The growth of patterned ceramic thin films from polymer precursor solutions

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CHAPTER 3

Film Analysis

Several methods have been used to analyse various physical properties of the manufactured films as well as their topography. These analysis methods are described in this chapter.

3.1 Microscopy

Apart from optical microscopy, the samples were imaged by the following methods.

3.1.1 Scanning Electron Microscopy

For scanning electron microscopy (SEM) the sample surface has to be conductive. The sample is placed into a high vacuum chamber and an electron beam, generated by applying a voltage (in the kV range) between the sample and a cathode, is focussed onto the sample surface by means of electric or magnetic fields serving as lenses. The spot diameter is approx. 10 nm, depending on the current. Electrons impinging on the sample release, due to their high kinetic energy, secondary electrons. Some of those are emitted into the space above the sample and are collected by a detector which has a positive bias with respect to the sample. The electron beam spot can be moved over the sample surface by applying additional magnetic or electric fields. For imaging the electron beam is scanned over the surface line by line and for each position \( x,y \) the intensity \( I \) of the detector signal is recorded and is displayed as an
image $I(x,y)$. Depending on material properties of the illuminated spot area, the amount of emitted secondary electrons varies and so does the intensity of the detector signal. Different materials thus differ in brightness in the scan image. Furthermore, the number of electrons that fall onto the detector depends on the presence and size of obstacles between the electron spot and the detector. A high feature causes a “shadow”, shielding the secondary electrons from beyond this feature on their way to the detector. Similarly, deep pits in the surface appear black, since secondary electrons created within the pit are nearly always adsorbed by the walls of the pit. Sharp protruding edges or peaks, where the electric field density is higher, on the other hand, appear brighter since the secondary electrons have a higher probability to leave the sample in locations of a higher electric field.

For the SEM images in this work, a Jeol 6320F field emission SEM was used with magnetic lenses (JEOL, Tokyo, Japan). The distance between the sample and the lowest lens, the objective lens, is the working distance and was usually set to 5-7 mm. The acceleration voltage was 1.5 kV.

3.1.2 Transmission Electron Microscopy

A transmission electron microscope (TEM) makes, just as the SEM, use of electron optics. The sample is placed into a vacuum chamber and exposed to an electron beam. Unlike in the SEM, in the TEM the beam is not focussed but the spot covers an area of about $2 \mu m$ in diameter. If the sample is sufficiently thin, electrons can travel through the sample with a finite probability. A sufficiently low sample thickness can be achieved by grinding a bulk sample to a fine powder of very small crystallites or by carefully milling a film to a local thickness of zero. Around this hole the sample has a wedge geometry and one can easily choose a spot, where the sample is thin enough for electron transmission but thick enough to provide electron contrast. Unlike the SEM, the sample does not have to be conductive. The transmitted electrons fall onto a fluorescent screen underneath the sample, where areas with a higher transmission rate appear brighter than areas with a lower one. By using a parallel electron beam and additional lenses between sample and screen one can obtain the diffraction image of all crystals within the spot area instead of the local transmissivity. For one of the films produced in this work ($Al_2O_3$) this technique was applied to determine the chemical composition of the films. The diffraction pattern evolving during electron irradiation was that of a crystalline
3.1 Microscopy

Al\textsubscript{2}O\textsubscript{3} phase, indicating that the molar ratio Al:O of the film amounted 2:3.

The TEM used for this purpose was a Jeol 2010F field emission TEM with an acceleration voltage of 200 kV (JEOL, Tokyo, Japan).

