Growth and characterisation of thin film Mott insulator p-n junctions

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Table of Contents

Abstract ................................................................................................................................. 1

1. Introduction .......................................................................................................................... 2

2. Sample preparation .............................................................................................................. 3
   2.1 Choice of substrate ............................................................................................................ 3
   2.2 Techniques for growth ...................................................................................................... 3
       2.2.1 Pulsed Laser Deposition ........................................................................................ 3
   2.3 Device structuring ........................................................................................................... 4
       2.3.1 Lithography ............................................................................................................... 4
       2.3.2 Etching ..................................................................................................................... 4
       2.3.3 Sputtering ............................................................................................................... 4
   2.4 Deposition ..................................................................................................................... 5
   2.5 Single layer sample ........................................................................................................ 9

3. Quality checks ..................................................................................................................... 10
   3.1 Quality of growth ............................................................................................................. 10
       3.1.1 X-ray diffraction: 2-theta-omega ......................................................................... 10
       3.1.2 X-ray reflectivity .................................................................................................... 11
   3.2 Atomic force microscopy ............................................................................................... 13
   3.3 Quality summary ........................................................................................................... 17

4. Theory .................................................................................................................................. 18
   4.1 Properties of used materials .......................................................................................... 18
   4.2 Mott insulators .............................................................................................................. 20
   4.3 Antiferromagnetic and superconducting regimes .......................................................... 21
   4.4 Semiconductor p-n junctions ......................................................................................... 22
   4.5 Superconducting p-n junctions ....................................................................................... 25
   4.6 Thin film characteristics ............................................................................................... 26

5. Measurement equipment ..................................................................................................... 27
   5.1 Measurement method ..................................................................................................... 27

6. Expected results .................................................................................................................. 29
   6.1 Single layer sample ........................................................................................................ 29
   6.2 Multilayer sample ........................................................................................................... 29
       6.2.1 From lead to central contact ............................................................................... 29
       6.2.2 From lead to other lead ...................................................................................... 31
7. Results ................................................................................................................................. 32
  7.1 Single layer p-n behaviour ............................................................................................... 32
    7.1.1 IVT curves of p-n contacts .................................................................................. 37
    7.1.2 pnp contacts .......................................................................................................... 38
  7.2 Multilayer sample .......................................................................................................... 41
    7.2.1 IV curves bath cryostat ...................................................................................... 41
    7.2.2 Resistivity curves bath cryostat .......................................................................... 43
    7.2.3 PPMS IVT curves ................................................................................................. 46
8. Discussion .......................................................................................................................... 50
9. Conclusion .......................................................................................................................... 51
10. Recommendations ............................................................................................................. 52
    10.1 Improvement of current experiments ..................................................................... 52
    10.2 New systems ............................................................................................................ 53
11. Appendix .......................................................................................................................... 54
    11.1 Appendix A: Used equipment .............................................................................. 54
    11.2 Appendix B: other measurements ........................................................................ 55
    11.3 Appendix C: growth and structuring conditions .................................................... 57
12. Acknowledgements .......................................................................................................... 61
13. References ........................................................................................................................ 62
Abstract
In this report of a BSc assignment, investigations of properties of the materials LSCO (x=0.09) and NCCO (x=0.10) grown on a LSAT substrate with an STO capping are described. In particular, the electrical properties of these materials in p-n junctions and in an alternating multilayer are characterised.

The growth of a new multilayer sample of Mott insulators LSCO and NCCO is described and analysed. Techniques to grow thin films are introduced and discussed. For the growth pulsed laser deposition, photolithography, sputtering and Argon etching have been used. The sample quality has been determined using atomic force microscopy, x-ray diffraction and reflectivity and resistance measurements. This quality is concluded to be fair, certainly for a first ever attempt to grow such a sample.

The theory to analyse the results is presented, which includes Mott insulator physics, p-n junction theory, thin film characterisation, theory on superconductivity and antiferromagnetism. A parallel is made between semiconductor p-n junctions and superconducting p-n junctions.

The measurement methods, which include four-point measurements, lock-in measurements and IVT-measurements are discussed. The results are presented as IV-curves, IV-diagrams and dV/dI curves to provide insight into p-n behaviour, transitions in the phase diagram and possible new effects arising from the properties of the sample.

The measurements done provided a large amount of information. For the single layer sample, p-n behaviour has been confirmed and material property transitions have been seen in the IVT-diagrams. Semiconductor-like pnp behaviour is confirmed as well, and the low bias resistance appears to be dominated by the first junction in the current path.

The multilayer sample displayed a wide variety of measurement results, despite only four junctions having been measured. Both ohmic and non-linear IV-curves have been observed at 300 K and superconductivity emerges in the LSCO at about 15-20 K. Indications for phase transitions have also been measured and provide clues for further research.
1. Introduction

This is the report of a bachelor assignment carried out at the University of Twente, in the research group Interfaces and Correlated Electron Systems. We have studied the physics behind a Mott insulator ramp type junction made of La$_{1.9}$Sr$_x$CuO$_4$ ($x=0.09$) (LSCO) or Nd$_{1.9}$Ce$_x$CuO$_4$ ($x=0.10$) (NCCO) leads on an alternating multilayer stack of LSCO and NCCO with a SrTiO$_3$ (STO) capping. This sample has been grown on a (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT) substrate, using pulsed laser deposition (PLD). Various other techniques such as lithography, argon etching, sputtering, atomic force microscopy and X-ray diffraction have been used to ensure a high quality sample. The first part of this report focuses on the preparation of the sample we have used for our measurements. Then, we will give descriptions on how the techniques work that we used. We conclude that chapter with the quality checks we have carried out. With the sample ready, we dive into the physics of semiconductors, Mott insulators and superconductivity so that we are able to justify our expectations for the electrical properties of the sample. Furthermore, we will attempt to link semiconductor-physics and superconductor-physics in an attempt to apply well known physics in an experimental area that is still shrouded in mystery. Armed with this knowledge we will analyse results from an older and simpler sample that has been tested before and explain what we expect from the sample that we have prepared.

From then on we will discuss the measurements we have performed on our sample and we will draw our conclusions from these measurements. Then, all that remains is a moment of retrospect on all the work. We will give our recommendations on how to improve the experiment and how the results may be refined. Lastly, we will give examples of what we think are possible applications of these kinds of systems in the future.
2. Sample preparation
In order to be able to do measurements on behaviour of interfaces between materials, a sample was designed. It is 5x5 mm, with layers of LSCO, NCCO, STO and gold on top. The process of creating this sample is described by introducing the growth techniques and settings applied to the setups that we have used, after which a description of the quality checks done during the process is given. At the end of this chapter, the quality of growth will be summarized.

2.1 Choice of substrate
The sample creation starts with a substrate, on which the growth of the different layers can be done most properly. The substrate chosen is \((\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}\) (LSAT). This is a crystalline substrate that is pre-fabricated. The electrical and magnetic properties are suitable for our goals; it is insulating and has a very low magnetic susceptibility. Another option would have been \(\text{SrTiO}_3\) (STO), however the lattice parameter of LSAT is closer to that of the materials to be grown on it (see table 1).

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice parameter (Ångstrom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCO</td>
<td>3.77520</td>
</tr>
<tr>
<td>NCCO</td>
<td>3.94900</td>
</tr>
<tr>
<td>LSAT</td>
<td>3.868</td>
</tr>
<tr>
<td>STO</td>
<td>3.9051</td>
</tr>
</tbody>
</table>

Table 1: a-axis lattice parameters of used materials

LSAT is a more suitable choice for the substrate than STO, because STO can become conducting when etched with argon ions and excess stress on the crystal structure is minimized. The crystal structure is deformed slightly as a consequence of this. The c-axis becomes slightly shorter, which should be visible in an x-ray diffraction measurement where the peaks of the LSCO will be moved slightly to a higher angle. This is to be found in XRD experiments.

2.2 Techniques for growth

2.2.1 Pulsed Laser Deposition
Following the choice of substrate, the p-n type cuprate multilayer needs to be grown. The multilayer was grown using Pulsed Laser Deposition (PLD). This technique incorporates deposition on a substrate using targets of the material to be deposited, which are illuminated by an Excimer UV-laser. The targets can be switched in order to grow materials in subsequent order. Using PLD, it is possible to use different targets in situ, which means the entire multilayer can be grown without exposure to external influences.

The parameters which can be altered to achieve good growth are substrate temperature, background pressure, laser fluency, laser frequency, ablation time, annealing time and of course target composition. From previous experiments, optimal growth conditions have been determined.
2.3 Device structuring
To enable measurements to be done, a structure needs to be defined on the sample. This structure should consist of leads to the multilayer, through which currents and voltages can be sent and measured. To create such a structure different techniques can be used. In this project we have used argon etching, lithography and gold sputtering to define the structure on the sample and make it ready for measurements.

2.3.1 Lithography
Lithography is used to define the areas that need to be structured by other techniques later on. A cleanroom environment is needed for all steps in the process. Lithography starts by applying a layer of photoresist material 906/12, 907/17 (thickness ≈ 3 µm) to the sample by spincoating at 6000 rpm.

After this is done, the photoresist is illuminated in several areas using a lithography mask. The effect on areas that are lit is that the chemical composition changes. As a result this area will be dissolvable in a developer; we used OPD 4262 for this. Now that we have removed the unwanted parts of the photoresist, the remaining photoresist is the etch mask which will protect the parts of the sample we want to keep intact.

2.3.2 Etching
With the mask ready, we can start etching to remove all grown material which has no photoresist on top using an argon-ion source. The precise settings we have used for all the etch steps can be found in appendix C. The mask itself will be etched, but it is at least an order of magnitude thicker than the thin films so this is not a problem. After this step, the remaining photoresist is removed using acetone and the sample is ready for the next step.

