Normal-State Properties and Laser Deposition of YBa$_2$Cu$_3$O$_{7-\delta}$ Superconductor Thin Films

Neng Yu Chen
Normal-State Properties and
Laser Deposition of YBa$_2$Cu$_3$O$_{7-\delta}$ Superconductor Thin Films

PROEFSCHRIFT
ter verkrijgen van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof. ir. K. F. Wakker,
in het openbaar te verdedigen ten overstaan van een commissie
aangewezen door het College van Dekanen, op

maandag 13 februari 1995 te 10:30 uur

door

Neng-Yu CHEN

natuurkundige ingenieur,
geboren te WuHan, Hubei, China
Published and distributed by:

Delft University Press
Stevinweg 1, 2628 CN Delft, The Netherlands
Telephone +31-15-783254
Fax +31-15-781661

CIP-DATA KONINKLIJKE BIBLIOTHEEK, DEN HAAG

Chen, Neng-Yu

Normal-state properties and laser deposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor thin films / N. Y. Chen - Delft: Delft University Press. - Ill.
Thesis Delft University of Technology - with summary in Dutch
NUGi 841
Subject headings: normal-state properties/ high-Tc film growth

Copyright © 1995 by N. Y. Chen
All rights reserved.
No part of the material protected by this copyright notice may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without permission from the published: Delft University Press, Stevingweg 1, 2628 CN Delft, The Netherlands.

Printed in The Netherlands
# Table Of Contents

**Introduction**  
1

**Chapter 1  Structure and thermodynamic stability of YBa$_2$Cu$_3$O$_{7.8}$**

   1.1 YBCO structure and oxygen stoichiometry  
   1.2 Phase stability of the YBa$_2$Cu$_3$O$_{7.8}$ compound  
   1.3 Compositional variation  
   1.4 Hole doping of the YBa$_2$Cu$_3$O$_{7.6}$  
   References  
7

**Chapter 2  Synthesis of the YBCO thin film by laser ablation**

   2.1 Thin film growth of YBa$_2$Cu$_3$O$_{7.5}$  
   2.1.1 Physical vapour deposition  
   2.1.2 Evaporation techniques  
   2.2 Pulsed laser deposition of thin films  
   2.2.1 Different process stages  
   2.2.2 System implementation and applications  
   2.2.3 Sample quality  
   2.3 Study of in-situ growth of Y$_2$Ba$_4$Cu$_8$O$_{16}$  
   Reference  
19

**Chapter 3  Growth of (110) oriented YBa$_2$Cu$_3$O$_{7.8}$ films by laser deposition**

   Abstract  
   3.1 Introduction  
   3.2 Film preparation  
   3.3 Results and discussion  
   3.4 Conclusions  
   References  
53

**Chapter 4  Low 1/f normal-state resistance noise in high-resistivity YBa$_2$Cu$_3$O$_{7.8}$ films**

   Abstract  
   4.1 Introduction  
   4.2 Experiment  
   4.3 Results and discussion  
   4.4 Conclusion  
   References  
65

**Chapter 5  Electronic phase diagram of the cuprates**

   5.1 Introduction  
   5.1.1 CuO$_2$ planes  
   5.1.2 Phase diagram  
   5.2 Normal-state transport properties  
77
5.2.1 The resistivity
5.2.2 The Hall coefficient
5.3 Two basic models
  5.3.1 The Hubbard model
  5.3.2 The Landau's Fermi liquid theory

References

Chapter 6  Scaling of the Hall coefficient and resistivity in
underdoped and overdoped RBa$_2$Cu$_y$O$_{7.8}$ films

  Abstract
  6.1 Introduction
  6.2 Experiment
  6.3 Results and discussion
  6.4 Conclusions
  References

Chapter 7  Search for deviations of time-reversal symmetry
in YBa$_2$Cu$_y$O$_{7.8}$ using transport measurements

  Abstract
  7.1 Introduction
  7.2 Experimental set-up
  7.3 Results and discussion
  References

Appendix A  Material removal rates by laser

Appendix B  Target Synthesis

Summary

Samenvatting

Curriculum Vitae
Introduction

The research described in this thesis started in May 1990. At that time, laser deposition (or laser ablation) was already recognised as one of the most promising techniques for high-$T_c$ thin film growth. Compared with most of the other techniques, laser ablation has several important advantages. The quality of the films made by this technique is reproducible. It is fast, easy to handle, relatively inexpensive and is suitable for deposition of oxide thin films where high oxygen pressure is needed. As the volume of the research on the high-$T_c$ cuprates expanded rapidly, more and more laboratories worldwide started to use this technique to produce cuprate thin films.

In order to satisfy the increasing demand for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) samples needed for various research purposes in our laboratory, it was decided to set up a laser deposition system. The laser deposition system was meant as an additional part of an existing integral system which consists of a MBE growth chamber and a surface analysis chamber. The special requirement for this system design was that it should be integrated with the other parts of the system. This meant that we should be able to transport samples from one part of the system to another without breaking vacuum.

After the system became operational, we were able to optimise the growth parameters to produce single phase (001) oriented YBCO thin films in a very short time. This is mainly due to the fact that the laser ablation process for this type of films had been investigated in a number of laboratories world-wide previously. Therefore, I will not give a lengthy story about the optimisation of growth parameters to grow (100) oriented YBCO films. Instead, I will first discuss more basic issues such as the crystal structure and the phase stability of the YBCO compound in Chapter 1 of this thesis, since they are of fundamental importance for the actual synthesis of this material.

The implementation of the laser ablation system and the characterisation of the sample qualities will be discussed in Chapter 2. Also in this chapter, I will present our study on in-situ growth of the $\text{Y}_2\text{Ba}_4\text{Cu}_8\text{O}_y$ thin films. The $\text{Y}_2\text{Ba}_4\text{Cu}_8\text{O}_y$ phase is potentially more attractive for application purposes due to the fact that it is
chemically more stable than the YBCO phase material (with $T_c$ of about 82 K). However, Y$_2$Ba$_4$Cu$_8$O$_y$ is also more difficult to synthesise using in-situ processes. In fact, no successful in-situ growth of a phase pure Y$_2$Ba$_4$Cu$_8$O$_y$ thin film has yet been reported.

In Chapter 3, I will describe our study on (110) oriented YBa$_2$Cu$_3$O$_{7.8}$ thin film growth. Unlike the (001) oriented YBCO, films which can already be routinely made in a large number of laboratories, the growth of this type of films is a more challenging one. The reason for this is two folds. First of all, the unwanted (103) oriented YBCO grains can easily be formed during the growth process, leading to inhomogeneous structural and electrical properties. Secondly, the (103) oriented grains cannot be easily identified and discriminated from the (110) oriented films using a simple X-ray powder diffractometer. Instead, other techniques which are more time consuming are necessary, such as the use of a Weissenberg camera.

It has already been observed that substrate temperature during film deposition is one of the major factors which determines the crystal orientation in the film, and that low temperature deposition will promote film growth with the c-axis oriented along the substrate surface. Therefore, we have tried to realise well oriented (110) YBCO films by doing film deposition at various low temperatures. We have looked at the crystal orientation using a X-ray powder diffractometer and a Weissenberg camera. We found that pure (110) oriented YBCO phase can only be grown at a temperature below 625 °C.

Besides the setting up of a laser ablation system in our laboratory and using this system to study growth of various types of films, we have used films made by this system to study fundamental issues such as the 1/f resistance fluctuation (Chapter 4), the anomalous temperature dependencies of the resistivity and the Hall coefficient (Chapter 6), and the possible time-reversal symmetry breaking (Chapter 7) in this material. In addition, our laser ablated samples were also used for a large number of other experiments in our laboratory and in various other laboratories which we will not discuss in this thesis.

The 1/f resistance noise in metal and semiconductor has long been studied. It has been observed that the noise level in a sample increases with decreasing number of carrier in the sample, i.e., it scales with the inverse of the sample volume. The presence of resistance noise becomes particularly disturbing for
design and fabrication of small structures, such as at DIMES (Delft Institute for Microelectronics and Submicron Technology). Although the basic mechanism leading to the characteristic 1/f spectra is still a subject of debate, it is generally agreed that the resistance noise is caused by thermally activated motion of defects in these materials. Measurement of the 1/f noise is mostly used to obtain information about microscopic defects and impurities. Recently, anomalously large 1/f noise has been observed in YBCO in the normal state. Even in single crystal YBCO samples, up to 5 orders of magnitude higher noise was measured compared with clean metallic samples. The question arises whether this extraordinarily high noise level was simply due to the presence of a large number of structural defects in YBCO such as minority phases, grain boundaries or has it a more intrinsic origin due to the crystal structure. We have looked at the noise in samples of different qualities. Our results indicate that the high noise level generally found in this material is due the presence of and the electrical conduction along the one dimensional Cu-O chains in the crystal structure (Chapter 4).

High-Tc superconductors show fascinating properties in many different ways. Besides the extremely high Tc's which are common to all these materials, their normal state also shows extraordinary transport properties. The temperature dependencies of the resistivity and Hall coefficient, for example, can not be explained using the currently existing theories and are frequently referred to as 'anomalous' behaviours. In Chapter 5, we will try to give the readers a short overview of a number of experimental results on the temperature dependencies of the resistivity and the Hall coefficient. The purpose of this is to illustrate why these materials are regarded as "anomalous" even in their normal state. This chapter is written as an introduction for Chapter 6. Due to the lack of a generally accepted theoretical explanation for this anomalous behaviour, I choose not to discuss the existing and mostly complicated theories dealing with this subject. Instead I will focus on two basic models, i.e., 1) the Hubbard model and 2) the Landau's Fermi liquid theory. Both of them are frequently used as starting points for forming of a theoretical description for the 'anomalous' normal state properties.

In Chapter 6, I will discuss our study on the temperature dependence of the normal state resistivity ρ(T) and the Hall coefficient RH(T) in (R)Ba2Cu3O7-δ (R = Sm or Y) thin films. These properties were studied as a function of carrier doping. Until recently, doping effects have mainly been studied in the underdoped regime
of this material using oxygen deficient YBCO samples. In our experiment, we have also studied the normal state transport properties in this low doped regime on oxygen deficient YBCO films made by laser ablation. In order to get a more complete picture of the doping effect, we extended our study for the first time into the overdoped regime by measuring Ca-doped SmBa$_2$Cu$_3$O$_{7-\delta}$ thin films grown by MBE. In the heavily overdoped (R)Ba$_2$Cu$_3$O$_{7-\delta}$ samples, we observed for the first time that $R_{eff}(T)$ saturates at high temperature.

In the last chapter of this thesis (Chapter 7), I will deal with the experiment which we carried out to test the possible time-reversal symmetry breaking in YBCO, as predicted from anyon models. One of the observable consequences of the possible breaking of the discrete space-time symmetries $P$ and $T$ in high-$T_c$ superconductors are anomalous transport properties similar to e.g. a Hall conductance. For example, an off-diagonal component in the resistivity tensor would exist even in the absence of an external magnetic field. We tried to reduce possible cancellation effects due to domain formation by using thin films with a lithographically defined sample area of a few square microns. The breaking of time reversal symmetry corresponds to an 'effective' magnetic field, which can be determined by calibrating the zero field off-diagonal resistivity with respect to the Hall voltage in an externally applied magnetic field. Our results indicate that the 'effective' internal field due to time reversal symmetry breaking is either absent or smaller than 75 gauss.

Acknowledgement

I would like to express my special thanks to Leo W. Lander for his major contribution in setting up the laser ablation system. Leo has made all laser ablated samples used in the various experiments described in this thesis. His invaluable experience in vacuum technology and his efforts to maintain the system in a superb condition allowed me to do my research work without disturbances.

Also my special thanks to Harold Assink for his contribution to improve various measuring system used for my experiments, and for his co-operation that lead to the publication of our results described in Chapter 7.
During my stay in this laboratory, I have enjoyed a great deal from working with Vladimir C. Matijasevic. I want to thank him for all the stimulating discussions. The ideas came out of these discussions have inspired me to initiate a number of the research works described in this thesis. I am indebted to 'my' students Kitty van Dijk and Rob Jonker who supported me during the measurements described in Chapter 6 and Chapter 4 respectively. I will never forget the pleasant hours we worked together.

I am grateful to my promoters Hans Mooij and Dick van der Marel who initiated the project and gave me the opportunity to work in the laboratory of the Solid State Physics group in Delft.

Finally, I want to thank all the people in this group for making my working enviroment so pleasant.
Chapter 1  Structure and Thermodynamic Stability of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

Compared to structures encountered in most areas of solid-state physics, those of the high-$T_c$ crystals are rather complicated. The common feature in the structures of all these superconductors is the presence of one or more adjacent $\text{CuO}_2$ layers in their unit cell. It is widely believed that superconductivity is a result of electron interactions in these layers. In our laboratory, we have mainly focused on growth and properties of one of these compounds, the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO). It is the first superconductor discovered with $T_c$ above the boiling point of liquid nitrogen (77.7 K).

