exact structure because the Bragg peaks become too spread out in reciprocal space.

The out-of-plane lattice parameters of the SrRuO$_3$ thin films (Figure 3.7) grown on NdScO$_3$ are smaller than those grown on GdScO$_3$ due to the increased tensile strain. Still, both lattice parameters are larger than the predicted lattice parameter of 3.86 Å (3.90 Å for GdScO$_3$) considering a reported Poisson ratio of 0.3, suggesting some defects that increase the unit cell.
increase of the width of the diffraction peaks for decreasing thickness increases the uncertainty in the lattice parameter. However, the trend is still visible that the lattice parameter decreases for film thickness. It suggests relaxation from the fully strained, small, lattice parameter at low thickness to more relaxed, larger, lattice parameters at larger thickness. This could be caused by an increase of defects for larger thickness to release the strain energy. So even though the in-plane lattice parameter still matches the substrate for the thicker films, defects have already caused strain relaxation along the out-of-plane direction.

A report by another group for SrRuO$_3$ films on a GdScO$_3$ substrate\cite{26} give the opposite thickness trend, where larger film thicknesses lead to smaller lattice parameters, due to a phase transition at 16 nm film thickness. Even at the large thickness tetragonal limit, their lattice parameter is 3.89 Å, which is significantly smaller than our 3.91 Å. It suggests that more defects are found in these films than those reported films. This is both caused by a decrease in oxygen pressure from the reported 0.13 mbar to 0.1 mbar in this study, and the fact that the growth was optimized for NdScO$_3$ and not for GdScO$_3$. So the defects found in the films studied here have changed the structure significantly, possibly even preventing the monoclinic structure and its associated increase in lattice constant. The FWHM of the rocking curve in the literature (0.07 °) is larger than found in these films (0.01 - 0.03 °), suggesting more disorder and thus defects in the literature films. However, the FWHM numbers reported in this study are limited by the resolution of the x-ray source, so probably the values reported in literature are also limited by their x-ray source. So no actual comparative conclusions can be drawn on the FWHM of the rocking curve.

Conductivity measurements of these SrRuO$_3$ thin films at different film thicknesses have been performed using the Van der Pauw Technique\cite{33} (Figure 3.8), calculated as

\[
e^{-\pi R_{\text{vertical}}/R_S} + e^{-\pi R_{\text{horizontal}}/R_S} = 1
\]

where $R_{\text{vertical}}$ and $R_{\text{horizontal}}$ are the resistances measured along the two measurement directions and $R_S$ is the sheet resistance,
SrRuO$_3$ growth on a NdScO$_3$ substrate

\[ R_S = \frac{\rho}{t} \]  

(3.2)

where \( \rho \) is the intrinsic material’s sheet resistivity and \( t \) the thickness of the film. The resistivity found for these films \( \text{(Figure 3.9a)} \) fall in the range of 500 – 1500 \( \mu \Omega \text{cm} \), which is significantly higher than the 200 – 400 \( \mu \Omega \text{cm} \) resistivity reported for SrRuO$_3$ films on common substrates such as SrTiO$_3$, LaAlO$_3$, Yttria-stabilized zirconia and DyScO$_3$[10] and also slightly higher than similar films reported in literature on the similar substrates as GdScO$_3$[26] or SmScO$_3$[12] which are 600 – 800 \( \mu \Omega \text{cm} \). It is known that oxygen vacancies can increase the resistivity of SrRuO$_3$ by one order of magnitude[10,34], so this larger resistivity is most likely caused by defects.

The lowest values of the resistivity are found in films with thicknesses around 6 nm. Thinner films have highly increased resistivity due to a metal-to-insulator transition at lower thickness, but also the 20 nm films have increased resistivity (note that they do have a lower sheet resistance due to the larger thickness). This is caused by an increase of defects for the thicker films which had also caused the increased lattice parameter. The huge difference in resistivity between the 6 nm high quality film on NdScO$_3$ and the 7 nm lower quality film is also caused by a difference in defect content. The resistivity of SrRuO$_3$ thin films in literature is lower for compressive strain than for tensile strain, and an increase of tensile strain also increases the resistivity.[12,26] The 6 nm and the 20 nm thick films, grown together on both substrates in a single batch, follow the rule that higher tensile strain gives higher resistivity. However contrary to that statement, the lowest resistivity of all films in this study has been found for the 7 nm thick film on NdScO$_3$. That 570 \( \mu \Omega \text{cm} \) resistivity is even lower than the literature values on lower strained films grown on GdScO$_3$ or SmScO$_3$. So a final conclusion cannot be drawn on the basis of these films alone because the differences in sample quality from sample-to-sample are too large. The defects can change a lot and even differences between layer-by-layer and step-flow like growth mode can influence the physical properties.[35] This large variation is caused by the difficulty to control the fluence precisely enough in the extremely narrow growth window for these highly strained films.