2.3.3 Sputtering
Sputtering is a technique used to deposit single metal materials onto a substrate or sample. It is done by bombarding a material target with highly energetic particles, which knock out single atoms which are collected on the sample. This technique is applicable in various ways, but in this project it was used to deposit gold atoms on the sample. This will create a uniform layer of material everywhere on the sample. To make a specific structure using sputtering, we again use lithography and a photoresist mask as described above, after which we can sputter the gold on the sample. Note though, that this mask is inverted. Next, another solvent can be applied to dissolve the photoresist. When the photoresist is dissolved, the gold on top breaks off, creating a structure on the places where the photoresist was removed earlier.
2.4 Deposition

The LSCO and NCCO targets have also been prepared beforehand. After polishing both targets they are loaded into the PLD chamber together with the LSAT substrate. We start with NCCO, which is deposited at 820 degrees Celsius, with a pulse frequency of 4 Hertz for 2 minutes and a pressure of 0.25 mbar O2. The second layer, LSCO, is deposited at 700 degrees Celsius, also at 4 Hertz, but for three minutes and at a pressure of 0.13 mbar O2. This is repeated three times to build a total of six layers on top of the LSAT substrate, as seen in figure 2. The reason for starting with NCCO is that it is deposited at a higher temperature than LSCO, which seems logical to do as we will anneal the sample after the deposition. To achieve 50 nm thickness we have grown the LSCO using about 720 pulses and the NCCO using about 480 pulses, with a respective growth rate of 0.69 and 1.04 Ångström per pulse. On top of this multilayer a STO cap is deposited, also 50 nm thick. The purpose of the STO capping is to prevent conduction in the c-direction from the current- and voltage-leads into the multilayer stack. As final treatment the complete multilayer is annealed in oxygen at 600 degrees Celsius for 15 min and again at 450 degrees Celsius for 30 min, both at 1 bar O2. After which the sample is cooled to room temperature at a rate of 10 degrees Celsius per min, see figure 3. Values for LSCO were obtained from the thesis by Van Zalk, 2009, p.19 and the values for NCCO from Ariando, 2005, p.35.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>p (mbar O₂)</th>
<th>Time (min)</th>
<th>f (Hz)</th>
<th>( v_{\text{dep}} ) (Å/pulse)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCCO</td>
<td>820</td>
<td>0.25</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>LSCO</td>
<td>700</td>
<td>0.13</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 2: Growth settings LM3NL01

---

Figure 2: Side view of LM3NL01

Figure 3: Temperature profile during growth of LM3NL01
When the multilayer was finished, we applied a photo resistive layer in a square (1740x1740 \( \mu m \)). Using an argon ion beam we will etch away all the excess STO, LSCO and NCCO. This was done under a 45 degree angle, to create a ramp-type junction [Smilde, 2001]. This is done to ensure good contacts between the contact leads that will be applied later on.

This, then, leaves us with a sample that looks like figure 4, which is a top down view of the sample after the first etch step. Using the crosses to align the next mask we deposited the NCCO and LSCO contact leads. These leads come in pairs and have different junction widths. The growth conditions of the NCCO and LSCO leads were the same as in the multilayer growth step.

However, while annealing the NCCO, the heater remained turned on for about 60 hours at 760 °C, 1 bar O\(_2\). This high temperature in combination with the oxygen pressure can have two major effects on the sample. The parasitic phase \((\text{Nd,Ce})_2\text{O}_3\) may be induced in the topmost layer of NCCO by the high oxygen pressure, which may reduce the quality of doping. The second possibility is high diffusion between the layers, mostly the cerium content of the NCCO diffusing into the LSCO layers, effectively reducing the doping level by eliminating holes. The cerium is able to flow into the LSCO because of the smaller ionic radius of cerium compared to strontium, enabling the cerium to fill sites where strontium or lanthanum is not present. Strontium does not fit into the cerium sites, making diffusion of strontium into the NCCO layers unlikely.

With the contacts applied, the sample looks like figure 5. The widths of the junctions are given in table 3.

<table>
<thead>
<tr>
<th>Lead</th>
<th>Width (( \mu m ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>11</td>
<td>200</td>
</tr>
<tr>
<td>12</td>
<td>200</td>
</tr>
</tbody>
</table>

Table 3: Junction widths LM3NL01
The next step is to etch two small squares in the multilayer, through the STO cap. After this we apply gold contacts to all leads and the two small squares in the centre. We however keep the junctions free of gold. This now looks like figure 6. The large pads of gold are to ensure a small contact resistance between the wiring and the leads.

During this step, the gold layer on the current lead of junction 5 flipped over and made a short with the voltage lead of junction 4. We removed it with a pair of tweezers.
This is the final step; the sample is complete. If a cross-section of a ramp would be made, it would look like figure 7.

A summary of all the steps in building the sample can be seen in table 4.

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PLD multilayer, including STO cap</td>
</tr>
<tr>
<td>2</td>
<td>Apply etch mask</td>
</tr>
<tr>
<td>3</td>
<td>Argon etch to define multilayer structure</td>
</tr>
<tr>
<td>4</td>
<td>PLD NCCO contact layer</td>
</tr>
<tr>
<td>5</td>
<td>Apply etch mask</td>
</tr>
<tr>
<td>6</td>
<td>Argon etch, only NCCO</td>
</tr>
<tr>
<td>7</td>
<td>PLD LSCO contact layer</td>
</tr>
<tr>
<td>8</td>
<td>Apply etch mask</td>
</tr>
<tr>
<td>9</td>
<td>Argon etch, LSCO &amp; STO cap</td>
</tr>
<tr>
<td>10</td>
<td>Gold lift-off mask</td>
</tr>
<tr>
<td>11</td>
<td>Sputter gold</td>
</tr>
<tr>
<td>12</td>
<td>Lift-off</td>
</tr>
</tbody>
</table>

Table 4: LM3NL01 preparation steps
### 2.5 Single layer sample

In this project, another sample (LSNL05) was measured for its possible p-n behaviour. This sample was created before the multilayer sample and is being measured for characteristics of p-n contacts in Mott insulators, ultimately to investigate novel properties of the phase diagram of these materials. This could later be used as reference material for the multilayer measurements. This sample is a single layer NCCO sample with LSCO leads with the same ramp type junctions, as shown below in figure 15.

![Figure 8: Side view LSNL05 ramp-junction](image)

Also, it was structured with a slightly different lithography mask. The only difference was in the junction widths. The comparison in junction widths is given below in table 7.

<table>
<thead>
<tr>
<th>Junction</th>
<th>Contact width (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LM3NL01</td>
</tr>
<tr>
<td>1/12</td>
<td>200 (NCCO)</td>
</tr>
<tr>
<td>2/11</td>
<td>200 (LSCO)</td>
</tr>
<tr>
<td>3/10</td>
<td>100 (NCCO)</td>
</tr>
<tr>
<td>4/9</td>
<td>100 (LSCO)</td>
</tr>
<tr>
<td>5/8</td>
<td>50 (NCCO)</td>
</tr>
<tr>
<td>6/7</td>
<td>50 (LSCO)</td>
</tr>
</tbody>
</table>

*Table 5: Comparison junction widths LM3NL01 and LSNL05*

The etching steps are identical to the ones used for LM3NL01, the PLD growth conditions can be found in appendix C.
3. Quality checks

The fabrication methods described before are tested methods [Ariando, Smilde, van Zalk], but the sample that we made has to be tested for material qualities. These quality checks have been done after several steps of the production process. Table 5 describes the different methods after each step.

<table>
<thead>
<tr>
<th>Step</th>
<th>Quality check method</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLD 3x (NCCO + LSCO) + STO</td>
<td>X-Ray Diffraction (XRD)</td>
<td>2-theta-omega, thickness</td>
</tr>
<tr>
<td>Every Ar-etch Lift-off after Au-deposition</td>
<td>Atomic Force Microscopy (AFM)</td>
<td>Smoothness surface, ramp heights</td>
</tr>
<tr>
<td>Sample ready</td>
<td>Check gold layer for cracks, missing gold, etc. Check for current shortcuts Lead resistivity measurements</td>
<td>Bad gold: redeposit, shorts: redeposit, bad resistivity: don’t use lead.</td>
</tr>
</tbody>
</table>

Table 6: LM3NL01 quality checks

The main measures for quality of growth of this sample are the ratio of compounds in sample, the thickness of the layers and the smoothness of sample surface. Also, the sample needs to be checked for measurability by confirming the absence of shorts on the substrate and by checking the resistivity of the leads themselves.

3.1 Quality of growth

3.1.1 X-ray diffraction: 2-theta-omega

The quality of the PLD growth is essential to the measurability of the sample. The quality of PLD growth has mainly been measured by performing an XRD measurement, where the chemical composition and the thickness of the different layers have been determined. First, a 2-theta-omega scan has been made to determine the materials deposited, the result of which is shown in figure 8.

![XRD material measurement with reference](image)

Figure 9: X-ray diffraction results of LM3NL01
The data above is counts of reflected photons plotted against the incident angle. This determines the c-axis lattice parameter in the measured material, since the growth is done in the (001) direction. We added a flat 10 counts to the entire signal to improve the readability the graph. This parameter can be determined by the Bragg diffraction law:

\[ n(\lambda) = 2d \sin(\theta) \]

Here, \( n \) is the order of diffraction, \( \lambda \) is the wavelength of the used X-rays, \( d \) is the lattice spacing of the out-of-plane axis and \( \theta \) is the diffraction angle.

In perovskite structures, this reflection is observed in every direction. However, the PLD allows for the growth in the (001) direction only (because of the substrate orientation) and the peaks observed need to be from c-axis parameters. A very large database with information about many compounds is available on the Radboud University website [Cheminf]. This can be used as a reference to check the XRD results. From this database, the peaks for c-axis NCCO, LSCO, LSAT and STO (in bulk) are retrieved and put into the graph above. Also, the parasitic phase \((\text{Nd,Ce})_2\text{O}_3\) is observed.

The values for theta coming from this X-ray diffraction spectrum deviate slightly from the bulk values for these materials. This deviation is known as strain, due to the fact that the materials tend to grow with similar a- and b-axis lattice parameters compared to those of the substrate, leading to different lattice constants in all directions. The lattice parameters in the a-direction can be found in table 1.

The largest lattice mismatch of connecting layers is between the LSCO and the NCCO (4.6%), which is considered suitable for experiments. We observed no double peaks for any of the materials from the XRD spectrum, indicating an identical strain for each material in every layer. As a result of these lattice mismatches, it is expected that the c-axis parameter of LSCO will drop (Poisson’s factor >0), and the diffraction peaks for LSCO are shifted to higher angles, from Bragg’s law. The c-axis parameter for NCCO will become slightly larger, which means the peaks for NCCO are shifted slightly to smaller angles. The shift of the LSCO peaks is clearly visible in this XRD spectrum, especially for the higher diffraction orders, the shift of the NCCO peaks is very small.