Although there are currently other cuprate superconductors known with even higher transition temperatures, YBCO is still attracting much of the research effort. There are a number of reasons for its popularity. First of all, it is relatively easy to make single-phase YBCO compared to $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($T_c = 110$ K) and Tl- or Hg-based compounds. Secondly, it is not toxic as is the case for $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_4\text{O}_y$ ($T_c = 127$ K) or $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ($T_c = 135$ K). Thirdly, due to a large number of extensive studies, the exact crystal structures of YBCO and related phases are very well known. On the other hand, one has to keep in mind that this compound is inherently unstable and can degrade or decompose in a humid environment. In this chapter, we will look at the YBCO structure, its phase stability and the restrictions this stability imposes on the actual synthesis of the YBCO compound.

1.1 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure and oxygen stoichiometry

We show the unit cell of YBCO in figure 1.1. The lattice parameters at room temperature are $a = 3.82$ Å, $b = 3.89$ Å and $c = 11.68$ Å.
It has two closely spaced (3.2 Å) CuO₂ plane layers lying in the a-b direction and separated by an yttrium layer. A one dimensional Cu-O chain, an unique feature of the YBCO structure, can also be seen along the b-direction. Distinction is often made between Cu atoms in the CuO₂ planes, and those in the Cu-O chains. They are denoted as Cu(2) and Cu(1), respectively. The oxygen atoms on the chain sites are mobile. Their mobility increases with temperature. In addition, the number of oxygen atoms in a single YBCO unit cell can vary between 6 (δ = 1) and 7 (δ = 0) depending on the chemical potential of oxygen. As a result, the oxygen content can

![Diagram of YBCO structure](image)

**Figure 1.1.** The structure of orthorhombic YBCO(δ=0). (a) shows the labelling of the relative atom positions; distinguishing the two CuO₂ plane layers and a one dimensional Cu-O chain layer; (b) emphasises the Cu coordination polyhedra.
be tuned by adjusting the temperature and the oxygen pressure in the environment.

When the crystal is fully oxygenated ($\delta = 0$), the oxygen atoms are perfectly ordered between chain copper atoms Cu(1) along the $b$ direction to form the one-dimensional Cu-O-Cu-O-... chains. The crystal structure is then orthorhombic. At the minimum oxygen concentration ($\delta = 1$), all oxygen sites along the chains are empty. The crystal structure becomes tetragonal. Between these two extreme cases, intermediate oxygen content states can have an ordered superstructure as a result of interaction between the oxygen atoms on the chain and interchain sites. This will give rise to a multiplicity of phases. de Fontaine et al [1.1] have calculated these phases using Monte Carlo simulation. The precise environmental conditions such as temperature and the oxygen partial pressure, as well as interactions within the chain layers, determine the thermodynamically most favourable oxygen state (i.e. the value of $\delta$ and the ordering of these oxygen atoms in the Cu-O chain). Figure 1.2 shows the calculated pseudobinary phase diagram of YBCO, adapted from de Fontaine et al [1.1].

It clearly shows that, even for a fixed oxygen content, different temperature can give

![Figure 1.2. Pseudobinary phase diagram for YBa$_2$Cu$_3$O$_{7.8}$, adapted from deFontaine et al [1.1].](image)
rise to different crystal structures. The structural phases OI and T are the usual orthorhombic and tetragonal phases. OII is an ordered orthorhombic phase in which full and empty Cu-O-Cu-O- chains alternate, giving rise to a supercell doubled along the crystallographic a axis. Note the tetragonal-orthorhombic transition near $\delta \approx 0.5$ at high temperature ($T > 600$K).

The change of the lattice parameters versus oxygen content has been determined experimentally by Jorgensen et al [1.2] and is shown in figure 1.3. These samples were prepared in various oxygen pressures at 520 °C followed by rapid quenching in liquid nitrogen.

1.2. Phase stability of the YBCO compound

The term 'phase' is frequently used when issues such as structural stability and thin film synthesis are discussed. Most oxide superconductors exist over a broad
range of composition with slightly differing transition temperatures. Therefore, their phases are frequently regarded as solid solutions. In this section, we will discuss the stability of the on-stoichiometry YBCO phase, Y:Ba:Cu = 1:2:3, where only the oxygen content can vary.

At Y:Ba:Cu = 1:2:3 composition, the YBCO phase is only stable in a certain part of the $P_{O_2}$-T phase space. Above the melting temperature, indicated as $m_1$ in figure 1.4, incongruent melting takes place. As the oxygen pressure is reduced to under 1 mbar, this melting line is intersected by a decomposition line, labelled $d_1$, see Lindemer [1.3]. Under $d_1$, YBCO decomposes into a mixture of three other phases, BaCu$_2$O$_2$, Y$_2$BaCuO$_5$ and YBa$_3$Cu$_2$O$_{7.5}$. Line $d_2$ indicates another important line determined by Williams et al [1.4]. In the region above $d_2$, YBCO is thermodynamically less stable compared to other phases (Y$_2$BaCuO$_5$ and BaCu$_2$O$_2$). Fortunately, the temperature in this region is already so low that metal atoms in the already formed YBa$_2$Cu$_3$O$_{7.5}$ structure cannot gain enough kinetic energy to break out from their positions to form the thermodynamically more favourable phases. However, this $d_2$ line does impose a low temperature limit to the region where YBa$_2$Cu$_3$O$_{7.5}$ is stable and where it can be grown during synthesis. Note, that line $d_2$ lies on the left side of the orthorhombic-tetragonal transformation line of the YBCO. This indicates that the orthorhombic YBCO is thermodynamically never favourable and thus inherently unstable anywhere in the thermodynamic phase space. Therefore, the high-Tc (orthorhombic) YBCO phase cannot be synthesised in a direct manner. Instead, a two-step process is necessary. During the first process step, an oxygen deficient tetragonal YBCO phase can be formed in the region between lines $m_1$, $d_1$ and $d_2$. A fully oxygenated, orthorhombic YBCO can than be obtained during the second step: a subsequent cooling in high oxygen pressure (ca. 1 bar).
Figure 1.4 Thermodynamic phase diagram of the $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$.
1.3. Compositional variation

In the former section we were able to see that, starting from an on-stoichiometry composition 1:2:3, tetragonal YBCO phase is only stable in a small region of the thermodynamic phase space. However, when the composition is off-stoichiometry, a mixture of minority phases can be formed in thermal equilibrium with the YBCO.

In figure 1.5, we show the a section of the pseudoternary phase diagram determined at 850 °C and at a series of oxygen pressures by Ahn et al [1.6]. Their study showed that at 1 mbar, denoted as (h), YBa$_2$Cu$_3$O$_{7-8}$ is in thermodynamic equilibrium with Y$_2$BaCuO$_5$, BaCu$_2$O$_2$, BaCuO$_2$ and "YBa$_3$Cu$_2$O$_y$" phases. This corresponds to there being stable tie-lines between these four phases and YBa$_2$Cu$_3$O$_{7-8}$ in this section of the Y$_2$O$_3$-BaO-CuO pseudoternary diagram. Note that 1 mbar is in the range of the oxygen pressure often used during in-situ YBCO thin film synthesis (see Chapter 2). This pseudoternary diagram indicates that a mixture of YBa$_2$Cu$_3$O$_{7-8}$ with small amounts of two of these minority phases will be formed if one starts from an off-composition material for in-situ thin film synthesis.
Figure 1.5 Pseudoternary sections versus oxygen pressure at 850 °C, from Ahn et al [1.6]. The pressure given close to each diagram determine the range of oxygen pressure over which each pseudoternary section is valid.
1.4 Hole doping of YBCO

The electrical properties of all high $T_c$ superconductors depend strongly on the carrier density in their CuO$_2$ plane layers. Within a small range of doping level, estimated between 1.6 to 2.0 holes per plane copper, many of the high $T_c$ materials can reach their respective highest Tc's [1.7]. Away from this 'optimum doping level', $T_c$ decreases. In order to change the carrier concentration in a given material, one can change the oxygen content in the lattice or substitute cations in the structure with other atoms having different valance.

Let's first look at the influence of the oxygen content in YBCO shown in figure 1.6, from Hass [1.8]. We will start with the largest oxygen deficiency ($\delta=1$). In this case, no oxygen is present in the chains. The YBCO compound is an antiferromagnetic insulator with the Neel temperature $T_N$ at about 500 K. By introducing oxygen onto the chain sites, the $T_N$ decreases monotonically. Over a certain point ($\delta < 0.7$), free carriers (holes) are induced in CuO$_2$ planes. The YBCO compound changes drastically from an insulator to a superconductor, accompanied by a tetragonal to orthorhombic structural transition. Further increase of chain oxygen can induce more holes in the material [ref], and increase the $T_c$ gradually, see $i_1$. Two plateaus in the $T_c$ can be seen, the 90 K plateau around $\delta = 0.1$ and the 60 K plateau around $\delta = 0.4$. When the YBCO compound is fully oxygenated ($\delta = 0$), the material reaches its highest $T_c$ of about 93 K, the hole concentration is said to have reached the optimum value, estimated at 0.16 holes per plane copper [1.9].

The second way to alter the carrier concentration is through cation substitution. A number of rare earth atoms can substitute Y$^{3+}$ in the YBCO structure. Sm$^{3+}$ and Gd$^{3+}$ are among others which can totally replace the Y$^{3+}$ to form the same structure having the same optimum $T_c$ (giving the same carrier density in the CuO$_2$ plane layers). In addition, the hole density in the sheet layers can be increased by partially substituting Ca$^{2+}$ for Y$^{3+}$. This can lead to overdoping the material and depress the $T_c$ when it is sufficiently oxygenated [1.9].
Figure 1.6. The phase diagram of YBa$_2$Cu$_3$O$_{7-\delta}$ as a function of oxygen deficiency $\delta$ and temperature $T$. From Hass et al [1.8].

References


Chapter 2 Synthesis of YBCO thin films by laser ablation

After the brief introduction of the YBCO crystal structure and its phase stability in Chapter 1, we now turn to the actual synthesis of this material. The YBCO compound has a relatively complex structure with different constituent atoms. This makes it susceptible to crystal imperfections such as oxygen loss, atom disorder, grain boundaries and minority phases. In addition, the fully oxygenated orthorhombic high-$T_c$ phase is inherently unstable everywhere in the thermodynamic phase space. On the other hand, the ability to make good quality high-$T_c$ material is of fundamental importance for both scientific research and technological applications.

Much effort has been made world-wide in numerous laboratories to synthesize YBCO using various techniques. It is made in basically three forms: polycrystalline bulk ceramic, single crystal and thin film. Large pieces of polycrystalline YBCO can be made already. However, the presence of an overwhelming amount of grain boundaries between the randomly oriented small grains of YBCO in these samples (typically about 1-2 \( \mu \text{m} \) in size) is responsible for the degraded electrical properties of such samples. Compared to single crystal samples or thin films, the critical current density \( j_c \) in polycrystalline YBCO is lower. They also have higher resistivity \( \rho \) and wider superconducting transitions. In order to study the intrinsic properties of this material, single crystal of YBCO is the ideal candidate. However, the process to make this type of sample is difficult and time consuming. Until now, only small single crystals of YBCO (mostly of the order of 1 mm\(^3\)) have been successfully grown. It must be noted that, even in these "ideal" samples, one still cannot rule out possible presence of imperfections such as inhomogenous oxygen distribution. Many experiments are therefore done on epitaxially grown YBCO thin films (thickness < 1 \( \mu \text{m} \)). Unlike in polycrystalline samples where each grain is randomly oriented, the CuO\(_2\) planes epitaxial in YBCO thin films are aligned throughout the whole sample.

Since the discovery of the high-$T_c$ superconductors, many different techniques have been used to synthesis oxide thin films. Among the physical vapour deposition techniques, single target laser ablation [2.1], single target sputtering [2.2] and coevaporation [2.3] are the most successful ones. In our laboratory, growth of YBCO
thin films by both laser ablation and coevaporation are studied. After a general
discussion about thin film growth in the first few sections of this chapter, a more
detailed description will be presented on the laser ablation technique used to grow
(001) oriented YBCO films. We will examine the electrical properties, the crystal
texture and the surface morphology of the films. At the end of this chapter, we will
also report an attempt to make $Y_2Ba_4Cu_8O_{16}$ using our laser ablation system.