The temperature evolution of the resistivity of (high quality) SrRuO$_3$ films on the two substrates is shown in Figure 3.9b. A linear slope, characteristic for a bad metal[36], is found from 300 K down to the ferromagnetic phase transition where there is a change in resistivity scaling towards a quadratic behavior arising from electron-electron scattering.[10] That transition temperature is commonly found at 160 K for bulk SrRuO$_3$, decreases for both compressive and tensile strain[12,37,38] and also decreases for smaller film thickness.[39] The transition temperature is 150 K for a 6 nm film and decreases to 130 K for a 20 nm film (not shown here) on GdScO$_3$. The same films in literature have found an increase from 100 K for a 20 nm film towards 110-130 K for thinner films.[26] So the transition temperature is increased drastically in these films with respect to the literature, likely due to the defects. The films on NdScO$_3$ have a decreased transition temperature with respect to the films on GdScO$_3$, as expected from their increased strain.[12]

A thickness-dependent metal-to-insulator transition can be seen in Figure 3.9c. The 7 nm film is metallic as can be seen from the increase of resistivity for higher temperature. The 3 nm film is metallic as well, but the resistivity is lower at low temperatures. The 4 nm film is in an intermediate state[36], with metallic conductivity at high temperature (increased resistivity when increasing the temperature) and insulating conductivity at low temperature (decreased resistivity when increasing the temperature). So SrRuO$_3$ grown on NdScO$_3$ will be insulating up to 8 unit cells, while on GdScO$_3$ it stays metallic down to the thinnest film measured here (3 nm). Also all SrRuO$_3$ thin films in literature are reported to be metallic down to 4 unit cell thickness.[10,39] A compressive strain is found to lower the transition thickness[40], so now it has been found that this large +2% tensile misfit strain increases the transition thickness drastically.

A low-quality SrRuO$_3$ film not only has increased resistivity at room temperature, but it also shows insulating behavior at low temperature \( \text{(Figure 3.9d)} \). While this low-quality sample is fully metallic down to ~80 nm and includes the ferromagnetic phase transition, it has a rather sharp increase of
resistivity as low temperature. This is most likely caused by defects that give an insulating phase inside the metallic matrix, hindering conductivity. The insulating phase shows up most clearly at low temperatures, but also contributes to a type of residual resistivity at higher temperatures.

3.5 Conclusion

High-quality SrRuO$_3$ thin films have been grown on REScO$_3$ substrates, where the growth conditions are extremely critical and small deviations, especially in the fluence, will lead to a large decrease in film quality. The growth mode is a combination of layer-by-layer and step-bunching modes, where a higher fraction of layer-by-layer growth was obtained with better growth conditions. The films have been stabilized up to 20 nm on a +2 % misfit strain NdScO$_3$ substrate. The lattice parameters,
conductivity and magnetic phase transition temperature have been found to be larger than similar films on the same GdScO$_3$ substrate in literature, due to more defects (most likely to be oxygen vacancies) in this study by a less optimized growth for GdScO$_3$. The lattice parameters increase as a function of thickness, similar to how the resistivity increases for increasing thickness, indicating the same large role of defects in both phenomena. Increasing the strain from +1 % on GdScO$_3$ to +2 % on NdScO$_3$ gives far more difficult growth and a huge increase in the thickness for the metal-to-insulator transition up to 8 unit cells. For future studies it is suggested to grow a series of high-quality SrRuO$_3$ thin films on both substrates with a well-defined amount of layers obtained from the RHEED data during growth. The conductivity should be measured locally with Hall bars to avoid lower quality material contributions from the sides of the sample due to an inhomogeneous laser plume in the growth and possible particles on the edges on the substrate. While it is not possible to extract absolute, low-error values for the lattice parameters, it will then be possible to see a trend which might point to possible structural phase transitions. Two possible phase transitions could possibly be found, one at the metal-to-insulator thickness and the other could be a monoclinic to tetragonal transition as also found on GdScO$_3$ and SmScO$_3$ in the literature. Higher quality films will also give more clear trends on the conductivity and could tell if the enhanced strain on NdScO$_3$ indeed increases the resistivity as expected from literature, or if there are some hidden parameters that will only be revealed when minimizing the defect concentration as far as possible. Further magnetic measurements could reveal more information on the character of the ferromagnetic phase transition.

3.6 Literature


Chapter 3

5177–5184 (2014)


SrRuO$_3$ growth on a NdScO$_3$ substrate