3.1.3 Atomic Force Microscopy

An atomic force microscope (AFM) is a scanning probe microscope that makes use of a small tip which is in close contact with the surface of the sample. Tip and surface interact by short range forces such as van der Waals forces (attractive) and the Coulomb force (repulsive). The tip has the shape of a cone with elliptical cross section and the cone angles of 40°-50° in one direction and 50°-60° in the other. The very end can be described as a hemisphere with a radius of less than 10 nm. The tip height is approx. 10-15 \( \mu \)m. The AFM used in this work to get information on the sample topography was a tapping mode AFM. Its principle is as follows: The probing tip, pointing downwards, is located at the free end of a tiny cantilever (length: 129 \( \mu \)m, width: 29.5-31.3 \( \mu \)m, thickness: 3.8-4.5 \( \mu \)m, the other end is fixed on a small piezo crystal (Fig. 3.1 (a)). By oscillating the piezo crystal in vertical direction with a frequency \( f_d \) close to the resonance frequency \( f_0 \) of the cantilever (usually several 100 kHz), the tip performs an oscillation with a large amplitude at frequency \( f_d \). The upper side of the oscillating cantilever serves as a mirror for a laser beam from a fixed laser diode, which is reflected into a segmented photo diode serving as detector. The output voltages \( U_{up} \) and \( U_{lo} \) of the two segments depend on how much light from the laser beam falls onto each of them. An oscillating cantilever causes the spot of the reflected laser beam to oscillate over the segments, generating an oscillating voltage in each segment. The normalized difference of the two voltages, \( \frac{U_{up} - U_{lo}}{U_{up} + U_{lo}} \), is an AC signal with the frequency \( f_d \). The amplitude is maximal for the given amplitude of the piezo crystal driving oscillation (Fig. 3.1 (b)). The oscillating piezo crystal is fixed to the lower end of a so-called scanner, which is a hollow tube of a piezoelectric ceramic. Under angles of 90°, four electrodes are placed on the outside of the cylinder. A fifth electrode is inside the tube. By applying a voltage between outer and inner electrodes, the tube stretches. A voltage between opposite outer electrodes causes the tube to bend [35]. The upper end of the scanner is fixed to the frame of the AFM. The scanner moves the cantilever and the tip horizontally and vertically. By mechanically lowering the scanner, the tip is brought into proximity of the sample surface. Due to the increasing
interaction between tip and surface, the oscillation amplitude of the cantilever is dampened. As a consequence the amplitude of the detector output signal decreases (Fig. 3.1 (c) and (d)). A feedback algorithm keeps the detector output signal constant (at a setpoint smaller than the maximum amplitude) by adjusting the vertical tip position. To scan the tip over the sample surface, the scanner moves the tip line by line over the sample, while the feedback loop, comparing setpoint and output signal, adjusts the vertical position of the tip by applying a voltage to the vertical component of the scanner. If the relation between the applied voltages to the scanner in horizontal ($x,y$) and vertical ($z$) direction and the corresponding deformations in these directions are known,
the tip-“height” $z$ (in nm) for each surface point $x,y$ (in $\mu$m) can be determined. This way the topography of the sample can be measured. The AFM software subdivides a single scan line into a fixed number of datapoints $x,y$ and logs the tipheight $z(x,y)$. One has to be aware that the vertical position $z(x,y)$ of the tip is not identical to the height of the surface since different materials of the sample surface can cause different dampings of the tip oscillation. A material with a strong damping causes the feedback loop to retract the tip more than a material with a weak damping. The first material will thus appear higher in the scan than the second. This is mainly a problem with soft materials, such as polymers. The samples that were scanned in this work consisted only of inorganic material and of only one phase so that here the heightscale of the scans is reliable.

AFM scans were performed with a Digital Instruments Dimension 3100 AFM (Digital Instruments, Santa Barbara, USA).

### 3.2 X-ray Diffraction

To investigate the phase composition of the inorganic films, as well as a preferential out-of-plane orientation of the crystals, standard $\omega$-$2\theta$ scans (sometimes called $\varphi$-$2\theta$ scans) were made, typically on a standard 2-circle-diffractometer or, in a few cases, on a 4-circle-diffractometer, namely when the sample had to be investigated in more detail at a later stage. To check for potential out-of-plane epitaxy of the films, $\omega$ scans (rocking curves) were taken on the same diffractometer. To investigate the in-plane orientation of epitaxial films, $\varphi$-$\psi$ scans (texture scans) were used, in addition to $\omega$-$2\theta$-$\psi$ scans (area scans). Three different x-ray diffractometers were used in this work:

- A Bruker Axs D8 2-circle-diffractometer (40 kV, 40 mA, software package Diffrac Plus Basic 4.02) was used for some of the $\omega$-$2\theta$ scans.

- A Philips 2-circle-diffractometer PW 1820 4-circle-diffractometer (40 kV, 30 mA, software APD PW 1877 3.6g) was used for some of the $\omega$-$2\theta$ scans and some of the rocking curves.

- A Philips X’Pert MRD 4-circle-diffractometer, type 3050/65 (40 kV, 40 mA, software X’Pert Data Collector 2.0b) was used for some of the $\omega$-$2\theta$ scans and rocking curves and for all texture scans and area scans.
The 2-circle-diffractometers were equipped with a monochromator for Cu Kα radiation, consisting of a graphite (002) single crystal (Bruker) that fulfilled the Bragg condition for Cu Kα radiation (see below).