2.1 Thin Film Growth of YBCO

2.1.1 Physical vapour deposition

The principle behind physical vapour deposition of YBCO thin films is very
simple. A suitable substrate should be chosen and placed in the vapour which has a
correct ratio of yttrium, barium, and copper atoms (i.e., $Y:Ba:Cu = 1:2:3$). When a
correct thermodynamic condition is created by adjusting the temperature and the
oxygen pressure, thin film of non-superconducting tetragonal $YBa_2Cu_3O_6$ can be
formed on the substrate. After a subsequent oxygen uptake during a controlled
cooling to room temperature, superconducting orthorhombic $YBa_2Cu_3O_7$ can be
made. Although the procedure appears to be very straightforward, it is not so easy
when it comes to the real processing steps.

The first concern is to make certain that the generated vapour does have the
correct composition. Deviation of over 1% can already lead to increased roughness
on the film surface [2.4] and to forming of minority phases, see Chapter 1. In
addition, since the electrical properties in this material are anisotropic, oriented
growth is often favourable. The choice of a suitable single crystal substrate material
and the smoothness of the substrate surfaces (on atomic scale) will determine
whether one can successfully achieve well oriented growth. Although tetragonal
YBCO is thermodynamically favourable throughout a region of the thermodynamic
phase space, samples grown in different parts of this region can still have different
structural and electrical properties. Uncertainties in actual temperature setting and
oxygen pressure during the crystallisation can additionally modify the film properties
in an unpredictable manner.

Depending on whether the crystallisation of the YBCO film takes place during
the actual deposition or afterwards, the process is called "in-situ growth" and "post-
annealing growth", respectively. In the case of post-annealing growth, atoms of
different elements with a proper ratio are first deposited onto the substrate in an amorphous or multilayer form by any vapour deposition technique. The following crystallization step takes place in an oven filled with oxygen up to 1 bar and at a corresponding temperature up to 900 °C. The resulting films have high transition temperatures of around 92 K. Their surfaces are generally not smooth on a micrometer scale. However, low oxygen pressure post-annealing at lower temperature has been found to give a smoother topography [2.5]. The high processing temperature generally used for the post-annealing process can also promote film-substrate interaction and lead to a degraded interface layer.

In this thesis, we will not go further into detail of the post-annealing process. Instead, we will focus only on in-situ film growth. In this case, crystallisation is achieved during the actual film deposition at a temperature typically one to two hundred degrees lower than needed for a post-annealing process. Therefore, the undesirable film-substrate interaction can be limited for a large number of substrate materials. Highly oriented growth can be easily achieved. When properly grown, these films have much smoother surfaces than the post-annealed films. Typically, in-situ grown films have $T_c$ of around 90 K. They also, typically, have higher critical current density than post-annealed films (on the order of $10^7$ A/cm² at 77 K). In addition, in-situ processes allow for epitaxial growth of multilayer structures, consisting of cuprate materials as well as other oxides, which can be insulators or conductors.

2.1.2. Evaporation Techniques

Before we move to the main subject of this chapter, namely laser ablation, we will first briefly discuss two other very successful techniques used to fabricate high-$T_c$ superconducting thin films. These are the sputtering and coevaporation techniques.

Similar to laser deposition, single target sputtering is also a very popular and relatively inexpensive technique. During this process, a target is bombarded with fast moving ions, breaking the material on the target surface into atoms (sputtering). The sputtered materials are collected on a substrate placed close to the target and form a thin layer on the substrate surface. The main drawback of this technique, when used in an oxygen environment, is the emission of high energy negatively charged oxygen ions which can cause backspattering of the film. This can lead to off-stoichiometric composition and ion damage to the film. The problem is largely solved by using
higher pressure and by placing the substrate off the rotation axis of the target. However, both of these measures can lead to a much lower deposition rate. The gas in the sputtering chamber is usually a mixture of Ar and O₂. Typical oxygen partial pressure for sputtering ranges from 10⁻² mbar to 1 mbar.

In contrast to the single target laser ablation and sputtering techniques, coevaporation film growth makes use of a number of separate sources, each for a different constituent element. The biggest advantage of this technique is that it readily permits independent control of the evaporation rate for each element. The composition of the film can be continuously varied during growth. However, this advantage can also be the main cause of difficulty. The major problem is the uncertainty of the evaporation rate for each of the sources. Electron gun evaporators which are necessary for evaporating metals with high evaporating temperatures generally cannot operate at the high oxygen pressure needed for in-situ YBCO growth. In our laboratory, this problem is solved adequately by: 1) using activated species of oxygen, such as ozone, which is more reactive and thus a lower pressure is needed and, 2) differential pumping in the system by introducing ozone close to the substrate and using a high pumping speed in the system (3000 l/s).

Fig 2.1 Oxygen pressure and temperature used for various in-situ techniques.
In figure 2.1, we compare the various regions of the thermodynamic phase space, where YBCO thin films have been successfully grown using these in-situ techniques. Note, that all these regions lie near the $d_1$ decomposition line (Chapter 1) and are inside the area where tetragonal YBCO phase is stable. Hammond and Bormann [2.6] have argued that, in order to grow high quality in-situ films, the growth temperature and pressure should be set near this decomposition line. The reason is that it is necessary to be in the stable region of the phase space to ensure the crystallisation of the tetragonal YBCO phase, and at the same time to take advantage of the higher temperature where all atoms have sufficient energy to overcome kinetic barriers in order to form the correct crystal structure.

2.2 Pulsed Laser Deposition of Thin Films

By focusing a laser beam onto a target substance, thin films with the same composition as the target material can be deposited onto a nearby substrate. This technique was first introduced in the mid-1960's, and has since been studied by researchers using ruby, CO$_2$, and YAG lasers [2.7]. It was after the discovery of the high-Tc cuprates in the late 1980's, when researchers realised that high quality thin films of these materials could be conviniently deposited using an excimer laser. A resurgence of this technique followed [2.8].

2.2.1 Different Process Stages

The process of in-situ laser deposition of high-Tc thin film is schematically shown in figure 2.2. It can be regarded as a repeated process cycle of three stages, followed by a final fourth stage: the oxygen uptake during cooling to room temeprature.
Fig. 2.2 Principle of laser ablation. 1) The laser-target interaction. 2) Plasma forming. A mixture of small particles such as atoms, ions and molecules of the same composition as the target material moves fast toward the substrate placed in front of the target. 3) Deposition and crystallisation on the substrate. After repeated process at stages 1 to 3 is completed, it is followed by a final stage: oxygen uptake during cooling (not on figure).

The first stage of the cycle is the laser-target interaction. High energy, pulsed laser beam with short wavelength is needed for this process. The photon energy of the laser should be absorbed in a thin layer on the target surface, explosively breaking the target material into atoms, ions and molecules, forcing them to move rapidly toward the substrate. In order to ensure stoichiometric growth, melting should be avoided on the target surface by using laser with sufficiently high intensity (≥10⁹W/cm²) [2.9]. During the second stage of the process, the actual flight of the small particles toward the substrate, a plasma-like plume can be seen. This plume is possibly caused by an ion discharge of the small particles in oxygen environment. At the third stage, crystallisation of the deposited material takes place. After the cycle of these three stages is repeated many times, a final step follows: Full oxygenation of
the film take place during cooling to room temperature in 1 atmosphere. The crystal structure transforms from tetragonal to orthorhombic and the material changes from an insulator to a superconducting.

Before we start with the actual laser ablation set up in paragraph 2.2.2, we will have a closer look at the different process steps of this technique.

2.2.1.1 The laser-target interaction.

By definition, laser ablation means material removal by high intensity laser radiation. The energy of the photon should be absorbed in only a thin layer on the surface of the target to ensure a sufficiently high local energy density. This is the precondition for laser ablation process to take place efficiently. Some materials can be readily ablated, while at the same time, a large number of materials cannot be treated by this process with high enough efficiency. This material dependency will certainly put a constraint on the applicability of this technique for growth of a number of materials. It is therefore helpful to have some basic understanding of what parameters are important for this process, and what kind of materials are inherently unsuitable for this technique.

According to the quantum theory, the energy of a photon can be absorbed by an electron in molecules or solids bringing it to a higher energy level, if the photon energy is equal to or larger than the energy difference of these two energy levels

\[
\Delta E = h \cdot \nu_{\text{abs}} \quad (2.1)
\]

Here \(\Delta E\) is the energy difference of the electron before and after absorption, \(h\) is the Planck constant and \(\nu_{\text{abs}}\) is the photon frequency. In many solids and molecules, this energy difference is about \(\Delta E = 4 - 7\) eV, which is in the range of UV photon energy. Absorption of UV radiation will therefore result in electronic transition in these materials.

On the other hand, absorption and reflection of light are determined by the complex refraction index \(n\) [2.10]:

\[
n = n_{\text{real}} + n_{\text{img}} = n_{\text{real}} - iK \quad (2.2)
\]
Fig. 2.3. Penetration of light in target material

where the absorption index $K$ is in turn defined through the Beer - Lambert law [2.11], see figure 2.3.

\[ I(z) = I(0) \exp(-4\pi Kz/\lambda) = I(0) \exp(-\alpha z) \quad (2.3) \]

where $I(z)$ is the intensity of light in the material at a distance $z$ away from the surface ($z=0$), $I(0)$ is the part of the incoming light absorbed at the target surface, and $\alpha = 4\pi K/\lambda$ is defined as the absorption coefficient of the material.

A larger $\alpha$ value means a smaller penetration depth. In this case, the material is able to absorb the incoming light in a thinner layer on the surface, leading to a high concentration of energy. It is therefore one of the key factors which determines whether a specific material can be ablated with high efficiency.

The second important factor is the thermal diffusivity $k$ (cm$^2$/sec) of the target material.

\[ k = K'\rho_d C \quad (2.4) \]
where $K'$ is the thermal conductivity (W/cmK), $\rho_d$ is the material density and C is the specific heat of the target material. The thermal diffusivity $k$ is a measure of how fast the absorbed laser energy will "spread-out", lowering the energy density in the ablated area and reducing the ablation efficiency.

In short, for a given laser frequency, the absorption coefficient $\alpha$ and the thermal diffusivity $k$ of the target material play major roles in determining the ablation efficiency. For a combination of a large $\alpha$ and a small $k$ will give a high ablation efficiency. In this case, a high energy density can be created in a relatively small ablation volume of the target (J/cm$^3$). In order to give an impression of how wavelength, absorption coefficient and diffusivity affect the ablation rate of the material in reality, we give the removal rates of some materials by different laser wavelength in Appendix A.

For the laser deposition technique, excimer laser is the most favourable type of laser. This is a class of electronically excited molecular gas lasers which emit high intensity, short duration pulses of UV light. It stands for "Excited homonuclear dimer". They have the following advantages: First of all, they are able to breakdown the irradiated material efficiently into atoms, ions, and molecules with the same stoichiometry as the target substance. This is necessary for proper film growth. Secondly, UV radiation is able to penetrate the plasma induced by laser-target interaction, so that it can irradiate the target surface continuously.

Both single crystal materials or materials in pressed pellet form can be used as target for laser deposition. Careful attention must be paid to surface quality. Rough, poor quality surfaces may result in vastly different local evaporation rates. Both commercial and self-made polycrystalline YBCO targets using citrate synthesis and pyrolysis method [2.12] were used in our laboratory. The steps for making the YBCO targets are given in Appendix B.

2.2.1.2 The laser induced plume

The most impressive sights of the laser ablation process is the plasma (plume) induced by the laser-target interaction, see figure 2.4. Numerous works have been reported on characterising the spectrum of the emitted light. Studies have been done to identify the different ionic particle species in the plasma. Different techniques, such as optical absorption, emission spectroscopy, mass spectroscopy, and fast
photography showed that the plume consists mainly of elemental and monoxide species, but large clusters have also been observed.[2.13-2.20]. The amount of ions has been estimates to a few percent.[2.14, 2.21]. Even if the amount of ions is comparatively low, it has been shown that most of the neutral Y₂O₃-molecules arriving at the substrate are in excited electronic states, and this probably applies also to other molecules [2.22]. The speed of the expanding plume constituents are very high. Typically speeds of 10⁶ cm/s have been reported for radiative species, and 10⁴-10⁵ cm/s for nonradiative species [2.23, 2.24]. The expansion in an ambient oxygen gas has been described in terms of shock waves and drag models [2.25].

Although the microscopic picture of the dynamics is complex and is still an area of research, one can use the plume as a first hand indication of whether the thin film growth can yield the desired result. In the case of YBCO ablation, starting with an on-stoichiometric target, one can tell whether the resulting film can have the highest $T_c$ (92 K) by looking at the shape and colour of the plume. This is because plasma colour depends on the presence and the ratio of different constituents being ablated. At the same time, the shape of the plume is a good indication of the correct focusing of the laser, given a specific oxygen pressure. In the optimum case, the plume has a full "egg" form and a bright white-blue colour. Deviation from this "optimum" plume can generally be corrected by refocusing the laser or by varying the laser pulse energy. The thin layer of material collected on the substrate will crystallise.