### 3.1.2 X-ray reflectivity

We did an X-ray reflectivity measurement was done to determine the thickness of each layer. This technique incorporates positive interference of X-rays reflected by the interfaces of the different materials, due to a different index of refraction. This difference is caused by electric properties. The intensities of the reflected X-rays exhibit an oscillating behaviour as a result of varying the incident angle \( \theta \). For this technique, low angles are used to avoid dominance of the Bragg reflection by the materials. This technique is expected to provide oscillations in the intensity, depending on incident angle. These oscillations are characterized by their periodicity and their amplitude. Higher amplitudes indicate a smoother interface in the multilayer.
In figure 9, clear oscillations can be seen for theta values between 0.5 and 1 degree. This indicates quite equal thickness of the layers across the sample. For small angles ($\sin(\theta) \approx \theta$), the layer thickness can be estimated by:

$$d = \frac{\lambda}{2} \frac{1}{\sin(\theta_1) - \sin(\theta_2)}$$

Using $\lambda = 1.54$ Ångstrom, and taking the distance between the first two peaks, a layer thickness of about 48 nm is found, which is consistent with the expected thickness from the layer grown by PLD.
3.2 Atomic force microscopy

Atomic force microscopy (AFM) is a technique which uses a very sharp tip (1 atom ideally) to scan a surface of a material. This tip is attached to a cantilever, on which a laser is projected. The reflection angle of the laser beam on the cantilever is measured by a detector, which provides very accurate information on the height of the cantilever.

The AFM in this project is used in Contact mode. The advantage of this mode is that it is the fastest way to measure with an AFM. It is deemed possible because the surface of the sample is not soft and the measurements are not done in liquid environments. However, this mode may damage the tip so caution is advised. In this mode, the cantilever is moved by piezoelectric elements in a feedback loop to keep the tip-surface distance constant, so the cantilever deflection is also constant. Within the feedback loop, the applied voltage is measured to determine the height of the surface. This way, the accuracy of surface height is in the order of Ångstroms and the in-plane directions can be measured within the range of 10 to 100 nanometres.

In this project, AFM has been used to check the height of the argon etches, smoothness of the surface and defects in the growth of the materials. First, after each etch step the etch depth is checked by scanning the edges of each new layer. This, in comparison with the XRD image, should confirm successful etching of the entire layer on the surface where no photoresist is applied. A scan of the ramp region is shown below in figure 10.

![AFM image ramp multilayer stack](image)

Figure 11: AFM image ramp multilayer stack
From this image, a height profile can be derived using the freeware Gwyddion. Across the entire image, the following profile is observed:

![Height profile](image)

Figure 12: Ramp height profile (left) & zoom of ramp (right)

As can be seen, the ramp profile is smooth and the height is almost 350 nm. The height indicates that it is possible that not the entire multilayer and the STO cap have been removed completely. The etching step had to be repeated to be sure the layer was removed in its entirety. So, after the new etch step, we observe the following height profiles, see figure 12.

![Height profiles](image)

Figure 13: Ramp height profile (left) & zoom of ramp (right)
This ramp is high enough and again smooth, but there appears to be a small peak near the edge of the multilayer, which is present on all sides of the sample. This is material, that has been removed during etching and accumulates at the edge of the photoresist on the multilayer. Because this is protected by the STO capping, we expect that this will not have any significant effect on the measurements. These AFM images are sufficient to conclude that the entire multilayer is etched away; the ramp is about 380 nm high.

Next, the smoothness of the surface is observed to estimate the quality of growth. Figure 13 is an image taken of an area of the multilayer sample and is representative for most of the sample.

In these pictures, it is observed that there seem to be some flakes, a byproduct of the growth, and small contaminants on the surface of the sample, but the surface is relatively smooth with deviations of about 2-3 nm maximum. This indicates constant growth of the different layers with some contamination on top.
While checking the sample quality with a microscope, we noticed small black dots on the surface with larger diameters than the ‘flakes’ observed above. These ‘holes’ were in the multilayer and close to, or in some cases, on the ramps. They appear to have a depth of the order of the multilayer and capping thickness (350 nm) in the multilayer and varying depth on the ramps. These defects may be caused by contamination of the substrate, preventing ablated crystal atoms to attach to the surface. Also, the very long annealing procedure may have broken (parts of) crystals off the sample, creating holes at these sites. It is unknown what exactly has caused these defects.

The holes in the bulk of the multilayer are assumed to have little effect on measurements, since they are small and their resistivity will be higher than that of the surrounding material and will thus have a negligible effect on the total current flowing through the sample.

However the holes in the leads and especially on the ramps could be a problem because the layers might intersect here and the lead might conduct a current in the c-direction, which is not desirable. Below in figure 14, a hole is shown in lead 2 with a depth of about 150 nm, which is the thickness of the LSCO lead. It is undeterminable by AFM whether these holes originate from the multilayer growth or from the lead growth. This could account for strange IV-measurements later on.

![Height profile of ramp](image)

**Figure 15: Height profile of ramp**

The junctions have each been classified for their lead status and for the existence of holes in the junction itself, which might cause strange IV-behaviour. These results are given in table 6.
3.3 Quality summary

From the XRD and AFM images we conclude that the growth quality of the multilayer and the leads is acceptable, but to check if the sample will work properly, the quality of the gold contacts that we applied has to be checked. Unfortunately, the sample did not show good adhesion for gold, so sputtering had to be done several times in order to obtain acceptable gold deposition. Still, we found some cracks, but from a resistivity measurement of the gold contacts, this does not seem to affect the resistivity of the contacts. So, concluding, the gold deposition was successful, but the low adhesion gives rise to some concern for the durability of the sample and the quality of the bonds to be set.

The check for shorts was done by placing a bond directly on the substrate and by placing one on the reference crosses for lithography, displayed in the bottom left corner of figure 4. Next, resistance of all the leads were measured with respect to these bonds and none showed a very low resistance, indicating that no shorts are present.

However, the resistances between the voltage and current contacts in the centre of the multilayer to all the leads differed strangely per lead. The results of a resistance measurement with a multimeter at 300 K are shown in table 6.

<table>
<thead>
<tr>
<th>Lead</th>
<th>Type</th>
<th>Contact width (µm)</th>
<th>Resistance (kΩ)</th>
<th>Gold contact quality</th>
<th>Ramp holes</th>
<th>Measurability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NCCO</td>
<td>200</td>
<td>25.76</td>
<td>Good</td>
<td>Good</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td>LSCO</td>
<td>200</td>
<td>48.91</td>
<td>Good</td>
<td>Fair</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>NCCO</td>
<td>100</td>
<td>0.90</td>
<td>Good</td>
<td>Good</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>LSCO</td>
<td>100</td>
<td>40.65</td>
<td>Good</td>
<td>Fair</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>NCCO</td>
<td>50</td>
<td>18.00</td>
<td>Poor</td>
<td>Good</td>
<td>No</td>
</tr>
<tr>
<td>6</td>
<td>LSCO</td>
<td>50</td>
<td>710</td>
<td>Good</td>
<td>Good</td>
<td>No</td>
</tr>
<tr>
<td>7</td>
<td>LSCO</td>
<td>50</td>
<td>26.23</td>
<td>Fair</td>
<td>Good</td>
<td>No</td>
</tr>
<tr>
<td>8</td>
<td>NCCO</td>
<td>50</td>
<td>52.90</td>
<td>Fair</td>
<td>Good</td>
<td>No</td>
</tr>
<tr>
<td>9</td>
<td>LSCO</td>
<td>100</td>
<td>440</td>
<td>Good</td>
<td>Good</td>
<td>No</td>
</tr>
<tr>
<td>10</td>
<td>NCCO</td>
<td>100</td>
<td>430</td>
<td>Good</td>
<td>Bad</td>
<td>Yes</td>
</tr>
<tr>
<td>11</td>
<td>LSCO</td>
<td>200</td>
<td>49.53</td>
<td>Good</td>
<td>Fair</td>
<td>No</td>
</tr>
<tr>
<td>12</td>
<td>NCCO</td>
<td>200</td>
<td>20.95</td>
<td>Fair</td>
<td>Good</td>
<td>No</td>
</tr>
<tr>
<td>-</td>
<td>Multilayer</td>
<td>500</td>
<td>1.01</td>
<td>Good</td>
<td>Good</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 7: Quality summary of LM3NL01 leads

From this summary, we can conclude that lead 1 should provide the best quality of measurements, besides the multilayer contacts. However, the ‘fair’ quality classification of the gold contacts is given when there are some artifacts present in the gold surface. This will most likely not have a great impact on the overall resistivity, because of the large contact surface of the gold and the lead. Furthermore it is expected that the junction resistance will be dominating the lead resistance, which will not be visible in 4 point measurements, but is of importance of the total impedance offered to the measurement setup, which might not work properly with too high total resistances. Therefore, leads 4, 7, 8, 11 and 12 should provide usable measurements as well.

Measurements done on leads 2 and 5 should be reviewed with caution and lead 3, 6, 9 and 10 are not expected to provide any usable result at all due to their very high or very low internal lead resistance.
4. Theory
Before the characteristics of superconducting (SC) p- and n-type cuprates can be analysed, a theoretical investigation is required. The relevant properties of the materials will be shown. The band structure of both materials will be described. Also a link with semiconductor physics will be made, to see if theory from this field is applicable in superconducting p-n junctions as well. The reason for this link is the good understanding of semiconducting p-n junctions compared to that of superconducting junctions. The behaviour of the junction will be described when the materials are brought in contact. Lastly, the effect of the size of the sample on its properties will be discussed briefly.

4.1 Properties of used materials
The materials used in this research are LSCO, NCCO, STO, LSAT, and gold. In table 8 are all lattice parameters of the materials.

<table>
<thead>
<tr>
<th>Lattice parameter</th>
<th>LSCO (x=0.09)</th>
<th>NCCO (x=0.1)</th>
<th>STO</th>
<th>LSAT</th>
<th>Gold</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-axis (Å)</td>
<td>3.7752</td>
<td>3.945</td>
<td>3.9051</td>
<td>3.868</td>
<td>4.0788</td>
</tr>
<tr>
<td>b-axis (Å)</td>
<td>3.80915</td>
<td>3.945</td>
<td>3.9051</td>
<td>3.868</td>
<td>4.0788</td>
</tr>
<tr>
<td>c-axis (Å)</td>
<td>13.213</td>
<td>12.113</td>
<td>7.796</td>
<td>7.729</td>
<td>4.0788</td>
</tr>
</tbody>
</table>

Table 8: Lattice parameters used materials LM3NL01

These materials crystallize in a perovskite structure. The structure of NCCO (left) is called T'-phase, whereas the LSCO (right) grows in a T-phase structure, the main difference between the two phases being the placement of the oxygen atoms which are not situated in a CuO-plane see figure 16. In LSCO there are two apical oxygen atoms because the other O-atom planes have ¼ O-atom situated in every unit cell per oxygen atom, whereas the other O-atom planes in NCCO have ½ O-atom per atom in the unit cell.