### 3.2.1 The Reciprocal Crystal Lattice

The vectors \( \vec{a}^* \), \( \vec{b}^* \), and \( \vec{c}^* \) of a reciprocal crystal lattice can be derived from the vectors \( \vec{a}, \vec{b}, \) and \( \vec{c} \) of the direct lattice by the following definitions:

\[
\vec{a}^* = \frac{\vec{b} \times \vec{c}}{V_{cel}} \quad \vec{b}^* = \frac{\vec{c} \times \vec{a}}{V_{cel}} \quad \vec{c}^* = \frac{\vec{a} \times \vec{b}}{V_{cel}}
\]

(3.1)

where \( V_{cel} \) is the volume of the unit cell, \( V_{cel} = \vec{a} \cdot (\vec{b} \times \vec{c}) \).

With these definitions e.g. \( \vec{c}^* \) is always normal to the (001) plane which is spanned by the vectors \( \vec{a} \) and \( \vec{b} \). Furthermore for all orthogonal crystal systems \( \vec{a}^* \parallel \vec{a}, \vec{b}^* \parallel \vec{b}, \) and \( \vec{c}^* \parallel \vec{c} \). Finally, for the trigonal and hexagonal crystal system \( \vec{c}^* \parallel \vec{c} \).

### 3.2.2 \( \omega-2\theta \) Scans

For a 2-circle- or powder diffractometer the angle of incidence, \( \omega \), is defined as the angle between the primary x-ray beam and the plane of the sample holder (Fig. 3.2). The angle of reflection, \( \vartheta \), is defined as the angle between the sample holder plane and the viewing direction of the detector. In a normal \( \omega-2\vartheta \) scan these two angles are varied simultaneously from \( \omega_{min} \) to \( \omega_{max} \). When a single crystal such as a SrTiO\(_3\) substrate is placed onto the diffractometer with its \( \vec{c} \)-axis (also \( \vec{c}^* \)-axis) normal to the sample holder plane, then the detector “sees” the radiation of a diffracted beam only if the Bragg condition is fulfilled:

\[ n \cdot \lambda = 2d_{(001)} \cdot \sin \omega, \ n \text{ being a natural number, } \lambda \text{ the x-ray wavelength, and } d_{(001)} \text{ the distance between adjacent (001) planes}. \]

Under the condition that the angle of incidence \( \omega \) is always equal to the angle of reflection \( \omega = 2\vartheta/2 \). This scan mode is therefore sometimes called \( \vartheta-2\vartheta \) scan and the angle of incidence is called \( \vartheta \), but in this work, for comparability with other scan modes and diffractometers, the expressions \( \omega-2\vartheta \) scan and \( \omega \) for the angle of incidence are used.

If the single crystal is covered with a film of unoriented crystallites, the diffractogram of the sample will show the (00l) reflections of the single crystal
substrate and all reflections of the film, resembling a common powder diffractogram. This is because for all lattice planes there are some crystallites in the film that have a lattice orientation parallel to the plane of the sample holder.

If a film that covers the substrate crystal was grown with a certain out-of-plane orientation (i.e. in the case of epitaxy), the set of observable reflections is reduced to those that come from the lattice plane which is parallel to the sample holder plane. For example, a film of crystals grown with their $a^*$-axis normal to the substrate surface and thus also normal to the sample holder plane, will only give (h00) reflections in the scan.

A film can also have a preferential out-of-plane orientation. In this case, e.g. the $a^*$-axes of the individual crystallites do not point in all directions with the same probability as in a non-oriented film. Nor do they point all in one direction as in an epitaxial film, but they point in one direction, (e.g. along the normal of the film plane) with a higher probability. In this particular case the diffractogram shows all the reflections of this phase as in the powder
Figure 3.3: Rocking curves of samples with correct alignment (a) and misalignment (b). For the sample in (a) the peak is be located at \( \omega = 2\vartheta/2 \). For the sample in (b) it is located at \( \omega = 2\vartheta/2 \) minus the angle of misalignment.

diffractogram, but the intensities of the peaks are changed so that the (h00) peaks have higher intensities compared to the non-oriented film and the (0kl) peaks have lower intensities.