2.2.1.3 The crystallisation and oxygenation of the YBCO

![Figure 2.4. A photo image of the laser induced plume.](image-url)
As already mentioned, the orthorhombic YBCO phase is thermodynamically not favourable anywhere in the thermodynamic phase space. Therefore, one cannot grow this high - $T_c$ phase of YBCO in a straightforward manner. Instead, a strategy is adopted by first creating a condition where tetragonal phase of the YBCO compound is stable. After the crystallisation of the correct tetragonal YBCO phase is completed during the deposition, the oxygen pressure should be increased to 1 atmosphere (moving up vertically in figure 2.1). During the subsequent cooling (move to the right of the figure horizontally), tetragonal to orthorhombic transition takes place at a temperature around 500 °C. Note that other phases are thermodynamically more favourable than the orthorhombic YBCO phase in the region right to the tetragonal-orthorhombic transition line (see Chapter 1). Nevertheless, YBa$_2$Cu$_3$O$_y$ superconductor is sufficiently metastable, so that it does not decompose into other, more favourable, phases which are not superconducting. Full oxygenation of the YBCO is achieved after the temperature is slowly cooled to room temperature.

2.2.1.4 The suitable substrate materials

To choose a suitable substrate material, we must consider the undesirable interaction and interdiffusion between the substrate and film material at such elevated deposition temperature. Another criterion is the lattice match. Due to the anisotropic properties of the YBCO material, epitaxially grown films are often desirable. In the case of epitaxial (001) YBCO growth, for example, the $c$-axis of the YBCO crystal stands perpendicular to the substrate surface while the $a$- and $b$-axis are aligned to the in-plane substrate lattices. This can be done by choosing substrate materials in single crystal form, which have comparable lattice parameters as the YBCO crystal along the substrate surface. At this point, we would like to note that, in plane oriented growth of YBCO has also been successfully achieved on polycrystalline substrates. In this case, a buffer layer of in plane oriented YSZ is first deposited using ion beam assisted deposition [2.26].

The third consideration for choosing a substrate material is whether this material has comparable thermal expansion coefficient as the YBCO. This is because film growth takes place at high temperature. During the subsequent cooling, different temperature dependence of the lattice constants can lead to tension near the interface between the substrate and the film. Eventually, this may lead to interface degradation. In figure 2.5, we show the temperature dependence of several substrate
materials suitable for the epitaxial growth of (001) oriented YBCO thin films. The temperature dependence of YBCO lattice parameters $a$ and $b$ are also shown for comparison.

![Graph showing temperature dependence of lattice constants](image)

*Figure 2.5 Temperature dependence of lattice constants of perovskite substrates and the YBCO superconductor at atmospheric oxygen pressure.*

### 2.2.2. System Implementation and Applications

In this section, we will show how the laser ablation technique is used in our laboratory. An overview of the electrical properties, crystal texture and sample morphology will also be given.

#### 2.2.2.1 Implementation

The laser ablation system in our laboratory was specially designed and made for the growth of superconducting oxide thin films and multilayer structures. It is part of a larger system for film growth and analysis, consisting of an additional growth chamber for multi-source co-evaporation and a surface analysis chamber. Samples can be transported from one chamber to another without breaking the vacuum, so
that one can avoid contaminating the film surface in air. A schematic overview of the complete growth and analysing system for cuprates superconductor is shown in figure 2.6.

We use a XeCl excimer laser (wavelength = 308 nm) for film deposition. The laser beam is focused onto the rotating target at 45° to the surface. The focusing point of the laser is away from the rotation axis of the target. This is done to avoid crater formation on the target surface. We use a laser fluence of about 2.5 J/cm². The repetition rate of the laser pulse is 9 Hz.

We prepared the on composition 1:2:3 YBCO target by citrate synthesis and pyrolysis method [2.12]. The actual procedure is described in Appendix B in detail. The smoothness of the target surface is maintained by polishing the target after every 2 deposition runs.

In figure 2.7a, we show the schematic drawing (top view) of our ablation chamber. Two key components can be seen: 1) the heater element needed for setting the substrate temperature, and 2) the multi-target holder. A maximum of six different targets can be placed onto the multi-target holder simultaneously. In order to avoid mutual contamination, all the targets are covered by a single 1 mm thick stainless steel.

Figure 2.6. A schematic overview of our complete growth and analysis system. It consists of a multi-source co-evaporation (MBE) chamber, a laser deposition chamber and a surface analysis chamber. Samples can be transported from one chamber to another without breaking the vacuum.
Figure 2.7 a) Schematic drawing of the configuration of the heater element and the multi-target holder inside the ablation chamber, viewed from the top of the chamber; and b) Multi-target holder, viewed from the heater element position.

steel front plate except the one being ablated by the laser. In addition, stainless steel separating plates are also placed between them. All targets are rotated by one single motor outside the ablation chamber simultaneously. Targets can be easily manoeuvred to the focused laser beam without breaking vacuum by rotating the the multitarget holder on its main axis manually. A schematic drawing of the front view of the multi-target holder is shown in figure 2.7b.
The heater element is positioned in front of the ablation target. The distance between these two elements can be adjusted from 2.5 mm to 7 mm. Two designs of the heater element have been implemented and tested.

For the first design, consideration is taken to enable sample transport in vacuum through out the whole growth and analysising system, i.e., from the laser ablation chamber to the MBE chamber or the surface analysis chamber. In this case, the substrates are glued onto 1.5 mm thick stainless steel disks with 25 mm diameter. In order to heat up the substrate to a desired temperature, the stainless steel disk is pressed onto a heater block. By radiatively heating the stainless disk through an opening in the heater block using a 1250 W quartz lamp (see figure 2.8a), the substrate temperature can reach 800 °C. The substrate temperature is monitored by a thermocouple inserted into the heater block. With this design it is also possible to grow several films after each other by placing a number of substrates onto a carriage inside the vacuum chamber before the ablation. One does not need to break the vacuum so frequently, and this reduces the chance for contaminating the chamber.

The major drawback of this design is the insufficient reproducibility of the temperature. This is due to the fact, that thermal contact between the stainless steel disk and the heater block is different for each deposition run. Although the thermocouple inside the heater block measured the same temperature each time, the actual substrate temperature can be up to 50 °C different during two separate deposition runs. This poor reproducibility is found during a temperature calibration run with a second thermocouple glued on the stainless steel disk with silver paint. The temperature distribution on the disk is also found to be inhomogeneous. Another problem with this design is the short life time of the quartz lamp. It burns out after about five deposition runs. In the MBE chamber a similar implementation, but with water-cooled reflector has a much longer life time of the lamp (over 300 runs without failure).
Figure 2.8  a) Heater element using quartz lamp radiation. b) Heater element using resistance wire.

A second design for the heater is shown in figure 2.8b. In this case, the stainless steel heater block is resistively heated by a thermocoax placed inside the block. The thermocoax is in direct contact with the block and produces a uniform (ΔT < 10 °C) temperature across the block. Substrates are directly glued on the heater block with silver paint. The temperature is monitored by a thermocouple glued on the heater surface, within 5 mm from the substrate. The disadvantage here is that the sample cannot be exchanged in-situ.

2.2.3. Sample Quality

c-axis oriented YBa$_2$Cu$_3$O$_y$ thin films can be made easily with our laser deposition system. The film qualities are basically reproducible. In this section, we will show and discuss some of the main features that characterize the sample qualities.
2.2.3.1. Film orientation and minority phases

We have done X-ray diffraction measurement on a large number of the laser ablated films. We use this technique mainly to determine the orientation of the majority YBa$_2$Cu$_3$O$_y$ phase and the presence of possible oriented minority phases. In some cases, we also used the X-ray data to calculate the c-axis lattice parameter of the c-axis oriented films. A powder diffractometer with Bragg-Brentano geometry [2.27] has been used. In figure 2.9, we show the X-ray diffraction data of one of our samples. This film is grown on an (100) MgO substrate. Except for the (002) diffraction line of the MgO substrate, all other diffraction peaks can be attributed to the (00l) diffractions of the YBa$_2$Cu$_3$O$_y$ thin films. This is a first indication that the sample is highly oriented, with the c-axis perpendicular to the substrate surface.

In figure 2.10, we display an infrared reflectivity spectrum of one of our films measured at room temperature. The strong feature below 100 cm$^{-1}$ and the peak at

![Figure 2.9. A typical Cu Kα X-ray diffraction data from one of the laser ablated films. Except the (002) diffraction line from the MgO substrate, all diffraction peaks can be attributed to the (00l) diffraction lines of the YBa$_2$Cu$_3$O$_y$ crystal.](image-url)
550 cm\(^{-1}\) correspond to phonons of the SrTiO\(_3\) substrate material. For a sufficiently thick film with a high reflectivity, these features are shielded by the YBa\(_2\)Cu\(_3\)O\(_y\) top layer and are no longer visible [2.28]. Phonons of the YBa\(_2\)Cu\(_3\)O\(_y\) are strongly screened by the Drude-like electronic response, except in \(ab\)-axis oriented grains and in secondary phases. The presence of the \(ab\)-axis oriented grains would for example result in a phonon-peak at 315 cm\(^{-1}\), which, however, we do not observe. Hence there is no indication for the presence of secondary phases or different orientations from figure 2.10.

![Graph](image_url)

"Figure 2.10. Infrared reflectivity of a YBa\(_2\)Cu\(_3\)O\(_y\) film on SrTiO\(_3\) substrate measured at room temperature."

Two cross-sectional Transmission Electron Microscope (TEM) pictures from two different films are shown in figure 2.11, with (a) a larger and (b) a smaller magnification. The brighter lines in the pictures are the Cu-O chain layers in the YBa\(_2\)Cu\(_3\)O\(_y\) structure. We can see that they are parallel to the substrate surface (SrTiO\(_3\)). This is another evidence that the films are \(c\)-axis oriented. A small step on the substrate surface can be seen in figure 2.11b. The regular texture of the YBa\(_2\)Cu\(_3\)O\(_y\) crystal is interrupted and disappears in a region right of the small step near the substrate surface. This shows that some minority phases are sporadically
distributed in this film. The reason that no additional reflection peaks from these minority phases are visible in the X-ray data (see figure 2.9) may be because they are either in a very small amount or are unoriented, or they are in an amorphous form. It is also possible that this region became disordered during the TEM sample preparation process.
Figure 2.11. Two cross-sectional TEM pictures taken from two different YBa$_2$Cu$_3$O$_y$ films on SrTiO$_3$. 
2.2.3.2 Resistivity versus temperature

The electrical properties of the films are routinely checked by measuring the electrical resistivity as a function of temperature. The measurements are done in a continuous flow cryostat using a four point technique. Electrical contacts are made by pressing four gold covered stainless steel pins on four Au contact pads which are laser ablated through a metal mask onto the film.

In figure 2.12, we show one sample resistance as a function of temperature. The sample becomes superconducting at temperature below 90 K. Above this transition temperature, the resistance varies linearly with the temperature to room temperature. We can write the temperature dependence of the resistivity as: $\rho(T) = \rho_0 + \rho' T$. Here, $\rho$ is the resistivity, $T$ is the temperature, $\rho_0$ is the residual resistivity of the sample due to impurity, and $\rho'$ is the linear coefficient of the temperature dependence of the resistivity. At room temperature, the resistivity of each of the samples lies between 300 $\mu\Omega$cm to 500 $\mu\Omega$cm. These are values frequently seen in literature for in-situ grown thin films. However, they are at least a factor two higher than the lowest value found for single crystal samples (ca. 150 $\mu\Omega$cm). The typical $T_c$ for our samples is about 91 K ($R = 0$). The transition width is usually less than 2 K.

![Resistivity versus temperature curve](image)

**Figure 2.12.** A typical resistivity versus temperature curve for our laser ablated samples.
2.2.3.3 Sample surface morphology

We have looked at the morphology of some of our films with Scanning Electron Microscope (SEM) and Scanning Tunneling Microscope (STM). A SEM picture is shown in figure 2.13a. Here a 100 nm thick and 5 μm wide YBa$_2$Cu$_3$O$_y$ line can be seen (vertical in the picture). The dark horizontal line is a 300 nm sharp step made on the substrate surface by ion milling. A large amount of small particles (white spots in the picture) are distributed all over the sample surface. The average size of the particles is about 0.25 μm and have a variety of shapes. We are not certain of what they are and how they are formed. Attempts to reduce their number by changing the laser pulse energy and by changing the spot size of the laser on the YBa$_2$Cu$_3$O$_y$ target had no visible effect.