![Crystal structures NCCO (left) and LSCO (right)](image)

The LSCO is a p-type material, which means it is hole-doped by replacing a lanthanum (La³⁺) ion with a strontium (Sr²⁺) ion in the crystal lattice, thereby eliminating an electron from the lattice, creating a quasi-particle called a hole. This hole is regarded as a positively charged particle, for it represents a missing electron. The opposite goes for the NCCO, which is electron-doped by replacing neodymium (Nd³⁺) with cerium (Ce⁴⁺), thereby putting another electron into the lattice. The doping constant x determines a lot of properties of the material.
By doping, one can make insulators like semiconductors or cuprates conducting. In the case of some cuprates (including LSCO and NCCO), some doping levels might lead to antiferromagnetic (AF) spin ordering or even to superconductivity (SC). For the LSCO and the NCCO, the effect of the different doping levels can be seen in the schematic phase diagram (not a real measurement) in figure 17.

![Figure 17: Schematic phase diagram of p- and n-type cuprates](image)

As can be seen here, the LSCO with $x=0.09$ should be in the superconducting regime and thus show superconductivity when cooled below its critical temperature ($T_c$, the black line above the yellow area) For this doping value, it is not expected that we see any antiferromagnetic effects. The NCCO has $x=0.1$ and this doping level should not be superconducting, but reveal antiferromagnetic behaviour below its Néel temperature ($T_N$, the black line above the red area).
4.2 Mott insulators

The materials we are working with are, as mentioned earlier, Mott insulators. This means that under conventional band theories these materials should conduct electricity. However, when measured, they turn out to be insulating. This effect is stronger at lower temperatures. The reason for this is the interaction of electrons with other electrons in the crystal lattice. A simplified way of describing this is by imagining a crystal lattice with one particle at every site (figure 18), each of which is in a classical ground state and has a repelling effect on all nearby particles. The repulsive force between them suppresses the motion of any of these particles to another site on the lattice.

![Figure 18: Schematic crystal lattice with one particle at every site](image)

More generally, Mott insulators occur when the repulsive Coulomb potential $U$ is large enough to create an energy gap. When a Mott insulator is doped with either electrons or holes, the AF phase is suppressed at low temperatures as can be seen in figure 17. Surprisingly the suppression is not symmetrical for hole and electron doping; the AF phase is much more robust on the electron doped side before a SC region arises. One view is that the carriers are more likely to be localized on the electron doped side [Lee et al., 2004]. Another possibility is that the next-neighbour hopping term favours AF on the electron doped side [Singh & Ghosh, 2002]. One of the simplest theories to describe this is the Hubbard model. In this model the electronic state of the cuprates can be described by a 3 band model. In this model, every unit cell has a copper $d_{x^2-y^2}$ orbital and two oxygen $p$ orbitals [Emery, 1987] [Varma et al., 1987]. Another result of this Mott insulating state is that there is order in the spins. This particular way of distribution is better known as the antiferromagnetic phase.
4.3 Antiferromagnetic and superconducting regimes

The phase diagram in figure 17 shows whether a material is antiferromagnetic or superconducting, but to be able to see these phases, an understanding of the characteristics of these phases is required.

In the antiferromagnetic phase, spins are oriented in an alternating way, up and down, cancelling total magnetization in the bulk object. This phase is insulating because of the Coulomb repulsion between electrons that prevents charge from moving and the spin frustration occurring when one tries to move a charge carrier with a certain spin to the next host atom. This is illustrated below in figure 19.

![Antiferromagnetic spin ordering](image)

In NCCO and LSCO, these spins lie in the copper-oxide planes, so in this case, the image above is in the ab-plane. However, if electrons are added or removed by doping, there will be an even number of spins on each side, zero in the case of hole doping, two in the case of electron doping. In the case of electron doping the two are always consisting of one spin up and one spin down electron, which is demanded by the Pauli Exclusion Principle. The result of doping is a change in the transition temperature of the anti-ferromagnetic phase, until the anti-ferromagnetic phase vanishes completely.

With certain doping levels the LSCO and NCCO can become superconducting when they are cooled below their critical temperature. This means that any current can flow without encountering resistance. Or in other words, there is no need to apply a voltage to keep the current flowing. These currents can persist indefinitely [Gallop, 1990]. There is a large difference between an ordinary conductor and a superconductor. In an ordinary conductor a current can be visualised as a fluid of electrons moving across a heavy ionic lattice. These electrons are colliding with the ions and lose energy due to these collisions. This is the cause of electrical resistance. In a superconductor the electrons can no longer be distinguished from one another. They form bound pairs, known as Cooper pairs. The energy spectrum of this ‘Cooper pair fluid’ possesses an energy gap, meaning there is a minimum amount of energy $\Delta E$ required to excite the fluid. Then, if this energy gap is larger than the thermal energy of the lattice the fluid will not be scattered by the lattice. The Cooper pair fluid is hence a superfluid and flows without energy dissipation.
4.4 Semiconductor p-n junctions

Two semiconductors of which one is p-doped and the other is n-doped can be joined together to form a p-n junction. This can be done with the same material to create a homogenous junction, or with two different semiconductor materials to form a heterogeneous junction. Since the superconducting p-n junction is heterogeneous the focus will be placed on heterogeneous semiconductor junctions.

There are three possible ways of forming a heterojunction in semiconductors.

- **Type 1.** The band gap of one semiconductor is completely contained in the band gap of the other one: \( E_C(2) > E_V(1) \) & \( E_V(2) < E_V(1) \). This is the case for an MgO and TiO\(_2\) interface, figure 20. The discontinuities of the bands are such that both types of carrier need a certain amount of energy to change from the material with the smaller band gap to the one with the larger gap.

  ![Type 1 band gap](image1)

  **Figure 20: Type 1 band gap [Zheng et al., 2010]**

- **Type 2.** The band gap still has some overlap, however both the \( E_C \) and \( E_V \) of material 1 are lower than the \( E_C \) and \( E_V \) of the other material. An example is show in figure 21, for a diamond and GaN interface.

  ![Type 2 band gap](image2)

  **Figure 21: Type 2 band gap [Shi et al., 2011]**
- Type 3. The band gap has no overlap, $E_v(1) > E_c(2)$. The situation for charge carriers is similar to type two, just more pronounced. An example is a GaInAsSb-InAs interface, figure 22.

![Figure 22: Type 3 band gap [Mikhailova et al., 2004]](image)

The three types of junctions are shown in figure 23 for arbitrary gap sizes and energy levels for comparison.

![Figure 23: Three possible band gap types](image)

When a p- and n-type material are brought in contact the band structure looks like one of the three cases mentioned before. Note that this is not in thermal equilibrium yet.
With the two materials now in contact the Fermi levels will shift so that they are at the same level, since they will exchange energy until the two materials are at the same temperature. However, when the Fermi levels are equal, the conduction and valence band will bend, because this state is not the most energetically favourable. The holes and/or electrons can lower their energy by crossing the junction. The bands will not match for any type 1 junction, as well as type 2 and type 3 junctions with different band gaps. There will be a discontinuity in the valence band or the conduction band. This can happen in two ways, depending on how the materials are doped, both of which are shown in figure 24.

![Figure 24: Energy band discontinuity at p-n interface](image)

A classic p-n junction is characterised by a lot of variables, which can be determined by measuring semiconductor characteristics such as mobility, charge carrier density and doping levels. The shape of an IV-curve coming from an ideal p-n junction is exponential and is given by

\[ I = I_s ( \frac{eV}{e k T} - 1 ) \]

Where \( I_s \) is the reverse bias saturation current for (relatively) large negative voltages, \( e \) is the elementary charge, \( V \) is the applied voltage across the junction (measured from p to n), \( k \) is the Boltzmann constant and \( T \) is the temperature.
4.5 Superconducting p-n junctions

Superconducting p-n junctions can be divided into two groups: conventional metals and other materials. The conventional metal group is not expected to be very interesting one, since the conduction band is half-filled and the carrier density and the Fermi energy are large (typically one electron per atom and several eV, respectively) [Mannhart, 1993]. The consequence is that the effects are only in very close proximity of the interfaces. No significant depletion or accumulation layers occur at contacts between conventional metals. A metal superconducting contact can, however, show interesting behaviour due to this proximity effect [Deutscher & Gennes, 1969], but it is not expected to be completely analogous to semiconductor behaviour.

In the non-conventional metal group the charge carriers have a clear electron or hole character, as is familiar from ordinary semiconductors [Tokura, 1991]. This makes this group a far more interesting one to study. Because of relative low carrier concentrations ($10^{21}$ cm$^{-3}$) compared to standard superconducting metals (But still high compared to semiconductors, even those doped to degeneracy ($10^{19}$ cm$^{-3}$)), the distinction between n- and p-type materials becomes relevant. [Pickett, 1989] With the ability to control electron and hole densities by changing doping levels, potential gradients over the junctions will occur with significant band bending as a consequence. [Mannhart, 1992] This bending can exist over large enough distances as to affect the properties of the junction.

Now to make the comparison with semiconductor physics several features of the superconductor system must be linked to semiconductor features. This, then, can give us insight in, or at least an expectation of, results for the measurements. At first glance the electronic properties are fairly similar, however taking the semiconductor approach and applying it to superconductors is a bit too simplified. A better way to describe the energy bands in a superconductor is the Hubbard model. The Hubbard model describes the transition between conducting and insulating systems. It still is a simple model, but it is a good approximation. In figure 25 a schematic overview of the energy bands in a superconductor is shown. In the materials used we assume that the majority of the current will flow through the planes oriented in the a-b direction that contain oxygen [Ando et al., 2001]. With this assumption a next step would be to see how two materials with oxygen bands at different energy levels interact when brought in contact. We think these bands will align in a way very similar to the level of the energy bands in semiconductors. The Fermi level will align when the two materials are in thermal equilibrium, and the energy level of the p orbitals of the oxygen atoms will have to bend to accommodate for this change. The resulting band diagram should, then, look similar to that of an ordinary semiconducting p-n junction.

Due to the fact we have p- and n-doped materials we expect diffusion of the electrons and holes, which will lead to a depletion or accumulation zone around the junction, this zone is expected to be of the order of magnitude of 1nm wide [Mannhart, 1993]. In our case we have multiple gaps, one between every layer of NCCO and LSCO between the multilayer stack and the ramp.

Figure 25: Hubbard band model in cuprate superconductor
To make a prediction about the type of junction that will form in this case we first look at the two possibilities in more detail. If we assume that a depletion zone forms at the interface of the materials, there will be three processes that carry current across the junction: thermionic transmission, direct inter-band tunnelling and defect-mediated tunnelling processes. When dealing with known superconductors, we are interested in temperatures below 100K, where thermionic emission is not expected to play a significant role.