### 3.2.3 Rocking Curves

Rocking curves (\( \omega \) scans) were taken to check for a preferential film orientation normal to the substrate plane: A (preferably strong) peak from the \( \omega - 2\vartheta \) scan was chosen, the detector was set to the corresponding value of the \( 2\vartheta \) angle and was kept fixed. \( \omega \) was varied in the range \([2\vartheta/2 - \delta; 2\vartheta/2 + \delta]\) with \( \delta \approx 3^\circ \).

In the case of an unoriented film, where for each value of \( \omega \) some crystallites have the right orientation to fulfil the Bragg condition, the scattered intensity is constant over the \( \omega \) range. On the other hand an epitaxial film gives rise to a single peak since the Bragg condition is fulfilled only for a single value of \( \omega \). A perfectly epitaxial film would give a peak with a width zero, but in reality, individual crystallites in the film have orientations deviating slightly from the perfect epitaxial orientation and the rocking curve consists of a peak with a finite width, mirroring the mosaic structure of the film.

The center of the peak does not necessarily lie at \( \omega = 2\vartheta/2 \). A small misorientation of the sample does not cause a peak shift in the \( \omega - 2\vartheta \) scan, because
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the position of a peak in terms of $2\vartheta$ is independent from the orientation of the sample, but causes a peak shift in the rocking curve (Fig. 3.3).

3.2.4 Texture Scans

Figure 3.4: The hemisphere in reciprocal space of a texture scan for the reflections \(\{hkl\}\).

If the rocking curves showed more-or-less sharp peaks (indicating an out-of-plane orientation), the in-plane orientation of the film was checked by a texture scan (\(\varphi-\psi\) scan). An \(\omega-2\vartheta\) scan only scans along one direction in reciprocal space, i.e. in the direction normal to the film plane (sample holder plane). It is therefore a one-dimensional scan in the reciprocal space. A texture scan is, however, a two-dimensional scan in reciprocal space, where instead of a line, the surface of a hemisphere (or part of it) in reciprocal space...
is scanned for the reflections \{hkl\}^1 off the substrate surface normal (Fig. 3.4). Due to the definition of the reciprocal lattice vectors \( \vec{a}^* \), \( \vec{b}^* \), \( \vec{c}^* \), each point in reciprocal space with the coordinates \( h \cdot \vec{a}^* + k \cdot \vec{b}^* + l \cdot \vec{c}^* \) corresponds to exactly one reflection \((hkl)\), with \( h,k,l \) integers (Fig. 3.5). If the direct crystal lattice is centered, however, several \((hkl)\) reflections are extinguished. The length of the reciprocal vector \( h \cdot \vec{a}^* + k \cdot \vec{b}^* + l \cdot \vec{c}^* \), with \( h,k,l \) integers is \( 1/d_{(hkl)} \), where \( d_{(hkl)} \) is the distance of adjacent lattice planes producing the reflection \((hkl)\). The vector \( h \cdot \vec{a}^* + k \cdot \vec{b}^* + l \cdot \vec{c}^* \), abbreviated \((hkl)\), is normal to the lattice plane \((hkl)\) and is therefore in the plane of diffraction, forming the bisector between the primary and the secondary beam. In Fig. 3.2, e.g. \( \vec{c}^* \equiv (001) \) is normal to the lattice plane \((001)\). For a texture scan, \( 2\theta \) is set to a value corresponding to the \( d\)-value of a suitable \((hkl)\) reflection and is kept fixed. By this, the

\[\text{Figure 3.5: Direct (a) and reciprocal (b) lattice of an orthogonal crystal, seen along the } \vec{a} \text{-axis.}\]

\(^1\{hkl\}\) represents the set of the \((hkl)\) plane and all symmetrically equivalent planes. In space group P 4mm (\( \text{PbTiO}_3 \)), e.g. \{101\} stands for \((101), (011), (\bar{1}01), \) and \((011)\).
Figure 3.6: The axes of a 4-circle-diffractometer. The \( \varphi \)-axis is closest to the sample, i.e. it is always parallel to the sample surface normal. Therefore it is affected by the movements around the \( \psi \)-axis and the \( \omega \)-axis. The \( \psi \)-axis is always in the plane of diffraction. It is affected only by movements around the \( \omega \)-axis, which is the furthest from the sample. For \( \psi = 0^\circ \), as shown here, the \( \varphi \)-axis is in the plane of diffraction. For \( \psi = 90^\circ \), the \( \varphi \)-axis is perpendicular to the plane of diffraction.