The STM picture in figure 2.13b shows large, atomically flat terraces and growth steps on the sample surface. The white line on the left is 50 nm long. The step height is typically a multiple of the c-axis parameter of the YBCO crystal. The observation of these terraces and steps has lead to speculation that the early stage of the film growth is characterized by island growth, instead of a layer by layer growth [2.29].
Figure 2.13 (a) a SEM picture; and (b) a STM picture of our laser ablated films
2.3. Study of in-situ growth of $Y_2\text{Ba}_4\text{Cu}_8\text{O}_y$

$Y_2\text{Ba}_4\text{Cu}_8\text{O}_y$ or simply '248', is another Y-Ba-Cu-O phase closely related to the '123' phase. It has two adjacent Cu-O chain layers between two sets of adjacent CuO$_2$ plane layers. This is in contrast to the '123' phase, which has only one Cu-O chain layer. The $c$-axis lattice parameter is roughly double that of the '123' structure. The unit cell of this compound is shown in figure 2.14.

Compared with the '123' phase, the oxygen content in the '248' phase YBCO material is stable. In figure 2.15, adapted from Lindemer [2.30], we can see that the oxygen content is essentially invariant until the decomposition temperature was reached. In 1 bar oxygen, for example, no oxygen loss is observed until the temperature reaches 850 °C. The additional stability of the '248' phase is widely attributed to the "double chain" configuration in the crystal structure.

![Figure 2.14. The unit cell of the '248' structure. It can be seen as a combination of two unit cells of the '123' phase, with two sets of double Cu-O chain layers adjacent to each other in each of the unit cells. The $a$, $b$, and $c$ lattice parameters were found to be 3.842 Å, 3.870 Å, and 27.250 Å respectively.](image-url)
The pure '248' phase is believed to be slightly hole underdoped in the CuO$_2$ planes. When the Cu-O chains are fully oxygenated, $T_c$ of this material is about 80 K. Incorporation of a small amount of Ca to the '248' material can increase the $T_c$ by up to 10 K, making it about the same value as that of the '123' material ($T_c = 92$ K). Due to the better phase stability and the comparable $T_c$, the '248' phase is potentially more attractive for application than the '123' material. Unfortunately, growth of '248' phase is also more difficult.

The '248' phase was originally discovered as a defect structure in powders of '123' material [2.31]. It was later synthesized as a majority phase in thin films using post annealing processes. Several groups have made '248' compound in bulk, including single crystals at very high oxygen pressures ($> 1.2 \times 10^5$ mbar) [2.32, 2.33]. The synthesizing oxygen pressure can be lowered to 1 bar if a catalyst is used [2.34]. For electronic applications, it is desirable to grow thin films of this material using an in-

![Figure 2.15. Typical changes in oxygen content (O/7M) of the '124' phase YBCO during decomposition. The results after decomposition at 0.01 MPa (100 mbar) oxygen (solid line) are compared with those expected from a '123' + CuO mixtures (dash line). Adapted from Lindermer[ref].](image-url)
situ process. Until now, no successful in-situ growth of the '248' material has been reported. In this experiment, we tried to examine the possibility to use our laser deposition system for in situ '248' thin film growth.

2.3.1. Phase stability and in situ growth

![Diagram showing the temperature and oxygen pressure dependence for phase equilibria for 2:4:8 composition. The line $d'$ indicates the equilibrium between the '248' phase and a mixture of '247' and CuO phases, determined by three different groups [2.30, 2.38, 2.39]. The shaded circles indicate the positions in the phase p-T phase space, where we have laser ablated on-stoichiometric '248' target for in-situ growth. For comparison, the melting line $m_1$ and decomposition line $d_1$ for phase pure '123' material at 1:2:3 composition are indicated. The widely used temperature and oxygen pressures for in situ laser ablation to grow '123' thin films are also shown.](image)
Numerous papers have been published on temperature and oxygen pressure dependence of phase equilibria for composition lying between '123' and CuO [2.30, 2.35-2.43]. They give somewhat conflicting results. In order to give an impression of the '248' phase stability, we show here only a selected set of data confirmed by a number of independent studies. The '248' phase decomposes at high temperatures and at low pressures into a mixture of CuO and \( \text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{y} \) (or '247') phase. We denote this decomposition line \( d' \) in figure 2.16. Three studies of equilibrium between the '248' phase and the mixture of '247'+CuO using three different techniques confirmed this line [2.30, 2.38, 2.39]. The melting line \( m \) and the decomposition line \( d_f \) for phase pure '123' are also shown for comparison. The position of the decomposition line \( d' \) in this pO\textsubscript{2}-T diagram shows that in situ growth of '248' should be realised at three to four orders of magnitudes higher oxygen pressure or at lower temperature than for '123' growth.

We made a target with a 2:4:8 ratio of Y:Ba:Cu for laser ablation using the procedure described in Appendix B. A number of films were then made in different areas of the p-T phase diagram, as shown in figure 2.16. We have tried to grow these films just at the equilibrium line. This is due to the same reason as given in section 2.1.2. The number near each of the circle corresponds to the individual film number grown at that position. Seven samples (numbered as 1 to 7) were made in the stable region for the '248' phase, close to the equilibrium line \( d' \). Sample 8 is made outside this 'optimum' region.

Sample 1 is ablated at 100 mbar oxygen at 760 °C. Flashing light spots induced by laser-target interactions could be seen on the target surface during ablation. No plume could be visible by doing ablation at such a high oxygen pressure. In order to allow more ablated particles to reach the substrate surface, we brought the substrate to 25 mm from the target (the minimum target substrate distance for our system). After 15 minutes of ablation (typical time for deposition of 300 nm thick film at 1 mbar oxygen pressure) and a subsequent cooling in 1 atmosphere oxygen, the colour of the substrate surface was the same as before the ablation, i.e., the film was not visible. X-ray diffraction showed only the diffraction lines of the MgO substrate. This suggests that no film was deposited under this condition.

Films 2, 3 and 4 were grown at 10 to 20 mbar oxygen at 700 to 720 °C. The length of the laser induced plume was ca. 15 mm at 10 mbar and reduced to ca 7 mm at 20 mbar. After 15 minutes of ablation, the film surface appeared grayish and
Figure 2.17. X-ray diffraction of samples 2, 3, and 4. The majority of the peaks in sample 2 could be attributed to the different diffraction lines of the '248' phase, although somewhat shifted from the expected position (as indicated). This film appears to be a mixture of '123', '248' and some other phases. Samples 3 and 4 show only a few diffraction lines that may be attributed to the '248' phase. This is an indication that they are not as well oriented as film 4.

shiny. The X-ray diffraction data of these samples are shown in figure 2.17. In addition to the (002) diffraction line from the MgO substrate, several other diffraction lines can be seen in all of the three samples.
In sample 2, the majority of the peaks could be attributed to the different diffraction lines of the '248' phase as indicated. However, these lines are slightly shifted from those positions expected for the '248' diffraction lines. This could occur if the '248' is heavily distorted by stacking faults in the structure [2.44]. The diffraction lines at 22.5°, 46.5° and 54.8° may be assigned respectively from the (003), (006) and (007) lines of the '123' phase present in the sample. Only a few diffraction lines can be seen in samples 3 and 4. Two of them may be the (004) and (0012) diffraction lines of '248' phase. The presence of the '123' phase is also vastly reduced. No '123' diffraction line can be observed for these two samples.

In order to increase the low growth rate at such high pressure, we have tried making two samples at 1 mbar and 640 °C (samples 5 and 6). The length of the plume in this case was about 25 mm. The resulting films had black colour and a shiny surface. But X-ray diffraction showed no presence of oriented '248' and '123' growth. This is also the case for sample 7.

We have tried one deposition (sample 8) at 1 mbar and at 760 °C with our '248' target. We note that this is in the region where '123' films were usually grown by laser deposition using on-composition '123' target. Except for the (002) diffraction from the MgO substrate, all other diffraction peaks can be assigned to the (001) diffraction of the '123'. This confirms the expectation that the '123' phase is stable in this region of the thermodynamic phase space even for 2:4:8 composition [2.37].

Except for sample 8 which is predominantly '123' phase and is superconducting (T_c=60 K), all films showed semiconducting behaviour in terms of the temperature dependence of their resistance. The resistance vs the temperature of sample 2, which probably contains the largest amount of '248' phase, is shown in figure 2.18. The resistance increased monotonically when the sample was cooled. This indicates that the '123' and '248' phases are either degraded or are only present in a number of isolated areas in the film.
Figure 2.18. The resistance of sample 2 goes up monotonically when it is cooled to lower temperature. The majority phase in this film behaves like a semiconductor. This indicates that the '123' and '248' phases present in the film are either degraded, or are only present in a number of isolated areas.

Electron Probe Micro-Analysis (EPMA) was done on samples 5, 6, and 8. A bulk polycrystalline '123' pellet was used as a reference. These three samples were the only ones which were thick enough. They were grown at low pressures (1 mbar) which allows sufficient growth rate. By comparing the deposition time and the oxygen pressure of other samples, we believe that the film thickness of these three samples was about 300 nm. This is the lowest limit for using EPMA without measuring a large signal contribution from the substrate as well. Five measuring points across the whole film area were taken on each film. The ratio of Y:Ba:Cu in
these samples were found to be 1:1.8:3.7, 1:1.9:3.6 and 1:1.7: 3.4 respectively. They seem to indicate that all these films were yttrium rich compared to 2:4:8 composition.

In conclusion, we have laser ablated several films using a ‘248’ target. Some films grown near the decomposition line $d'$ showed X-ray diffraction lines which may be attributed to partial ‘248’ growth. The resistance of these films decreases with increasing temperature, resembling the semiconducting behaviour. No single phase ‘248’ films were made using these growth conditions. Although the ‘248’ phase is stable in this region of the p-T phase space (for 2:4:8 composition), the temperature on the decomposition line $d'$ may not be high enough to overcome the kinetic barrier for ‘248’ phase formation. Catalyst incorporation in the target may be needed to reduce the kinetic barrier. c-axis oriented ‘123’ film can easily be grown with the ‘248’ target at temperature and oxygen pressure for usual ‘123’ growth (where on-composition ‘123’ target material is used). This confirms the suggestion that the ‘123’ phase is thermodynamically stable in this region of the p-T phase space for the 2:4:8 composition.

References


Chapter 3  Growth of (110) oriented YBa$_2$Cu$_3$O$_{7.8}$ films by laser ablation

N. Y. Chen, G. Rietveld, L. W. Lander,  
V. C. Matijasevic, P. Hadley, and J. E. Mooij

Delft University of Technology, Applied Physics, 2628 CJ, Delft, The Netherlands

Abstract

Several attempts have been made by different groups to grow (110) YBa$_2$Cu$_3$O$_{7.8}$ thin films on (110) substrates. In most of the cases, both (103) and (110) orientations of YBa$_2$Cu$_3$O$_{7.8}$ have been found in the film. The substrate temperature during the film deposition is one of the major factors that determines the crystal orientation of the YBa$_2$Cu$_3$O$_{7.8}$. In our experiment, effort is made to examine the influence of the initial substrate temperature from 595 °C to 660 °C on the relative amount of the (110) and (103) oriented grains. The amount of (103) oriented YBa$_2$Cu$_3$O$_{7.8}$ is reduced systematically with decreasing substrate temperature. At the lowest deposition temperatures we find only (110) oriented growth.
3.1 Introduction

The high-Tc superconductor YBa$_2$Cu$_3$O$_{7-δ}$ (YBCO) is a layered compound. The presence of the CuO$_2$ plane layers in the $a$-$b$ direction of this crystal results in anisotropical materials properties. The resistivity, the critical current density, the electrical field, and the superconducting coherence length all depend on the crystal orientation. The anisotropy is the greatest when a material property along the $c$-axis is compared to the same property in the $a$ or $b$ direction. For instance, the superconducting coherence length is 0.3 nm along the $c$-axis, while it is 2 nm in the $a$ and the $b$ direction.

Until now, most of the thin films of this material have been made with the $c$-axis oriented perpendicular to the substrate surface. The in-plane transport measurements of these films probe the properties of the material in the $a$ and $b$ directions where no large anisotropy exists. For fundamental as well as technological reasons one would like to make films with the $c$-axis parallel to the substrate surface, so that the two crystal orientations with the greatest difference in material properties could be measured on the same thin film sample. In order to do this, various groups have produced films with (100) [3.1], (105) [3.2], and (110) [3.3, 3.4] orientations on (100), (305) and (110) SrTiO$_3$ substrate respectively. Typically, the (100) films are oriented with the $c$-axis lying in two perpendicular directions along the substrate surface in the different grains. In order to make film with the $c$-axis aligned along the same direction throughout the whole film, we have decided to work with (110) films, where all the grains have the $c$-axis only in the [001] direction of the substrate. Here we report on the growth of (110) films of YBCO by laser ablation.