As stated before, the depletion zone is expected to be very thin at the relevant carrier concentrations. Because of this thin barrier, direct elastic tunnelling can occur from the valence band of the p-type material to the conduction band of the n-type material (or vice versa). Indirect tunnelling, typically an inelastic process, can also be important, even dominant [Duke, 1969]. Examples of the latter are multi-step tunnelling via impurity states in the gap and phonon-assisted tunnelling. These two inelastic processes act together in the more common case of variable-range hopping via impurity states with slightly different energies. [Mannhart, 1993] The relative importance of these different tunnelling processes is influenced by factors such as the width of the barrier, the amount of, and the nature of defect states.

The other case is the formation of an accumulation layer. In p-n junctions with accumulation layers the Fermi level crosses the junction without traversing the band gap. Such junctions behave like ohmic contacts.

To check for the presence of either a depletion layer or an accumulation layer we will analyse the IV curves of the sample. If a gap is visible in the curve there is a depletion zone. If, on the other hand the curve is ohmic, the contact formed an accumulation layer.

4.6 Thin film characteristics

Guo et al. demonstrate that the thickness of films can affect the $T_c$ of superconductors. [Guo et al., 2004] However this oscillation in $T_c$ is only visible for films that have a thickness of 30 atomic layers or less. [Chiang, 2004] Since the layers of LSCO and NCCO we have grown are approximately 50 nm thick and the c-axis of the unit cells of the molecules are between 12.1 Å (NCCO) and 13.2 Å (LSCO) we expect no change in critical temperature for the LM3NL01 sample. This is a somewhat naïve interpretation of their data though, since Guo et al. used lead on a silicon substrate and measured the supercurrent through the bulk. As a consequence, they have no interface effects, which in our case are likely to have an effect on, or even dominate the superconducting properties. There are however no references we could find that described film thickness in a multilayer stacked p-n junction.

It is therefore an interesting idea for additional study, since thin film superconductors could lead to higher $T_c$ values. [Gozar et al., 2008]
5. Measurement equipment
The characterisation of the junctions is done by measuring IV-characteristics in two measurement setups, namely a bath cryostat and physical property measurement system (PPMS).

In the bath cryostat, it is possible to do measurements at fixed temperatures. The cooling is done by placing the sample in a bath of liquid helium (T=4.2 K). The pressure on the liquid helium can be lowered by pumping, which will decrease temperature to about 1.5 K. The bath cryostat setup has the advantage that up to 12 IV-channels can be connected at the same time, enabling quick measurements of all junctions. The disadvantage is the lack of range in the temperature, only room temperature (T=300 K), liquid helium temperature and the (pumped) liquid helium temperatures can be investigated properly.

Therefore, the PPMS is used after measuring in the bath cryostat. The advantage of the PPMS is to measure temperature dependence of IV curves, because the sample temperature can be controlled very precisely. The IVT-curve obtained can provide intuitive insights into the phase diagram of the LSCO and NCCO. A disadvantage is that only two channels and a minus channel can be connected at one time.

5.1 Measurement method
The simplest way of measuring an IV-curve in a system would be a two-point measurement. This measurement method is very basic and incorporates a voltage meter and an Ampère meter as shown in figure 26.

![Figure 26: two-point measurement](image_url)

This provides a fairly reliable measurement of both the voltage and the current. However, this method is insufficient for measurements on superconducting systems, as well as some others such as Schottky barriers and systems with large contact resistances. In our case the resistance of the wires is in principle infinitely larger than the resistance of the sample, so to compensate for this resistance a four-point measurement should be used, see figure 27. This will provide more reliable measurements.
In both the bath cryostat and the PPMS, mainly four-point measurements are performed.

To determine the resistances in the junctions, one can take a derivative of the IV-curve, as well as performing a lock-in measurement on the junctions. The lock-in measurement technique incorporates an IV-sweep, where the incoming current is a DC current, modulated with an AC voltage. Using a Taylor expansion for the current as function of this modulated voltage:

\[
I(V + v \cos(\omega t)) = I(V) + \frac{dI}{dV}(v \cos(\omega t)) + O(2)
\]

From this formula, \(dI/dV\) is found proportional to the signal at frequency omega, which can be found using a Fourier transform. The phase information is lost in this approximation, but the \(dV/dI\) measurement is found to provide sufficient accuracy to perform measurements with.
6. Expected results
In order to estimate whether measurements have been successful, it proves useful to state expectations of the measurements for reference.

6.1 Single layer sample
The single layer sample is expected to exhibit p-n behaviour during all measurements between 300 K and 1.5 K. This means a higher resistance for negative biases and a resistance peak close to zero bias. This can turn to ohmic behaviour when there is enough thermal excitation. Where this will happen is to be investigated, but is not expected to happen at 300 K.

6.2 Multilayer sample
The expectation for the behaviour of the multilayer sample is based on several probable governing phenomena. The system is a very complicated one in terms of fabrication, amount of junctions in one channel and of course possible interactions between the parallel LSCO and NCCO layers. Therefore, the single layer sample, as it is a simpler design, is used as a reference for possible p-n interactions and total resistances to arise. Other effects that may be

The materials used are under doped Mott Insulators: the LSCO is on the edge of the superconducting regime and the antiferromagnetic regime in the phase diagram. The NCCO is doped at a level with a transition to the AF regime at low temperatures. This leads to a low probability of a supercurrent and an expected rise of resistivity at low temperatures, due to the emergence of the AF phase. Also, the bulk of the materials outside the AF and SC phases is expected to behave as a metal, but not an ordinary one, since there is a pseudogap present [Mannhart, 1993].

The current-path is to be investigated to know where interesting physics can happen and where defects can occur that may provide unexpected results. Since the measurement can be done from a lead to the central minus contact and from a lead to another lead, this will be discussed separately.

6.2.1 From lead to central contact
In the image below, the major steps which will influence the resistivity and the current path are displayed. These are discussed in detail in the following paragraphs.

![Figure 28: Schematic flow of current through LM3NL01](image-url)
1. **Gold contact to LSCO/NCCO leads**

The contact surface should be large enough for the barrier to be considered insignificant. However, the gold appears to be removable very easily and has peeled off several times during sample preparation. This indicates a bad contact and therefore the lead resistance can be very high. This can be measured easily by performing a two-point measurement on the voltage and current leads.

2. **LSCO/NCCO leads**

The leads themselves are not expected to exhibit a high resistivity from sheet resistance, which are given in the figures below for LSCO (x=0.09) and NCCO (x=0.10), respectively. The resistances observed for the junctions are a few orders of magnitude higher.

![Figure 29: Sheet resistance LSCO (left) & sheet resistance NCCO (right)](image)

However, the leads may have been damaged during growth, leaving holes in the surface. Again, this can be confirmed or rejected by the measurements of the lead resistance.

3. **Junction ramp**

In this step, the first interesting physics can take place. The barrier between the different materials is expected to be high. The barrier between the same materials in the stack and the lead (e.g. LSCO/LSCO contacts) is expected to be low, since this is the same material.

However, if the current is forced to go through such a barrier, there are two options where this can happen: at the junction ramp and in the stack. The conductance in the c-direction is expected to be lower, based on the electronic structure of cuprates. However, the contact surface in the stack is several orders of magnitude larger than the contact surface at the ramp. This leaves us with the problem of not being able to determine the current flow path in the lead-central contact measurements.

4. **Multilayer stack**

In the multilayer stack itself, there are holes present, which are not expected to give rise to significant resistances, as described in the chapter on the sample quality. However, the question remains how the current actually moves through the sample. The top layer, which is in contact with
the gold contact, is LSCO. This suggests ohmic behaviour for LSCO leads with some possible interaction with the NCCO layer as well as some pseudogap behaviour.

The current from NCCO leads will have to cross a p-n barrier in order to flow through the central contact. The behaviour exhibited by the NCCO lead junctions is expected to be p-n like, as will be investigated using the single layer sample. What effect the parallel orientation of the p-n contact surface to the current direction will have, is to be investigated.

5. Multilayer to gold contact
The gold contact on the multilayer is large and therefore we expect it to have an insignificant resistance like the lead gold contacts. This was confirmed by the low resistance between the voltage and current leads.

6.2.2 From lead to other lead
This measurement setup is expected to follow the same steps as described above, except for the multilayer to gold contact. The other steps are repeated backwards.

The junction ramp/multilayer stack step is special in this case. One option is a different material for every lead (e.g. from LSCO to NCCO). The LSCO and NCCO can be seen as two interwoven combs coming from either side with one made of LSCO and one made of NCCO. This is expected to exhibit p-n behaviour like the single layer sample, with a larger contact surface. Such a measurement could provide some qualitative information on the ratio of contributions of the perpendicular contacts and those of the parallel contacts. This is because the size of the cross sections of the perpendicular contacts are of the same order of magnitude as those in the single layer sample, only now there are three of those.

When two leads of the same material are connected, this p-n behaviour is not expected to occur. The contact between the same materials is ideally ohmic, the barrier being zero. A barrier will arise in the p-n contacts, however, making it very unlikely that the current will start flowing through the other material. Therefore, an ohmic IV-curve is expected for these measurements. Non-ohmic behaviour most probably indicates bad deposition, but it may also indicate interface effects. To confirm or reject the latter, more research needs to be done on LSCO grown on different substrates, one of which will have to be NCCO.
7. Results
Now the samples have been prepared, the supporting theory has been described, the measurement setups have been analysed and the possible outcomes of the measurements have been discussed. Measurements to determine the behaviour of the samples have been performed. On the next pages, the graphs resulting from these measurements will be displayed and discussed.

7.1 Single layer p-n behaviour
The p-n behaviour of the single layer sample was investigated to use as a possible reference to the measurements on the multilayer. This was done both in the bath cryostat setup and in the PPMS. In the bath cryostat, all junctions have been measured to characterise the IV-behaviour. The results are given below for both 300 K and 4.2 K.

![Figure 30: IV curves LSNL05 junctions 1-6 at 300 K](image-url)
Figure 31: IV curves LSNL05 junctions 1-6 at 4.2 K

Figure 32: IV curves LSNL05 junctions 7-12 at 300 K
In all the junctions, a non-linear resistance is observed. The shape of these curves is a clear indication of a depletion layer formed at the interface, since the curves are asymmetric with a lower current in the negative direction. This indicates a depletion layer formed at the interface due to the p-n contact. An accumulation layer would exhibit ohmic resistance behaviour.

Also, the general resistance at 4.2 K is higher than the resistance at 300 K (comparable voltage range, lower currents). This could indicate the emergence of the AF phase in the sample.