The radius of the scan hemisphere in reciprocal space is defined. The sample is moved so that each radius vector of the scan hemisphere (Fig. 3.4) is once the bisector between the primary beam and the viewing direction of the detector. If this radius vector points to a reciprocal lattice point (i.e. \( h,k,l \) are integers), the corresponding lattice plane fulfils the Bragg condition and the detector measures the intensity of a diffracted beam.

Texture scans were carried out on a 4-circle-diffractometer that allows to move the sample around three mutually perpendicular axes: \( \omega \), \( \varphi \), and \( \psi \) (Fig. 3.6). The axis of the detector, \( 2\vartheta \), coincides with the \( \omega \)-axis. The
movement of the sample for a texture scan with sample inclination $\psi$ in the range $\psi \in [\psi_{\text{min}}; \psi_{\text{max}}]$ and rotational positions $\varphi$ in the range $\varphi \in [\varphi_{\text{min}}; \varphi_{\text{max}}]$ is as follows. After $2\vartheta$ and $\omega$ are set to the fixed values, the sample is brought into the position $\varphi_{\text{min}}, \psi_{\text{min}}$. The sample is rotated around the $\varphi$-axis to the position $\varphi_{\text{max}}, \psi_{\text{min}}$ while the intensity is logged. Such a scan, corresponding to a parallel of latitude of the scanning hemisphere, is called $\varphi$-scan. After the $\varphi$-scan for $\psi_{\text{min}}$ has been taken, the sample is brought back into the position $\varphi_{\text{min}}, \psi_{\text{min}}$. Then $\psi$ is increased by an increment $\Delta\psi$ and another $\varphi$-scan is taken between $\varphi_{\text{min}}$ and $\varphi_{\text{max}}$. In this manner $\psi$ is stepwise increased and $\varphi$-scans are taken until $\psi = \psi_{\text{max}}$ is reached. Fig. 3.4 corresponds to the situation $\varphi \in [0^\circ; 360^\circ], \psi \in [0^\circ; 90^\circ]$.

### 3.2.5 Area Scans

Reciprocal lattice planes that include the surface normal of the sample may be of interest e.g. because they have a higher symmetry or because they are common for both substrate and (epitaxial) film. These lattice planes can be investigated by area ($\omega$-$2\vartheta$-$\psi$) scans. Similar to texture scans they are scans of a two-dimensional subspace in reciprocal space. Unlike texture scans, in area scans an uncurved plane is examined (Fig. 3.7). Strictly speaking not the (infinite) reciprocal plane is scanned but a sector around the origin, delimited by $1/d_{\text{max}}, 1/d_{\text{min}}$ and $\psi_{\text{min}}, \psi_{\text{max}}$ (Fig. 3.7).

To take an area scan of e.g. the $\overrightarrow{b}\overrightarrow{c}^*$-plane of a $\overrightarrow{c}$-axis oriented orthogonal sample (which contains all (0kl) reflections), the sample is rotated to the position $\varphi$ where the $\overrightarrow{b}\overrightarrow{c}^*$-plane is perpendicular to the plane of diffraction (i.e. where $\overrightarrow{a}^*$ is in the plane of diffraction). $\varphi$ is kept constant during scanning. The sample is brought into the position $\omega_{\text{min}}, \psi_{\text{min}}$ and the detector is set to $2\vartheta = 2\omega_{\text{min}}$, where $\omega_{\text{min}}$ is related to $1/d_{\text{max}}$ by the Bragg condition). $\omega$ and $2\vartheta$ are increased, while the intensity is logged, until $\omega = \omega_{\text{max}}$ is reached. Then, the sample is rotated back to $\omega_{\text{min}}, \psi_{\text{min}}, \psi$ is incremented and the next $\omega$-$2\vartheta$ scan is taken (Fig 3.7).

### 3.3 Critical Temperature Measurements

The most important property of a superconducting sample is the absence of a measurable electric resistance below a certain critical temperature $T_c$. Other
3.3 Critical Temperature Measurements

Figure 3.7: The plane in reciprocal space of an area scan.

properties, such as the occurrence of the Meissner effect, i.e. the displacement of a magnetic field from the interior of a superconductor [36], can also be used to check for superconductivity but are technically less easily accessible than the conductance behaviour.