Several groups have grown (110 oriented YBCO films on (110) SrTiO$_3$ substrates. In most of the cases, both (103) and (110) orientations of YBCO were observed in the films, see figure 3.1. Wu et al reported successful in-situ growth of (110) YBCO on (110) SrTiO$_3$ by sputtering [3.4]. The sputtering were done in an mixture of 0.22 mbar Ar and 0.17 mbar O$_2$. During deposition the substrate temperature was maintained at 705 °C. Habermeier et al achieved (110) growth with laser ablation [3.3] by setting the substrate temperature initially to 650 °C in order to nucleate a seed layer for (110) growth, and the substrate temperature was then increased to 720 °C for the rest of the deposition process. Superconducting films with high transition temperature were achieved by this method.
Figure 3.1. (110) and (103) oriented YBCO unit cell on (110) SrTiO$_3$ substrate.

The substrate temperature during deposition is one of the major factors which determines the crystal orientation, i.e., with the c-axis perpendicular or parallel to the substrate surface. For example, it is known that a YBCO film deposited by laser ablation on a (100) SrTiO$_3$ substrate at oxygen pressure between 0.25 mbar to 1 mbar will grow with (001) orientation when the substrate is heated to 750 °C, but (100) oriented growth is induced at lower temperatures. To ensure successful growth of pure (110) oriented films, it is important to get a clear view of how the relative amount of (110) and (103) orientations changes as a function of substrate temperature during film growth. In our experiment, we examine the influence of the initial substrate temperature during seed layer growth in the range of 595 °C to 660 °C. To characterise the in-plane structure of our thin films, we made use of a standard Weissenberg camera in the rotating mode. Weissenberg camera in the oscillating mode [3.5] and Raman technique [3.3] have been used for the same purpose by other groups. Special attention was paid to making accurate temperature measurement of the substrate during film deposition.
3.2 Film preparation

We deposited films of YBCO on (110) SrTiO$_3$ substrates by laser ablation, using a XeCl excimer laser. The set up is shown in figure 3.2. The laser power density at the target was 2.5 J/cm$^2$, with a pulse repetition rate of 9 Hz.

![Diagram of laser deposition system]

*Figure 3.2. Schematic of the laser deposition system. The thermocouple glued adjacent to the substrate ensures an accurate temperature measurement of the substrate temperature.*

In order to ensure accurate temperature measurement and a homogeneous temperature distribution on the substrate during deposition, our (110) SrTiO$_3$ substrates were glued with silver paint to the stainless steel heater heated by a thermocoaxial wire. Care was taken for homogeneous silver paint distribution between the heater block and the substrate. The substrate temperature was measured by gluing a platinum-13% rhodium vs. platinum thermocouple on the heater block with silver paint adjacent to the substrate; see figure 3.2. The accuracy of the
temperature measurement was checked by gluing a second identical thermocouple in the middle of the substrate surface with silver paint. The two thermocouples gave the same temperature to within 5 °C. The substrate temperature ($T_s$) quoted in this paper is the temperature of the thermocouple as shown in figure 3.2. While the substrate temperature was kept constant during each deposition run, ranging from 595 °C to 660 °C, an identical background oxygen pressure of 1 mbar was used for all film growth during our study. Below 595 °C we were not able to make good film with a shiny surface.

3.3 Results and discussion

The first step in the characterising of our film is a standard θ-2θ scan on a X-ray powder diffractometer using Cu $K_\alpha$ radiation with Ni as a filter. Although polycrystalline secondary phase are hardly detectable due to the small amount of material in the film, these scans are still useful when oriented material with an unwanted orientation is present. In figure 3.3 we give a typical scan of one of our films, grown at substrate temperature ($T_s$) of 625 °C. Only peaks from the (110) SrTiO$_3$ substrate and the (110)/(103) oriented YBCO film are present, together with small Cu $K_\beta$ peaks due to imperfect filtering of the Ni foil; no other peaks are visible in the noise (note the logarithmic intensity scale).
Figure 3.3 $\theta$-2$\theta$ scan of film made at $T_s = 625$ °C

A first try to discriminate between (110) and (103) orientation of the YBCO films was the determination of the d-spacing of the films from the $\theta$-2$\theta$ reflection peaks. The result is given in figure 3.4, where also the values for fully oxygenated bulk material are indicated. A clear trend is seen in this figure that cannot be related to the change of orientation of the film, because from other X-ray measurements (see below) we know that at lower temperature more (110) orientation is present. This trend to larger d-spacing at low temperature is larger than would be expected from just chain oxygen deficiency [3,5]. It may therefore be related to some kind of (cation or oxygen) disorder in the films.
The second step in our characterisation was carried out with a Weissenberg camera. Here, the points in a plane of the reciprocal lattice perpendicular to a certain sample rotation axis are measured. In our case, this rotation axis was chosen perpendicular to the substrate surface. We thus measure the reciprocal lattice points of planes parallel to the surface of our films. In figure 3.5 we give two example of such scans. The first is the result of a measurement of the (110) plane of the film grown at 625 °C. Clearly visible are the intense SrTiO$_3$ diffraction spots, showing the two-fold symmetry of the (110) SrTiO$_3$. The arrow in the figure indicate the [001] direction of the substrate surface. In between each of two points in this direction, two other (weaker) spots are visible that originate from parts of the film with the c-axis lying in the studied plane and therefore is due to the (110) oriented part of the YBCO film. This, however, does not exclude (103) orientation to be present in the film as in the plane of the reciprocal lattice reflection from this direction coincide with the much stronger substrate reflections. Therefore, another scan was made of a different plane in the reciprocal space (again parallel to the substrate surface) where among others the (005) reflection of any of any (103) oriented material will be visible. In this plane, no reflection of the substrate or any (110) oriented YBCO are present. The result of such a scan is shown in the second part of figure 3.5, now from a film grown...
at 665 °C. In this film (103) oriented material is clearly present. Again the two fold symmetry of the layer is visible; also the two possible orientations for the (103) case (see figure 3.1) are both present. For all of our films we have made both scan shown in figure 3.5.

In order to get a quantitative idea of the relative amount of (110) and (103) orientation in our films, we measured the intensity of two different diffraction spots, one typically for each orientation, with a photometer. As can be seen in figure 3.6, these intensities show a clear trend as a function of growth temperature of the film. Note that only intensities relative to those of the film grown at the highest temperature are given. The intensity of the peak related to (103) orientation of the film decreases monotonically with temperature and was essentially in the noise level for films grown below 620 °C. We therefore conclude that for these low growth temperatures, no (103) orientation is present in our films. The intensity of the (110) related peaks has a maximum at 625 °C and is generally increasing for lower growth temperatures. In order to find out whether the maximum is real, we made two more films at 625 °C and 615 °C. The intensities found for these films are comparable with the previous ones, but reveal a less pronounce peak at 625 °C. Note that these temperature are much lower than the ones Wu et al used for their sputtered films (T_s = 705 °C) and still 30 °C lower than the laser ablated films grown by Habermeier et al (T_s = 650 °C). This difference may be partly explained by the different construction of the heaters that are used. If the thermocouple is not closed to the substrate and if the substrate is not glued to the heater, large temperature difference between thermocouple and substrate are easily obtained.
Figure 3.5. Weissenberg exposures a) of the (110) plane of the film grown at $T_s = 625 \, ^\circ C$; and b) of another plane in the reciprocal space (again parallel to the substrate surface) where only reflections from (103) oriented YBCO crystal can be seen.
SEM pictures of the films showed the presence of small droplets, typical for all films we made so far, including (001) oriented YBCO films grown on (100) SrTiO$_3$. Apart from the structure, we also measured the electrical resistance as function of temperature for some of the films. The sample made at $T_s = 660$ °C was superconducting with a transition temperature $T_c = 70.5$ K. $T_c$ decreases with decreasing deposition temperature $T_s$: the sample made at 595 °C showed semiconducting behaviour.

![Graph showing relative intensity versus growth temperature]

*Figure 3.6. Relative intensity of reflection from (110) and (103) oriented YBCO in the films as function of growth temperature*

### 3.4 Conclusions

We have performed a systematic study on the relative amount of (110) and (103) oriented YBCO in thin films grown on (110) SrTiO$_3$ substrates by laser ablation, as a function of substrate temperature during deposition. $\theta$-2$\theta$ scans shows that only (110)/(103) oriented YBCO was present in these films. Further characterisation with a Weissenberg camera showed that, the amount of (103) oriented YBCO is reduced systematically with decreasing substrate temperature. Pure (110) oriented growth is only possible if the growth temperature is lower than 620 °C. Films made at temperatures lower than 595 °C have rough surfaces.
References


Chapter 4  Low 1/f normal-state resistance noise in high-resistivity YBa$_2$Cu$_3$O$_y$ films

N. Y. Chen, R. Jonker, V. C. Matijasevic, H. M. Jaeger$^{a)}$ and J. E. Mooij

Department of Applied Physics and DIMES, Delft University of Technology,
Delft, The Netherlands

Abstract

We have measured 1/f resistance noise at room temperature in laser-ablated YBa$_2$Cu$_3$O$_y$ (YBCO) thin films over a wide range of normal-state resistivities. Surprisingly, the high resistivity films exhibit lower normalized noise powers than the low resistivity films. The lowest normalized noise power is 100 times lower than any previously reported values for the YBCO compound and is comparable to the lowest noise levels found in other cuprates. Upon oxygen reduction, the noise power in the high resistivity films increases monotonically whereas it decreases in the low resistivity films. We conclude that the high noise level in YBCO may be intrinsic to the structure and due to conduction along the Cu-O chains. The low noise power in high resistivity films appears to indicate a degraded chain conductivity.
4.1 Introduction

Low-frequency 1/f resistance fluctuations (1/f-noise) have been intensively studied in homogeneous materials such as metals and semiconductors [4.1, 4.2]. Since the discovery of high-Tc cuprate superconductors, a number of groups have reported noise measurements in the normal state of these materials [4.3-4.7]. In general, the observed noise power has a large magnitude compared to clean metals even for single-crystalline samples. In YBa$_2$Cu$_3$O$_y$ (YBCO), in particular, noise levels 7 orders of magnitude higher than in metals have been reported[4.6]. Recently, this strong 1/f noise in YBCO has been attributed to conduction along the one-dimensional Cu-O chains[4.7]. In our experiment on laser-ablated YBCO thin films, we have studied 1/f-noise in samples over a wide range of normal-state resistivities and oxygen content. The observed behavior of the noise can be understood in terms of variations in the chain conductivity for the different samples.

4.2 experiment

All our samples were grown on (100) SrTiO$_3$ substrates by laser ablation in 1 mbar of oxygen. Substrates (2.5 × 10 × 1 mm$^3$) were glued with silver-paint to a heater block and heated to 700–750°C during deposition. Immediately after film growth, the deposition chamber was vented with 1 bar of oxygen. X-ray diffraction measurements showed that films made by this system were single phase, c-axis oriented YBCO. Five equally spaced 1 x 2.5 mm$^2$ gold contact pads were ablated onto each sample in-situ through a metal mask. Electrical connection to a film was made by pressing contact pins onto the pads, resulting in a typical contact resistance of 0.1 Ω.

Resistance fluctuations were measured using a standard 5-terminal ac technique [4.8]. The sample current density was smaller than 1000 A/cm$^2$. We found that the 1/f noise power scaled with the square of the bias current, indicating that the noise was due to resistance fluctuations.
In order to investigate the influence of oxygen content on the films' noise power, we systematically subjected the samples to a series of repeated anneals at various oxygen pressures. The samples were placed in an oven filled with oxygen to a preset pressure. After heating up to 450°C in two hours, the temperature was kept constant for another 30 minutes. The samples were then cooled to room temperature in 15 minutes.

4.3 Results and discussion

We describe here four samples, labeled A, B, C, and D. They represent a range of normal-state resistivities, $\rho$, and superconducting transition temperatures, $T_c$, as shown in Table I. The resistances as a function of temperature for the as-made samples are shown in Fig. 1. Samples A, B and C have high $T_c$'s of around 90 K and sharp transitions ($\Delta T_c= 2$ K). The resistivities of these three samples vary roughly linearly with temperature from $T_c$ to room temperature. This indicates that the YBCO majority phase is responsible for the electrical resistance. Sample D exhibits a higher resistivity (2800 $\mu\Omega$cm at room temperature) and lower $T_c$ of about 78 K ($\Delta T_c=6$ K). The downward curvature in the resistivity in D indicates that the sample is hole-underdoped relative to the optimum doping. For all samples we can write the measured resistivity as $\rho(T)=\rho_o + \rho'T$. Here $\rho_o$ is an effective residual resistivity, and $\rho'$ the linear temperature coefficient of resistivity. In Table I we also list the values of $\rho_o$, and $\rho'$ for the four as-made samples. The room temperature resistivities of all of our samples are high, and even the lowest (380 $\mu\Omega$cm) is still about three times higher than the resistivity found in clean single crystals [4.9]. Similarly, the temperature coefficient $\rho'$ is between 3 and 24 times (for samples A and D, respectively) higher than the value reported for single crystals. Although we do not know the cause of the increased resistivity in our films, these values are typical for in-situ films.
Figure 4.1 Resistivity vs temperature for the four as-made samples.