The IV-curves for junctions 7-12 scale with junction width at 300 K, which can be observed in the scaled plot, figure 34. At 4.2 K most curves overlap without scaling. The 50 μm curve (cyan) exhibits strange behaviour as it does not scale with the other curves. It is considered defect during this measurement. The overlap without the scaling, however, is interesting. This might indicate degradation, but since these measurements were not done with a long time in between, this is unlikely. A more interesting thought is that the gap in the NCCO has been fully developed and the junction width has become the smaller factor in the total resistance, unlike in the 300 K curves.
The curves for junctions 1-6 are not scalable for junction width. This can have several causes. The stoichiometry of the materials in the PLD plume has a radial dependence and due to a small misalignment, the material composition can deviate greatly. For NCCO, this would cause only a minor problem in composition, since the atomic masses of the neodymium and the cerium are very close (144:140). For the LSCO, a major deviation in dopant concentration may occur, since the strontium is lighter than lanthanum (88:139). [Van Zalk, 2009].
Also, dV/dI curves for junctions 7-12 have been measured, using lock-in measurements. This provided figure 36, which also indicates a correlation between junction width and resistance. Also, the base of such a curve might be used later to investigate the band gap of these materials, when the sample design is done in such a way that all resistances are known and the junction resistance can be measured directly.
### 7.1.1 IVT curves of p-n contacts

In order to qualitatively analyse this p-n behaviour in the temperature range, an IVT curve has been made with the PPMS. These curves have been made with a measurement sequence, which made IV-curves while cooling down. The temperature interval for every measurement was 10 K from 300 K till 10 K, from then on the temperature interval changed to 1K till 4.2 K.

The figures below show the IVT curves obtained for the different junctions, where the colour shows the absolute value of the current.

![IVT curves LSNL05](image)

In these graphs, the p-n behaviour is clearly visible for the entire temperature range, since the increase in current as function of bias voltage does not indicate an ohmic resistance behaviour in any of the graphs. Also, the widths of the curves differ per junction, but the general shape is the same. In each curve, the resistance increases in the 300 K – 180 K range and below 40 K again. In between, the width of the curve, and therefore the resistance, is fairly stable.

In the first transition stage, a gap appears to be opening linearly in all graphs. This is most presumably due to the reduced thermal excitation at lower temperatures, since it appears to be a linear relation. Below 25 K, the transition might occur in the LSCO, but the physics behind this transition are to be investigated. A spin glass phase may occur here.
7.1.2 pnp contacts

pnp contacts were also measured in this sample, by connecting one junction to another instead of placing the minus leads on the NCCO square. However, most pnp contacts delivered unsatisfying results. An IV-curve of a pnp contact is expected to behave very symmetrically. A possible exception here may occur when the p-n and n-p junctions are of different sizes. Therefore the slope may be slightly different on one side, due to the higher ramp resistance from this side.

The collection of IV-curves that were obtained is displayed below:

From this measurement, it is clearly seen that the pnp behaviour in these junctions is present. All the curves are symmetric in the origin. Some measurements show similar strange features as the p-n measurements regarding the dV/dI dip around zero bias, as can be seen in the lock-in measurement of the dV/dI curves for the pnp contacts of junctions 3, 4, 9 and 10:
Figure 39 shows the p-n and pnp contacts of these junctions and two major features arise from this graph. First, the width of the curves seems to scale by a factor two for the p-n and pnp- contacts. This is as expected, because of the double energy gap which has to be traversed by the current. Second, a peculiar fact arises when a close up is made of the peaks at zero bias voltage.
In this graph, we observe a peak value for every starting junction: junction 3 in black, junction 9 in red and junction 10 in green. This suggests that the first junction is dominant in the total resistance at zero bias voltage, e.g. J3-J10 is black and J10-J3 is green. It is unknown to us what physics are behind this.
7.2 Multilayer sample
For the multilayer sample, all junctions have been tested, however junctions 7, 8, 11 and 12 show interesting and reproducible results. This is in agreement with our expectations that we described earlier in the quality table in the section on quality checks. The junctions and some relevant attributes are listed below.

<table>
<thead>
<tr>
<th>Junction</th>
<th>Material</th>
<th>Contact width (µm)</th>
<th>Measurability</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>LSCO</td>
<td>50</td>
<td>Good</td>
</tr>
<tr>
<td>8</td>
<td>NCCO</td>
<td>50</td>
<td>Good</td>
</tr>
<tr>
<td>11</td>
<td>LSCO</td>
<td>200</td>
<td>Good</td>
</tr>
<tr>
<td>12</td>
<td>NCCO</td>
<td>200</td>
<td>Good</td>
</tr>
</tbody>
</table>

Table 9: Specifications of discussed junctions

Furthermore these junctions give an overview of the two different lead-materials and they have two different widths, so we may be able to say something about the resistivity as function of junction width as well. In this chapter we will therefore discuss mainly these four junctions.

7.2.1 IV curves bath cryostat

![IV curve Junction 7 to ground - 50µm LSCO @300K](image1)

![IV Curve Junction 11 - 200µm LSCO @300K](image2)

![IV curve Junction 8 to ground - 50µm NCCO @300K](image3)

![IV Curve Junction 12 - 200µm NCCO @300K](image4)

Figure 41: IV curves LM3NL01 junctions 7, 8, 11 and 12 at 300 K
Junctions 7 & 8 show ohmic behaviour, but we had expected non-ohmic behaviour indicating some kind of gap. Since the current has to cross over several planes in the c direction to reach the minus lead, both in the LSCO leads and in the LSCO top layer, a pseudogap in the out-of-plane direction is expected to play at least a small role. It is possible that this gap is very small due to the large amount of thermionic electrons still present, but this is unclear.

Junction 12 shows expected behaviour at room temperature. Junction 11 shows a resistance drop at low voltages, while the opposite should be true if the junction behaves as a p-n contact. The IV curve of junction 12 has the expected resistance increase around low voltages for a p-n contact. Furthermore, arguing from the way the sample is built, the junctions with LSCO leads should always behave ohmic, or at least identical to an IV curve of pure LSCO, since the top layer of the sample is LSCO and we expected the lead-to-stack contact to be of high quality. However, from this argumentation, both junction 8 and 12 should show some signs of the p-n behaviour.

When looking at the IV curves in the bath cryostat at 4.2K we see that a lot has changed.

Figure 42: IV curves LM3NL01 junctions 7, 8, 11 and 12 at 4.2 K
With the assumption that all LSCO leads should show ohmic behaviour with an energy gap around low bias, because of the loss of thermionic excited electrons, junction 7 is working as expected. It is worth noting that the resistance of all junctions, except junction 11, is quite high. Especially junction 12 has a very high resistance around low voltages. To see this more precisely the lock in measurements of the resistivity are shown next. Furthermore the NCCO leads should show p-n type behaviour, as the current from a NCCO lead has to cross over into an LSCO layer at least once. It may also be the case that the current is flowing into the bottom layer of LSCO or NCCO straight away and then flows upwards through the multilayer, creating the p-n behaviour. This is in agreement with what we see here either way.

7.2.2 Resistivity curves bath cryostat

![Resistivity curve Junction 7 - 50μm LSCO @4.2K](image1)
![Resistivity curve Junction 11 - 200μm LSCO @4.2K](image2)
![Resistivity curve Junction 8 - 50μm NCCO @4.2K](image3)
![Resistivity curve Junction 12 - 200μm NCCO @4.2K](image4)

Figure 43: dV/dI curves LM3NL01 junctions 7, 8, 11 and 12 at 4.2 K

A very interesting difference between the leads is that the LSCO leads show a zero bias resistivity peak, whereas the NCCO leads show a sharp dip. This may be caused by the measurement setup and will be discussed in the Discussion section. Junction 7 is behaving strangely. It has a sharp dip, but within that dip there is a small peak. As mentioned before, the peak resistances of the junctions vary greatly. This confirms our expectations of the large variation in quality of the leads, especially since we assume any defects or variations in stoichiometry in the stack have only a minor effect on the resistivity compared to those in the leads themselves.
In junction 8 there are two lobes, symmetrically around +0.07V bias and again some unexpected variation in the resistivity around +0.10V. The origin of this increase in resistivity is unknown to us. To determine whether it was some form of supercurrent we measured the sample in the PPMS and applied a magnetic field. However, in the PPMS there was no sign of these lobes at all, so the results are inconclusive. The absence of this behaviour in the PPMS measurements may be caused by degradation of the sample, because the PPMS measurements were performed more than two weeks later. More results of the PPMS will be shown further on, but first we will look at resistivity curves at 1.5K in the bath cryostat.

Junction 11 shows a smooth dV/dl curve, with the range of the bias being very small since the resistivity is low. The sharp peak indicates that there is a pseudogap in the junction. This result seems to provide another basis to our claim that the current flows into a lower layer of the multilayer stack first and has to cross the NCCO layers as well, giving rise to this increased resistance.

Junction 12 also displays the strange lobe structure around zero bias. A resistivity rise is observed at +0.2 V and another feature is seen at 0.3 V. Again, these features have not been observed in the PPMS measurements, maybe due to degradation of the sample.

Figure 44: dV/dl curves LM3NL01 junctions 7, 8, 11 and 12 at 1.5 K
In this series of measurements we found the following behaviour.

Junction 7 showed an increase in resistance, but only slightly. The peak became very sharp compared to the measurement at 4.2K. It still has a very small dip around zero bias, but it is unclear why.

The resistivity curve of junction 8 became very smooth, however the dip in the centre was gone completely; it gave way for a spike. The lobes are also still present. An interesting thing happened to the resistance of junction 8 in general: it dropped from 19.5KOhm to 14KOhm at low bias, but the effect was even stronger for higher biases: the resistance dropped from 15KOhm to 2.5KOhm there.

Junction 11 showed large hysteresis at 1.5K and an increase in resistance. Low bias resistance increased from approximately 650 Ohms to 1650 Ohms. For larger voltages the increase in resistance was smaller, about 125 Ohms, from 275 to 400 Ohms.

Junction 12 had the largest resistance at 1.5K by far, about 55KOhm. This is a clear indication that a phase change into the AF phase definitely occurred, or was occurring. The shape of the curve is as we expect: a high resistivity around low bias and a decrease for higher biases.
7.2.3 PPMS IVT curves

The first IVT curve shows some expected and some unexpected behaviour. As stated, we expect the resistance to increase for lower temperature since the thermionic transmission decreases. This can be clearly seen in the graph as the widening of the blue central bar. What is somewhat unexpected though, is the decrease in resistance at around 140 K. This could be explained from the NCCO that has a phase transition into the AF regime for temperatures under approximately 140K for the level of doping used but has a decrease in resistance until then, see figure 46. The sheet resistance as function of temperature of NCCO and LSCO can be seen in figure 29. These do not indicate a large resistance transition at 140K.