The resistance of a small sample is best measured in the four point mode, where four contacts on the sample form a rectangle or a line (Fig. 3.8 (a) and (b)). The contacts are made by thin metal wires glued onto the sample with a conductive paste, e.g. silver paste. Through the outer contacts (for a line arrangement) or two neighbouring contacts (for the rectangular arrangement) a defined constant current is provided. For a sample with a resistance $R > 0$ the potential difference between these two source contacts creates a voltage not only between them but also between the two inner contacts or opposite contacts, respectively. This voltage between the so-called sense contacts can be measured and is proportional to the resistance of the sample.

If, e.g. due to lack of space on the sample surface, one source and one sense
contact are unified to one single contact (two point mode, Fig. 3.8 (c)) the voltage between the sense contacts is proportional to the sum of the sample resistance and the resistance of the silver paste dots and thus not proportional to the first only. In both cases, however, the resistance of all wires between voltmeter and sample does not enter into the measurement. The multimeters HP3458A and HP3478A (Hewlett Packard, Palo Alto, USA), which were used in the experiments, can also measure the resistance in a two point mode, making use only of the source contacts. In this case the measured resistance is the sum of sample, contacts, and wire resistance.

For resistance measurements, the sample has to be cooled down in a cryostat while the resistance is logged. Usually, four contacts were placed onto the sample, describing roughly a square, by gluing the ends of thin platinum or copper wires with silver paste onto the sample. The other ends of the wires were connected to the sample holder of the cryostat, which was equipped with a temperature sensor. Two different cryostats were used: 1. A self-made cryostat without a temperature control, in which the sample chamber was surrounded by a reservoir for liquid nitrogen. Upon filling this reservoir, the sample temperature dropped very quickly from room temperature to approx. 77 K. After the nitrogen had fully evaporated, the temperature rose slowly to room temperature (Fig. 3.9). The sample temperature was measured by a PT100 resistance thermometer, combined with a HP3478A ohmmeter. The cooling or heating rate of the measurement could not be controlled, nor was the measurement performed in vacuum, giving rise to potential condensation of water on the sample. Nevertheless, several successfull measurements were made with this simple and low-cost device. 2. The second cryostat was a commercial PPMS Mod. 6000 (Quantum Design,
3.4 Critical Current Density Measurements

San Diego, USA). Here, the sample chamber was surrounded by a liquid helium reservoir, which was embedded in a liquid nitrogen reservoir. A heating element allowed to control the sample temperature, which was measured by a PT100 and an internal ohmmeter.

Both cryostats were equipped with a computer that recorded the temperature and resistance measurements and, for the commercial cryostat, controlled the heating. For both cryostats the measurement was performed while heating the sample slowly up from the lowest temperature. For the self-made cryostat the heating rate was between 0 K/min and approx. 0.7 K/min, as estimated from Fig. 3.9. Every minute, the sample temperature, the resistance in the four point mode, and the resistance in the two point mode were measured within approx. 10 seconds, while the temperature continuously increased.

For the commercial cryostat the heating rate was usually set to 1 K/min. Every 2 K the temperature was stabilized and the resistance in the four point mode and in the two point mode was measured.

3.4 Critical Current Density Measurements

The conductance behaviour of a sample of a potential superconductor does not only depend on its temperature but also on the electric current through the sample. If the current density in the sample exceeds a certain value, the critical current density $j_c$, the sample shows a non-superconducting behaviour. $j_c$ is a function of the sample temperature and the strength of a magnetic field surrounding the sample. $j_c$ increases with decreasing temperature and decreasing strength of an external magnetic field. Values for $j_c$ were determined by transport and magneto-optical measurements.
3.4.1 Transport Measurements

For transport measurements, photolithography was used to etch four measurement bridges with well-defined geometry into the superconducting film (Fig. 3.10). Both ends of each bridge ended in wider contact pads. The sample was contacted with four contacts (Pt wire, silver paste) in a line and was cooled down with a Sterling cooler. At a set temperature below $T_c$, an electric current through the sample was established. The current was stepwise increased until the voltage measured in the sense contacts exceeded $10 \mu V$ ($10 \mu V$ criterion). This current was the critical current $I_c$. By dividing $I_c$ by the cross-sectional area of the measurement bridge, $j_c$ was obtained. The transport measurements were carried out by F. Zygalsky at the Technische Universität Berlin on samples made in Groningen. The photolithographic work in preparation of the measurements was done by I. von Lampe at the same university.