In order to compare our noise results with those reported by other groups, we normalize the noise spectral density in the conventional manner following the Hooge formula [4.10]. \( S_V(f)/n = S_V(f)\Omega^\alpha/V^2 = \gamma/n_c \) Here \( S_V(f)/n \) is the normalized noise spectral density, \( S_V(f) \) is the measured noise spectral density, \( \Omega \) is the sample volume, \( V \) is the measured voltage drop over the sample, \( f \) is the frequency, \( \alpha \) is an exponent close to unity, and \( n_c \) the carrier density of the sample. The parameter \( \gamma \) for each sample is calculated using the carrier density \( n_c = 5.75 \times 10^21/cm^3 \) [4.11]. The values of \( \gamma \) and the exponent \( \alpha \) for each sample are also presented in Table 1. Remarkably, samples with high resistivities, \( \rho \), and high effective residual resistivity, \( \rho_0 \), exhibit significantly less noise than the samples with lower resistivity and residual resistivity. This is in contrast
to the usual expectation that higher resistivity samples of the same material, containing more defects and/or a smaller number of carriers, should also produce a higher noise level. In YBCO, apparently, defects such as grain boundaries or possibly additional scattering centers inside each grain, which may be the cause of the larger effective residual resistivity in samples C and D, do not increase the resistance noise. We note that Zheng et al. also have reported lower noise levels in their YBCO thin films with higher resistivity [4.12].

The effects of oxygen annealing on the superconducting transition temperature are shown in Fig. 2. After annealing at a reduced oxygen pressure (ranging from 1 bar down to 0.1 mbar), the $T_c$ of samples A and C are reduced in a manner comparable to bulk samples [4.13]. Sample C was only annealed over a smaller pressure range due to the fact that further annealing at lower pressure led to a large sample resistance, that exceeded the maximum resistance value suitable for our noise measurement setup. In sample B, $T_c$ appears to be comparatively insensitive to the annealing treatment, staying at around 90 K over a large annealing pressure range and only dropping down to 80 K at 1 mbar, indicating that the CuO$_2$ planes are hole-overdoped. The $T_c$ of sample D, on the other hand, starts at 78 K and falls off rapidly to below 70 K after annealing at relatively high oxygen pressure (100 mbar).
Figure 4.2 $T_c$'s of samples A and C as a function of oxygen annealing pressure.

Figure 4.3 Normalized noise power for samples A and C as a function of oxygen annealing pressure.
Since samples B and D show different annealing behavior for $T_c$, this may be an indication of different carrier doping in the CuO$_2$ planes. We therefore choose to focus our attention here only on samples A and C, which should have the same oxygen content in the Cu-O chains. Interestingly, in addition to the striking relationship between $\rho$ and $\gamma$ for the as-made films discussed above, samples A and C also show clearly different annealing behaviors; see Fig. 3. Upon oxygen reduction from the fully oxygenated state, the normalized noise in sample A, which had originally a higher noise level, decreases first to a minimum. Further oxygen reduction appears to lead to a noise increase. In contrast, the normalized noise for sample C, which had already a lower level, increases monotonically upon oxygen reduction. The annealing behavior of sample C is what one would expect qualitatively in comparison with noise behavior in normal metals, where both the reduction of the number of carriers in the sample and the increase in defect concentration can lead to noise increase. We note that the normalized noise in sample D, which had originally a large resistivity and low noise, shows qualitatively similar behavior as sample C. At the same time, noise in sample B resembles sample A.

In a recent paper, Liu et al. reported noise measurement on YBCO thin films grown by pulsed organometallic-beam epitaxy, each having a different oxygen deficiency [4,7]. They observed a lower noise with initial oxygen reduction and a minimum at $y = 6.5$ corresponding to a $T_c \sim 60$ K, similar to our sample A. They proposed a model based on parallel conduction paths along the chains and the planes to account for the observed anomalous noise variation, and suggested that the extraordinary high noise level, which is generally found for the YBCO compound, is intrinsic to the crystal structure of this material. Due to the one-dimensional character of the chains and the mobility of the oxygen atoms on the chains sites, chains are assumed to produce much more noise than planes. Since oxygen reduction will degrade the chains by introducing more vacancies on the chain oxygen sites, the conductance of the chains decreases much faster than that of the planes. Effectively, the reduced conductance of the chains can reduce the noise contribution of the chains, while the noise originating from the planes becomes increasingly dominant.
Table I. Sample characteristics, including thicknesses, $d$, superconducting transition temperatures, $T_c$, resistivities at 300 K, $\rho(300\text{ K})$, linear temperature coefficients for the resistivity, $\rho'$, Hooge parameters, $\gamma$, and the frequency exponents, $\alpha$.

<table>
<thead>
<tr>
<th>Samp</th>
<th>$d$ (nm)</th>
<th>$T_c$ (K)</th>
<th>$\rho(300\text{ K})$ ($\mu\Omega\text{cm}$)</th>
<th>$\rho'$ ($\mu\Omega\text{cm/K}$)</th>
<th>$\rho_o$ ($\mu\Omega\text{cm}$)</th>
<th>$\gamma$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>400</td>
<td>89</td>
<td>380</td>
<td>1.11</td>
<td>39</td>
<td>51</td>
<td>1.26</td>
</tr>
<tr>
<td>B</td>
<td>780</td>
<td>90.5</td>
<td>495</td>
<td>1.68</td>
<td>-0.61</td>
<td>632</td>
<td>1.32</td>
</tr>
<tr>
<td>C</td>
<td>650</td>
<td>89</td>
<td>730</td>
<td>2.09</td>
<td>112.3</td>
<td>0.9</td>
<td>1.31</td>
</tr>
<tr>
<td>D</td>
<td>240</td>
<td>79</td>
<td>2800</td>
<td>7.81</td>
<td>476</td>
<td>0.19</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Our lower resistivity samples confirm the observations of Liu et al. We see no other explanation for the decrease in noise upon oxygen reduction. If one accepts that the noise in the low resistivity films is due to the intrinsic chain conduction, then it appears that the only possibility for the lower noise in the high resistivity samples is that the chains there do not contribute to the conduction. This is also consistent with the fact that their noise increases upon oxygen reduction. The noise increase in sample C may reflect the intrinsic noise of the planes or it may be of some other extrinsic origin. The proposed absence of chain conduction in sample C could also account for the increase in resistivity and in the temperature coefficient $\rho'$ compared to sample A (see Table I), since the chain conductance is found to be roughly equal to the plane conductance in single crystals [4.9]. Another interesting feature is that the higher resistivity samples have a noise level which is comparable to the lowest noise previously reported for cuprate materials without CuO chains, such as in Tl$_2$Ba$_2$CaCu$_2$O$_8$ thin films by Misra et al [4.14]

The detailed microscopic origin of the degradation of the chain conductance in our high resistivity films is unclear at present. However, the reason cannot simply be
oxygen deficiency since (1) the as-made samples have high $T_c$'s and (2) the samples were annealed several times at high oxygen pressures. We therefore find disorder in the lattice, quenched-in during growth, to be the most probable cause. Since oxygen is rather mobile in the chains, this disorder has to be related to the metal-atom lattice in YBCO.

In writing this paper we became aware of the noise measurements done by Scouten et al. on laser-ablated YBCO thin films [15]. They report low resistance noise which is even lower than for our sample D. Similar to our low noise samples, they also see a noise reduction after increasing the oxygen content by a plasma treatment.

4.4 Conclusion

In conclusion, we have investigated the normal state resistance noise in laser-ablated YBCO thin films. Extrinsic structural defects, such as grain boundaries or impurities in these samples do not lead to higher normalized noise level. Strong 1/f noise generally found in high-quality YBCO material likely is caused by the well-conducting chains intrinsic to the crystal structure, confirming the conclusion of Liu et al. Instead of indicating a higher purity of the crystal, as is normally the case in normal metals, low 1/f noise in YBCO samples appears to be an indication of degraded chain conductance.

We would like to thank Peter Hadley, Rick Kraaijeveld and Ad Verbruggen for many useful discussions, and Leo Lander for technical assistance. This work is supported by Dutch National Research Program for High Tc Superconductivity (NOP-HTS). HMJ acknowledges support from the National Science Foundation (DMR 91-20000) through the Science and Technology Center for Superconductivity.
References

[a) Permanent address: James Franck Institute and Department of Physics. The University of Chicago, Chicago, Illinois 60637, USA.


[4.11] We used the same value as Liu et al., Ref. 7, in order to compare our data more readily. We believe this value to be 30% too high. However, we note that choosing a smaller $n_C$ value will lead to even smaller $\gamma$'s.


Chapter 5  Electronic Phase Diagram of the Cuprates

5.1 Introduction

The properties of high-$T_c$ cuprates can be altered dramatically by doping. They go through regions where they are antiferromagnetic, semiconducting, superconducting, or show metallic properties depending on the carrier doping. When heavily doped, these materials have transport properties that, to a certain extent, resemble those predicted by a Fermi liquid picture. We illustrate these regions in figure 5.1. From the point of view of solid state physics research, these materials are fascinating because a complete understanding of how the electron properties evolve with doping is still lacking. It is interesting to remember that before 1986 it was widely believed that solid-state physics was a mature field. The discovery of the high-$T_c$ cuprates has revealed the weakness of our understanding of strongly correlating electron systems.

![Phase Diagram](image)

*Figure 5.1 Generic phase diagram for the cuprates. AF = Antiferromagnetism, SC = Superconductivity, and $T_N$ = the Néel temperature.*
In the early days, much attention was focused on the extraordinarily high superconducting transition temperatures found in these materials when optimally doped. This is the region near the centre of the horizontal axis in figure 5.1. Gradually, more and more attention was also turned to the normal-state properties at temperatures above their $T_c$'s (up in the centre region of figure 5.1). It turns out that these materials also show properties in the normal state, which are not so "normal" in the sense of a conventional metal.

Much of the theoretical and experimental research is accumulating on the low-doping region of the phase diagram (left in figure 5.1). The region of higher hole doping, i.e., overdoped side, has been less studied and there exist less experimental data. This is probably due to the fact that there are less abundant samples available in this region (on the right part in figure 5.1).

In this chapter, I will discuss the normal-state transport properties of the cuprate materials at different doping levels. A discussion of the electronic states and the phase diagram are given first. I choose not to discuss the numerous theoretical models which are offered to explain the behaviour of the cuprates. Instead, we will look at two different, but basic, models for electron transport, the Hubbard model and the Fermi liquid model. This is because the current theoretical approaches for the high-$T_c$ normal state can be mainly divided into two categories: those which are based on a Fermi liquid picture[5.1-5.6] and those, whose starting point is the strongly correlated electron system where an antiferromagnetic state is observed [5.7, 5.8]. We will look at the limitations of these two basic models and see how far these models are able to describe the electron transport properties in the high-$T_c$ materials.

5.1.1 CuO$_2$ planes

The common structural feature of all the cuprates are the CuO$_2$ plane layers along the $a$-$b$ direction. They are responsible for the superconductivity as well as the anomalous normal state transport properties of these material. Regions between these layers are insulating and act as charge reservoir for these CuO$_2$ planes. In order to understand the electrical properties, it is important to examine the molecular orbitals of these material first.

Appreciating the formal ion charges can be helpful, but the structural backbone of the superconductor cuprates is the strongly covalent CuO$_2$ planes. Due to the
complexity of their structures, it is important to make some simplifying assumptions when we look at the molecular orbitals. The short distance between adjacent copper and oxygen atoms in the CuO$_2$ plane layers indicates covalent and not ionic bonding. For the CuO$_6$ octahedron in the La$_2$CuO$_4$ structure for example, see figure 5.2, there are 17 orbitals. Five from the 3d orbitals on Cu, which are d(x$^2$-y$^2$), d(z$^2$) and the three d(xy) type. The Cu atoms have two oxygen neighbours along the c-direction, one above and one below, these in addition to the two neighbouring planar oxygen atoms (the other two nearest neighbour planar oxygen must be considered in the next unit cells) These four O atoms have three p orbitals each, which contribute 12 orbitals for a total of 17 orbitals.