Figure 45: IVT curve LM3NL01 junction 7
Figure 46: NCCO phase diagram

Figure 47: IVT curve LM3NL01 junction 8

Junction 8 does not have the diminished resistance at around 140 K, as we have seen in junction 7. The graph is highly symmetrical and the applied bias at low temperatures is much larger than that of junction 7, in other words the resistance is higher. The increase in resistance as function of temperature is minor until 100 K, after which it increases rapidly.
The IVT curve of junction 11 has some interesting features. Again we see the decrease of the resistance until approximately 140 K. But there appears to be a transition to the superconducting phase at around 12K. Why the junction does not become completely superconducting is unclear, as the top layer is LSCO. It may be the case that the LSCO has degraded as a consequence of the small strain on the lattice. Another possibility is that the lowest layer of LSCO is of higher quality than the top layer, and this layer becomes superconducting before the NCCO layers above enter the AF regime. If we sum the sheet resistances of NCCO and LSCO this seems to be a very likely possibility.
Figure 49: IVT curve LM3NL01 junction 12

The IVT curves of junctions 8 and 12 are similar. The resistance increases strongly from temperatures of 100K and lower and the graphs are very symmetrical.

If we look at the IVT curves from the NCCO junctions of the multilayer sample and the IVT curves from the single layer sample we see similarities and differences. Both the 40 µm and 200 µm junction in the single layer sample have the increase in resistance at high (300-180 K) temperatures. They also show another increase in resistance at low temperatures. This latter is also clearly visible in the multilayer stack for NCCO junctions, but the former is not. Furthermore the IVT curves of the multilayer sample are very symmetrical whereas the ones of the single layer sample are not.

Looking at the multilayer LSCO junctions we see a decrease in resistance as the temperature decreases until approximately 140 K. After that the NCCO enters the AF regime and the resistance increases. An interesting thing we can see in the IVT curve of the LSCO 200 µm junction is the drop in resistivity for temperatures less than 20 K. This resistance drop indicates a superconducting transition in the LSCO.
8. Discussion

It became apparent that growing a high quality multilayer sample is a difficult task. The choice conditions of the PLD growth has mostly been an educated guess, since there was not a lot of information available on growing LSCO and NCCO on top of each other, especially about annealing conditions. However, these growth methods appear to have acceptable quality and some measurements with reasonable results have been done.

On top of the difficult fabrication process itself, we made a major error in the timing of the annealing-period in the growth process. This error was the 60 hour stay of the sample at 760°C in the PLD chamber during the second lead deposition stage. This may have destroyed crystals in the sample, creating holes in the multilayer and leads. Also, the gold contacts were not sticking to the surface very well. The gold peeled off very easily on its own or by wire bonding.

The lead resistances in the multilayer sample are quite high, which is compensated for by four-point measurement. However, the bath cryostat setup displayed strange behaviour for values around zero voltage bias. This can be caused by new physics, but most probably this is due to the relatively high resistance of the sample compared to the internal resistances of the measurement setup, which is built for superconductivity measurements rather than high resistances. This behaviour can be investigated by measurements of semiconductor p-n junctions with comparable IV-curves, which are well understood. To confirm or reject new physics taking place, the PPMS was used.

The lock-in measurements provide direct measurement of the dV/dI characteristics of the samples. However, a first order Taylor approximation is not a very accurate quantitative measurement. Since no hysteresis took place, this did provide some qualitative measurements, indicating the double gap size in the pnp contacts of the single layer sample, for instance.

On a concluding note of the discussion part, we state that multilayer Mott insulator samples are still a leap of faith with not enough background information to make sound conclusions about the physics happening in these samples. Essential background information includes the growth of LSCO on NCCO and vice versa, investigation of the p-n behaviour of these materials and a better mapping of the phase diagram including possible new phases.

Despite these efforts, more work still needs to be done, interesting features have certainly been found and will be discussed in the conclusion and recommendations sections. Outlooks for this kind of multilayer samples include possible new interface effects, investigations of the pseudogap phase and out-of-plane conductance and, in the far future, exciton research.
9. Conclusion
For as far as we know this is the first time a multilayer stack with three layers of both LSCO and NCCO was grown using PLD and measured at low temperatures. This multilayer stack has been grown with acceptable quality for some of the junctions and these junctions have shown some interesting results.

The results from the single layer sample are reproducible in different setups and provide possible evidence about the nature of the energy structure and phase diagram. p-n behaviour in this sample is confirmed and possible material property transitions have been seen, including thermal excitation and a transition at low temperatures, the nature of which is unknown. Indications for improvement of the growth of these samples have also been found, the most important being the deviation of optimal doping during deposition by misaligning the PLD plume.

When we connected the junctions as pnp contacts, we saw some interesting features. The first connected junction seems to dominate the height of the peak in the dV/dI curve and the width of the dV/dI peak is about twice that of the p-n curve. This latter fact indicates a double energy gap in the pnp contact, compared to the p-n contacts.

The measurements were done properly and are reproducible. They have provided interesting results for further research. Considering IV-curves, at 300 K, both ohmic and nonlinear IV-curves have been observed. The distinction in these appears to be the junction width and not the lead material, the physics behind which are unknown.

At 4.2 K, all four measured junctions exhibited different behaviour. The NCCO curves appear to have dV/dI lobes for distinct absolute voltages, the nature of which is unknown. The 200 µm LSCO junction has a very low resistance, which is not caused by shorts. The IVT-measurements indicate a transition at about 15-20 K, which was confirmed to be a superconducting transition in the top LSCO layer by a two point RT-measurement. The other IVT-curves all look symmetric, with a change in the trend at about 140 K. This may be due to the AF transition in the NCCO or a pseudogap in the LSCO, but this is still inconclusive.
10. Recommendations

The recommendations below are separated in two parts. The first part is about how more insight into the done experiments can be obtained. The second part is about which systems could be investigated in the future to further characterise the properties of the used materials.

10.1 Improvement of current experiments

After analysis of the data, we found that it is hard to describe precisely what parts of the sample are the causes of the observed IV-characteristics. We think that it can be helpful to design the sample in such a way that the only way the current can flow is directly through the junction and the multilayer stack. To this end, we suggest an improvement in the preparation of the sample. Instead of the current STO capping layer we suggest using LSAT or LAO as top layer instead. The reason is the possibility of STO becoming conducting after argon etching, and thus there may be a conducting interface between the STO and the leads in the ab-plane.

A very simple second recommendation is to prepare another multilayer sample where the PLD setup is not turned off before the weekend and the sample is not kept at 760 °C for 60 hours. This may provide information about the effect of long-term heating of these samples. Also, growing a similar sample can provide additional measurements of the wide variety of strange effects seen, such as the lobes on the dV/dI curves of the NCCO samples at 4.2 K and the superconducting transition in the 200 µm LSCO junction.

Furthermore we found very large variations in junction quality in the sample we have prepared. We think that this may be caused by the way the material is deposited in the PLD-chamber. To be able to discuss this properly we think it would be useful to make another multilayer sample, but this time with equal junction widths for all junctions. That way any stoichiometric variations in the ab-plane can be mapped as function of location on the substrate.

To be able to measure these kinds of samples in a better way in the future, we suggest adapting the bath cryostat measurement setup to higher resistance samples. This might be done by using semiconductor p-n contacts with similar resistance values.

Another recommendation we have is measuring these materials at temperatures above 300 K, instead of measuring at very low temperatures. This may lead to a better understanding of the thermionic excitation of the electrons and their effect on resistivity of the leads for all temperatures as the pseudogap may turn out to vanish for high enough temperatures.

To understand the nature of the growth effects better, it may be interesting to investigate the behaviour of the top LSCO layer, when grown on NCCO. Effects of strain on the electronic properties of materials need to be investigated further, as are possible interface effects, which have not been investigated further in this report.

We think it can give greater insight in the working of these samples by making a setup where the leads are being investigated by measuring their IV-characteristics. With this new sample it would be possible to not only verify the things we have measured with our sample, but also to map in greater detail the origin of the resistance in the leads.
10.2 New systems

The complex multilayer system calls for a lot of improvement, but new systems can also be built to investigate several properties of the multilayer components.

A first suggestion is to create a system where there are only two layers, one NCCO and one LSCO and part of the bottom layer is being exposed, so this can be reached with gold contacts. This kind of experiment can provide insight into interface effects happening at these materials as well as insight in possible exciton condensates to emerge. This kind of experiment will certainly contribute to better understanding of the results of this multilayer sample. Such a system should not be made very complicated with a lot of junctions with variable junction width. A simpler design like a Hall bar would be sufficient and because of the simplicity, better.

More layer systems can be grown in the same fashion to investigate interfaces between the layers of similar multilayer systems. This can provide a mapping of possible physics happening at these interfaces, like the strength of coupling of the layers when more layers are introduced. To this end, layer thickness can also be varied. However, the growth of contacts for every separate layer will introduce more etching steps and more complexity in sample design. This means that the results will be harder to reproduce and may therefore be considered more unreliable, since the sample will be harder to reproduce correctly with every step added.

The third and last system suggestion would be to create a multilayer sample with leads that only make contact to the same type of material. This way, only the surface parallel to the current direction is in contact with the other type of material, providing information about the c-axis conductance of these systems. We suggest doing this in a bilayer first and in a multilayer system later on. Sample design should be like the one in this project, providing possibilities to investigate junction width dependence.
11. Appendix

11.1 Appendix A: Used equipment

Hardware
- PLD setup
- X-ray diffraction measurement setup
  - Bruker D8
  - Cu-source, lambda = 1.54 Ångstrom
- Argon etcher
- Spincoater
  - Cleanroom environment
  - Photoresist OLIN 906/12, 907/17
  - Solvent OPD 4262
- Sputter cannon
- Wire bonder
- Bathcryostat
  - Cooling to 4.2 K, pump till ~1.5 K
- Measurement/control boxes PXI (specs?)
- Physical property measurement system (PPMS)
  - Quantum Design

Software
- LabVIEW
  - Virtual instrument made for PLD control & bath cryostat control
- CleWin v4
- Gwyddion
- Origin 8.6
- MATLAB 7.11.0 (R2010b)
11.2 Appendix B: other measurements

1.5 K measurements of multilayer J7, 8, 11 and 12
For completeness, the results of the multilayer measurements of junction 7, 8, 11 and 12 are added here. These results provide no additional features to the results acquired at 4.2 K, only a slight change in resistivity, which is expected based on the sheet resistance values and the rise of antiferromagnetism.