3.4.2 Magnetooptical Measurements

This method makes use of both the Meissner effect (i.e. the fact that a type II superconductor expels a magnetic field from its interior), and of the Faraday effect. The Faraday effect is the rotation of the polarization plane of light when travelling parallel to a magnetic field (rotation angle $\alpha = V \cdot l \cdot H$, $V$=Verdet constant or Verdet tensor, $l$=length of the path in magnetic field, $H$=magnetic field strength).

If a superconducting thin film on a paramagnetic substrate is exposed to a magnetic field perpendicular to the film plane, the magnetic field penetrates the superconducting film only close to the film edges. The field free inner part of the superconducting film is called the Meissner phase, the edges which
are penetrated by the magnetic field lines are called the Shubnikov phase. The partial penetration of the magnetic field arises from a supercurrent of the maximum or critical current density $j_c$ near the film edges [37]. The local density of magnetic field lines can be made visible by means of the Faraday effect: Linearly polarized light that falls perpendicularly onto the sample and is reflected by it rotates its direction of polarization in those regions of the sample that are penetrated by field lines (non-superconducting parts and Shubnikov phase). Light that falls onto the superconducting areas, which are field free (Meissner phase) does not change its polarization direction. Between crossed polarizers, the Meissner phase of the sample appears black, the non-superconducting areas and the Shubnikov phase have different shades of grey.

Figure 3.11: Magnetooptical measurement of $J_c$: The brightness profile was taken along the white line. Black area: superconducting film; grey area: no film. The bright areas on the very left of the image originate from magnetic domain structures in the garnet film. Image size: $2.3 \times 2.3 \text{mm}^2$. 
Since the Verdet constant of air is quite small, the contrast of the magneto-optical images can be enhanced by placing a non-doublebreaking material with a high Verdet constant onto the sample. In the present case, a thin layer of doped ferrimagnetic iron garnet (cubic, optically isotropic) with a high Verdet constant was used on a gadolinium-gallium-garnet substrate [38]. The lower face of the substrate was covered with a thin gold layer that reflected the light into a CCD camera.

At the sharp edge of a superconducting region, the magnetic field lines penetrate the superconductor only partially (Shubnikov phase). The field line density at the edge is even higher than in the non-superconducting region. The edge therefore appears as a bright line between a darker area (non-superconducting) and a black area (superconducting) in Fig. 3.11. The light intensity is proportional to the square of the magnetic flux density in the sample. By taking an image of the sample and measuring the light intensity along a line perpendicular to the film edge, a profile of the flux density $B$ along this line is obtained (Fig. 3.12). Under the assumption that the edge belongs to a long narrow stripe of superconducting material, the flux density profile in the Shubnikov phase is given by

$$B(y) = \mu_0 \cdot \frac{J_c}{\pi} \cdot \tanh^{-1} \left[ \left( y^2 - b^2 \right)^{1/2} \cdot y / \left( 1 - \frac{b^2}{a^2} \right)^{1/2} \right]$$

(3.2)

where $y$ is the position along the line, $\mu_0$ is the magnetic field constant, $J_c$ is the product of $j_c$ and the film thickness $d$, $b$ marks the position of the boundary between Meissner and Shubnikov phase within the superconductor and $a$ is the position of the superconductor surface. For the exterior, the flux density is given by

$$B(y) = \mu_0 \cdot \frac{J_c}{\pi} \cdot \tanh^{-1} \left[ \left( 1 - \frac{b^2}{a^2} \right)^{1/2} \cdot y / \left( y^2 - b^2 \right)^{1/2} \right]$$

(3.3)

By fitting the parameters $a$, $b$, and $J_c$, $J_c$ is obtained. The critical current density $j_c$ is $J_c$ divided by the film thickness.

The polarizer and analyzer were part of a microscope that was used to image the sample with a high magnification. The sample and the garnet film were placed in a cryostat, which had a window for optical access. Unfortunately, the resolution of the set-up used in this work was not high enough to observe
3.4 Critical Current Density Measurements

Figure 3.12: Profile of the flux density $B$ along the line in Fig. 3.11, taken at $T=33$ K with an external field of 1.48 mT. The curve is a fit to the data (Eqs. 3.2 and 3.3) with $b=56.23 \, \mu m$ and $a=281.46 \, \mu m$.

one micrometer wide lines of superconducting Bi$_2$Sr$_2$CaCu$_2$O$_x$. Therefore, this method was only used to confirm the results of transport measurements of $j_c$. The magneto-optical measurements were carried out by B. Biehler at the Universität Konstanz, Germany, on samples made at the University of Groningen.