Figure 50: IV-curves J7, J8, J11, J12 at 1.5 K
RT measurement central pads
A two-point measurement of resistance versus temperature was done to determine whether the LSCO top layer is exhibiting a superconducting transition.

![RT-measurement central pads multilayer stack](image)

Figure 51: RT-measurement central pads multilayer stack

This figure indicates a superconducting transition taking place between about 20 and 25 K. The resistance does not drop to zero because of the resistance of the connecting wires and gold contacts, being measured with the two-point measurement. This transition provided some explanation to the junction 11 IVT-measurement, which exhibits a similar transition below 25 K.

In the graph below, the sheet resistances of LSCO (x=0.09) and NCCO (x=0.10) being mentioned earlier are plotted, connected parallel \( R = \frac{R_1 \times R_2}{R_1 + R_2} \). A comparison with the graph above indicates that the LSCO grown on the NCCO has a higher \( T_c \). Otherwise, this graph does not provide any qualitative or quantitative information, despite of the resistance values being very alike the graph above.

![Theoretical parallel resistance LSCO + NCCO](image)

Figure 52: parallel connected 50 nm thick sheet resistance of LSCO and NCCO
11.3 Appendix C: growth and structuring conditions

LM3NL01

PLD growth conditions

For the multilayer LM3NL01, the expanded PLD growth conditions have been given below. Unfortunately, the exact LSCO lead deposition data has not been retrieved from the system, but the conditions were very similar to the LSCO deposition during the multilayer deposition in the second column.

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<th>Multilayer</th>
<th>STO cap</th>
<th>NCCO electrode</th>
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<td>10-2-2012</td>
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<tr>
<td>Deposition temperature</td>
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<td>Cooldown</td>
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System info

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Calculate optics

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Warming up

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<td>0.25 &amp; 0.13 mbar</td>
<td>0.1 mbar</td>
<td>0.25 mbar</td>
</tr>
</tbody>
</table>
Warming up procedure:

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Temperature range</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>WU to 300°C PID</td>
<td>300-820°C @ 20°C/min</td>
<td></td>
</tr>
<tr>
<td>Wu to 300°C</td>
<td>300-700°C @ 20°C/min</td>
<td></td>
</tr>
<tr>
<td>WU to 300°C</td>
<td>300-820°C @ 20°C/min</td>
<td></td>
</tr>
</tbody>
</table>

Measure laser energy

<table>
<thead>
<tr>
<th>Energy behind lens</th>
<th>Laser voltage</th>
<th>Laser energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>74.7 +/- 0.88</td>
<td>19.7 kV</td>
<td>340 mJ</td>
</tr>
<tr>
<td>93.2 +/- 0.59</td>
<td>21.5 kV</td>
<td></td>
</tr>
<tr>
<td>75.0 +/- 1.1</td>
<td>19.7</td>
<td></td>
</tr>
</tbody>
</table>

Preablation & Deposition

<table>
<thead>
<tr>
<th>Preablation</th>
<th>Deposition</th>
<th>Estimated thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 min @ 10 Hz</td>
<td>2 min @ 10 Hz</td>
<td>50 nm</td>
</tr>
<tr>
<td>NCCO</td>
<td>STO</td>
<td>50 nm</td>
</tr>
<tr>
<td>LSCO</td>
<td>NCCO</td>
<td>150 nm</td>
</tr>
</tbody>
</table>

Anneal procedure

<table>
<thead>
<tr>
<th>Gas flow</th>
<th>Process pressure</th>
<th>Cool down</th>
<th>Annealing temperature</th>
<th>Cool down</th>
<th>Annealing temperature</th>
<th>Cool down</th>
</tr>
</thead>
<tbody>
<tr>
<td>chamber vented</td>
<td>1 bar, oxygen (@650°C)</td>
<td>700-600°C @ 10°C/min</td>
<td>15 min @ 600°C</td>
<td>600-450°C @ 10°C/min</td>
<td>30 min @ 450°C</td>
<td>450-RT @ 10°C/min</td>
</tr>
<tr>
<td>chamber vented</td>
<td>1 bar, oxygen (@780°C)</td>
<td>700-600°C @ 10°C/min</td>
<td>15 min @ 600°C</td>
<td>600-450°C @ 10°C/min</td>
<td>30 min @ 450°C</td>
<td>450-RT @ 10°C/min</td>
</tr>
</tbody>
</table>

Etching

The etching procedure has also been logged. The etch procedures for the multilayer, NCCO electrode layer and LSCO electrode layer had to be redone after AFM showed that the ramp heights were insufficient. This means two sets of data for each.

Some settings were constant for every etch step:

<table>
<thead>
<tr>
<th>Ar flow</th>
<th>X pos</th>
<th>Y pos</th>
<th>Z pos</th>
<th>On/off</th>
<th>V_{beam} (V)</th>
<th>V_{acc} (V)</th>
<th>V_{dis} (V)</th>
<th>I_{dis} (A)</th>
<th>I_{beam} (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>20</td>
<td>15</td>
<td>18</td>
<td>8/12</td>
<td>500</td>
<td>100</td>
<td>40</td>
<td>0.38</td>
<td>10</td>
</tr>
</tbody>
</table>
For the other steps, values for settings are given below:

<table>
<thead>
<tr>
<th>Etch step</th>
<th>Multi1</th>
<th>Multi2</th>
<th>n-lead1</th>
<th>n-lead2</th>
<th>p-lead1</th>
<th>p-lead2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>NCCO</td>
<td>NCCO</td>
<td>NCCO</td>
<td>NCCO</td>
<td>LSCO</td>
<td>LSCO</td>
</tr>
<tr>
<td>Date</td>
<td>09/02/2012</td>
<td>10/02/2012</td>
<td>13/02/2012</td>
<td>14/02/2012</td>
<td>15/02/2012</td>
<td>17/02/2012</td>
</tr>
<tr>
<td>P_{back}(mbar)</td>
<td>4 e-7</td>
<td>5.6 e-7</td>
<td>1.1 e-7</td>
<td>1 e-7</td>
<td>1 e-7</td>
<td>4.7 e-7</td>
</tr>
<tr>
<td>Angle</td>
<td>45 rot</td>
<td>45 rot</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>P_{etch}(mbar)</td>
<td>1.6 e-3</td>
<td>1.6 e-3</td>
<td>1.6 e-3</td>
<td>1.6 e-3</td>
<td>1.6 e-3</td>
<td>1.5 e-3</td>
</tr>
<tr>
<td>I_{fil}(A)</td>
<td>5.78</td>
<td>5.73</td>
<td>5.77</td>
<td>5.71</td>
<td>5.64</td>
<td>5.79</td>
</tr>
<tr>
<td># pulses</td>
<td>75</td>
<td>7</td>
<td>41</td>
<td>24</td>
<td>42</td>
<td>4</td>
</tr>
<tr>
<td>Etch time</td>
<td>8+8+9 min</td>
<td>2min20s</td>
<td>7+6min10s</td>
<td>8min</td>
<td>7+7min</td>
<td>1min20s</td>
</tr>
</tbody>
</table>

**LSNL05**

For the single layer LSNL05 sample, the PLD growth conditions are listed below.

<table>
<thead>
<tr>
<th>Deposition temperature:</th>
<th>820 C - 740 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition pressure:</td>
<td>0.25 mbar-0.1 mbar</td>
</tr>
<tr>
<td>Laser fluency:</td>
<td>1.2 - 1.5</td>
</tr>
<tr>
<td>Annealing:</td>
<td>1 bar oxygen</td>
</tr>
<tr>
<td>Cooldown:</td>
<td>10 C/min</td>
</tr>
</tbody>
</table>

**System info**

<table>
<thead>
<tr>
<th>System:</th>
<th>PLD-Combi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target:</td>
<td>NCCO 0.10 &amp; STO</td>
</tr>
<tr>
<td>Target notes:</td>
<td>Ce = x=0.10, STO mooie, LSCO x=0.09</td>
</tr>
<tr>
<td>Substrate:</td>
<td>LS046</td>
</tr>
<tr>
<td>Substrate Treatment:</td>
<td>LSAT 5.0x5.0x0.5 mm, one side polished</td>
</tr>
<tr>
<td>Substrate Notes:</td>
<td>annealed at 1050 for 210 minutes, cleaned with acetone &amp; ethanol</td>
</tr>
</tbody>
</table>

**Calculate optics**

| Desired fluency:       | 1.2 - 1.5     |
| Desired laser spot:    | 5.70 mm2      |
| Efficiency:            | 0.92 N not checked |
| Mask type:             | 7h            |
| Desired energy behind lens: | 74.3 - 93 |
| Mask position:         | 710.16 mm     |
| Mirror position:       | 140 mm        |
| Lens position:         | 31.65 mm      |

**Warming up**

<p>| Background pressure:   | 3.1 e-7 mbar  |
| Gas:                   | oxygen        |
| Gas flow:              | 25 - 20       |
| Deposition pressure:   | 0.25 mbar - 0.1 mbar |
| Warming up procedure:  | to 400 C PID  |</p>
<table>
<thead>
<tr>
<th>Preablation &amp; Deposition</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Preablation:</strong></td>
<td>2 min @ 10 Hz</td>
</tr>
<tr>
<td><strong>Material:</strong></td>
<td>STO</td>
</tr>
<tr>
<td><strong>Deposition:</strong></td>
<td>105 sec = 1 min 45 sec @ 4 Hz</td>
</tr>
<tr>
<td><strong>Estimated thickness:</strong></td>
<td>~50 nm</td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>0.1 mbar</td>
</tr>
<tr>
<td><strong>Preablation:</strong></td>
<td>2 min @ 10 Hz</td>
</tr>
<tr>
<td><strong>Material:</strong></td>
<td>NCCO Ce:0.1</td>
</tr>
<tr>
<td><strong>Deposition:</strong></td>
<td>2 min @ 4 Hz</td>
</tr>
<tr>
<td><strong>Estimated thickness:</strong></td>
<td>480 pulses ~50 nm</td>
</tr>
</tbody>
</table>

**Anneal procedure**

- **Cool down:** 1 bar O2 @ 700°C
- **Gas flow:** 700-600 @ 10 C/min
- **Annealing temperature:** 15 min @ 600°C
- **Cool down:** 600-450 @ 10°C/min
- **Annealing temperature:** 30 min @ 450°C
- **Cool down:** 450-RT @ free cooling
12. Acknowledgements

This assignment has been a very interesting challenge for us, however without all the help we received; it would not have been a success. Obviously we are very grateful for all the people who helped us with any questions or problems we had.

Most notably we want to thank Hans Hilgenkamp and Marcel Hoek.

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