![CuO$_6$ octahedron](attachment:image.png)

**Figure 5.2. The structure of a CuO$_6$ octahedron in La$_2$CuO$_4$ parent compound.**

By applying the principle that maximum interaction occurs for orbitals that have maximum overlap, we can focus on the in-plane covalent bonding alone. On the central Cu atom, we only use the d(x$^2$-y$^2$) orbital, since it is correctly oriented to
have the overlapping with its neighbouring planar oxygen atoms. The \( p \) orbitals of the two planar oxygen atoms are directed toward the central Cu atom. We only need to use these three orbitals, since to the first approximation the other 14 orbitals can be taken as non-bonding relative to these orbitals.

Figure 5.3 shows a CuO\(_2\) plane with \( d(x^2-y^2) \) orbitals attached to the Cu atoms, and with \( p_x \) and \( p_y \) orbitals attached to the oxygen atoms. The orbitals on Cu are all the same, and those on the O atoms are the same in the a and b directions, so that the repeat distance is the unit cell size (=\( a \)). This molecular orbital diagram corresponds to the \( k = 0 \) or \( \Gamma \) point in the Brillouin zone (\( k \) is the wave vector). Bonding between the charge-lobes of the orbitals occurs when the orbitals have the same phase (shaded-shaded or white-white). Antibonding occurs with opposite phase (a shaded and a white orbital). For the molecular orbital in figure 5.3.a, there are as many bonding and antibonding overlaps. Since the bonding and antibonding energy are approximately the same but opposite in sign, this molecular orbital is non bonding. The orbital diagram in figure 5.3.b has a repeat distance = 2\( a \) in both the x and y directions; This is the point \( M \) in the Brillouin zone. The CO\(_2\) plane has a square lattice and the first Brillouin zone is shown in figure 5.3.c, where the \( \Gamma \), \( X \) and \( M \) special points are indicated. At the point \( M \), three different types of orbitals can be drawn, see figure 5.3.d. The bonding orbital (B) has the maximum amount of overlap and hence the lowest energy. The antibonding orbital (A) has the minimum amount of overlap and hence the highest energy. Finally, the non bonding orbital (NB) has as many bonding and antibonding overlapping orbitals, hence, there is little energy change from the atomic case. The other 14 orbitals we take as nonbonding, so they have energy levels that are essentially independent of \( k \).
Figure 5.3. (a) A CuO$_2$ plane viewed from above, shows σ binding between the Cu(x$^2$-y$^2$) and oxygen p$_x$ and p$_y$ orbitals. This repeat distance is $a$; therefore, the bonding refers to $k=0$ or the $\Gamma$ point in the Brillouin zone. (b) is the same except corresponding to the $M$ point in the Brillouin zone. (c) The reciprocal lattice (solid line) of a square lattice with the first Brillouin zone outlined by solid lines. The special points $\Gamma$, $X$, and $M$ are indicated as is the irreducible wedge with dashed lines. (d) A sketch of $E$ versus $k$ for the bonding (B), antibonding (A), and nonbonding (NB) orbitals. Adapted from Burns[5.9]
The occupancy of the 17 orbitals by electrons are as follow: Cu atoms contribute 11 electrons from the 3d^{10}4s^1 configuration, each of the four oxygen contributes four electrons from its 2p^4 configuration, making it 27 in total. Finally, the two La^{3+} contribute further 6 electrons. There are a total of 33 electrons. Each of the 17 orbitals can accommodate at most two electrons (Pauli principle). Thus all of the orbitals will be filled except for the antibonding orbital which has the highest energy. In the atomic state, the ionisation energy of a p electron from the 2p^4 oxygen orbital is larger than that of a 3d Cu orbital. Therefore, the antibonding orbital A has mainly Cu d(x^2-y^2) character. It is this orbital that carries the missing electron (i.e., the hole) that give the Cu ions in the CuO_2 plane layers their spin s=1/2.

Since the d(x^2-y^2) Cu orbital is only half filled, the parent LaCuO_4 compound is expected to be a conductor based on a non-correlated electron picture. However, this material is found to be an insulator. Essentially the same situation is found for the parent compounds of all the other high-T_c cuprates. This basic fact indicates the failure of the independent electron picture.

5.1.2 Phase diagram

While the parent compound for the high-T_c material is insulating, its properties can be changed in a dramatically way by inserting additional holes into their CuO_2 plane layers. For the sake of simplicity, we use La_{2-x}Sr_xCuO_4 as an example to illustrate the effect of doping. In figure 5.4, we show the generic phase diagram of this compound, adapted from Keimer et al [5.10]. At half filling (x = 0), we have an antiferromagnetic insulator, see left in the figure. The Cu ion moment in the CuO_2 plane layers order antiferromagnetically due to superexchange interaction of the Cu spins.

By doping the material with Sr atoms, La^{3+} ions are randomly replaced by Sr^{2+} and thus fewer electrons are donated to the CuO_2 plane layers. Thus CuO_2 layers are hole doped. Approximately one hole is added for each Sr atom. The Néel temperature, which was 300 K in the undoped material, decreases with increasing hole doping. The long range antiferromagnetic ordering decreases and disappears at x = 0.04, when the Néel temperature is reduced to zero. When x exceeds 0.06 this material becomes a superconductor. The superconducting transition temperature increases with x until it reaches its maximum value at x = 0.15. The doping level at which the T_c reaches its maximum is called the 'optimal' doping level. Further increase of hole concentration suppresses the T_c. When x is larger than 0.3, this
material loses its superconducting properties completely. Hall effect measurements showed that the Hall coefficient changes sign at such high doping level, indicating that carriers change from holes to electrons. In addition to the impressive transition in electronic properties of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compound upon doping, its crystal structure also changes from tetragonal to orthorhombic.

![Phase diagram](image)

**Figure 5.4.** Generic phase diagram of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, Adapted from Keimer et al [5.10].

Similar transition also occurs in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. In this case, the parent compound is the tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_6$ phase ($\delta=1$). No oxygen atoms are present on the chain sites (see Chapter 1). Just as in the $\text{La}_2\text{CuO}_4$ case, the Cu ion moment is also ordered antiferromagnetically in the CuO$_2$ plane layers. By introducing oxygen atoms onto the chains, the number of holes on the CuO$_2$ plane layers can be increased. The generic phase diagram has already been shown in figure 1.6 of
Chapter 1. The range of variation of oxygen content in this compound is one atom per formula unit, allowing the properties to change from an antiferromagnetic insulator to a superconductor (but not further than optimal doping). Note that in figure 1.6, the doping level is indicated with oxygen deficiency $\delta$ along the horizontal axis. We must keep in mind that the hole doping in the CuO$_2$ plane layers is not only determined by the oxygen deficiency in the Cu-O chains alone, but is also influenced by the ordering of these oxygen atoms on the chain sites [5.11]. When this oxygen ordering effect is taken into account, the superconducting transition temperature of this material will increase with doping until the maximum $T_c$ is reached, in the same way as in the La$_{2-x}$Sr$_x$CuO$_4$ case. The optimal doping is reached when the chains are almost completely occupied by oxygen atoms ($\delta = 0.05$). In order to increase the hole concentration in its CuO$_2$ plane layers even further, one needs to resort to heterovalent substitution. By substituting a fraction of the Y$^{3+}$ by Ca$^{2+}$, the number of holes in the CuO$_2$ plane layers can be increased beyond the 'optimal' doping level and into the overdoped regime [5.12].

5.2 Normal-state transport properties

5.2.1 The resistivity

In this section, we will briefly describe the temperature dependence of the resistivity and the Hall coefficient of the high-$T_c$ cuprates. These two physical properties, among other things, are frequently used to argue that these materials behave in an uncommon manner, or 'anomalously', even in their normal state. This is in addition to their surprisingly high superconducting transition temperature $T_c$'s.

In figure 5.5, we show the in-plane resistivity of La$_{1.85}$Sr$_{0.15}$CuO$_4$, YBa$_2$Cu$_3$O$_7$, Bi$_2$Sr$_2$CuO$_6$ and Bi$_2$Sr$_2$CaCu$_2$O$_8$ compounds, adapted from Battalogg et al [5.13]. These are all optimally doped cuprates. The linear temperature dependence in the region above the transition temperature can be clearly seen. Note that the scale is the same for all these four compounds. The linear temperature dependence of the resistivity, which persists over a wide temperature range, is highly unusual and make these cuprates distinctively different from conventional metals even above the transition temperature.
Figure 5.5. Temperature dependence of the in-plane resistivity $\rho_{ab}$ measured on crystals of various cuprate superconductors. 123 90K denotes $YBa_2Cu_3O_{7-\delta}$, while 214 LSCO corresponds to $La_{2-x}Sr_xCuO_4$ with $x = 0.15$. Adapted from Battlogg et al [5.13]

In conventional metals, the transport properties are governed by electron-phonon scattering. There are two temperature regions relative to the Debye temperature $\theta_D$.

For the high temperature region the resistivity $\rho$ varies linearly with temperature:

$$\rho = A + BT \quad (T \geq 0.2\theta_D) \quad (5.1)$$

where $A$ and $B$ are constants. At such a high temperature all phonon modes are excited. The electron-phonon scattering, which causes the resistance, is proportional to the square of the amplitude of the atomic vibration about their equilibrium positions. This leads to the linear temperature dependence.

However, as the temperature decreases the resistivity drops faster with temperature:
\[ \rho \propto T^5 \quad (T \ll 0.2\theta_D) \quad (5.2) \]

This is due to the fact, that when the temperature reduces to below 0.2 \( \theta_D \), an increasing number of phonons with high excitation energy start to freeze out. This reduces the electron-phonon scattering and thus reduces the resistivity faster than in the high temperature region. The Bloch-Grüneisen formula extrapolates between the low and high temperature limits. As an illustration, we show the resistivity temperature dependence of five different metals in figure 5.6, adapted from Madelung [5.14].

![Resistivity vs Temperature Graph]

Figure 5.6. The electrical resistivity of several metals as a function of temperature (in reduced units, \( \Theta = \) Debye temperature). The points are experimental resistivity data. The solid line is a result from the Bloch-Grüneisen formula. Adapted from Madelung [5.14]. Note that the room temperature resistivity of these metals is two orders of magnitudes smaller than those found in high-Tc cuprates (shown in figure 5.5).
The Debye temperature $\theta_D$ for the high-$T_c$ cuprates lies between the 300 K to 450 K. Deviation from linear resistivity (excess conductivity) should be expected at temperature between 60 K to 90 K. However, none of the curves in figure 5.5 shows such a deviation. The results for Bi$_2$SrCuO$_6$ which is denoted as Bi2201 in figure 5.5, is particularly interesting. The linearity persists to the temperature just above $T_c = 7$ K. This is about 50 K below the temperature where the deviation would be expected from the Bloch-Grüneisen formula. The absence of an excess conductivity indicates that another scattering mechanism, besides the electron-phonon scattering, may play a prominent role in these materials. It should be noted, though, that even in the case that other scattering mechanism is more dominant, a cross over from $T$ to $T^5$ behaviour that would have arisen from a phonon "background" contribution should still be visible somewhere below 60 K. That there is no deviation from linearity at all is thus amazing.

The linear temperature dependence of the resistivity, however, is only observed in a small doping region near the 'optimal' doping level. As an example, we show the doping and temperature dependence of the resistivity of La$_{2-x}$Sr$_x$CuO$_4$ in figure 5.7.a, adapted from Battlogg et al [5.15]. Note, that they are all in the doping range below or equal to the 'optimal' doping level, the so-called 'under-doped' regime ($x < 0.15$). A similar behaviour found for our YBa$_2$Cu$_3$O$_{7-\delta}$ samples is given in figure 6.3a of Chapter 6. The general features are as follow: As $x$ decreases the resistivity becomes larger. This is consistent with the expectation that resistivity goes up when carriers concentration decreases. Also, while $x$ becomes smaller, the resistivity continues to show a high temperature regime where it varies linearly with the temperature. The slope at high temperature goes up with decreasing $x$. Deviation from the linear temperature dependence can be seen at lower temperature, showing excess conductivity. The temperature $T_p^*$, where the deviation sets in, decreases with increasing doping (larger $x$). At optimal doping level ($x = 0.15$), $T_p^*$ appears to be below the superconducting transition temperature.
Figure 5.7. (a) In-plane resistivity $\rho_{ab}$ as a function of temperature for several composition of $La_{2-x}Sr_xCuO_4$, adapted from Battlog et al [5.15]; (b) In the overdoped regime, the resistivity of the $La_{2-x}Sr_xCuO_4$ ($x=0.2, 0.25$ and $0.3$) show up turn curvature at high temperature, adapted from Battlog et al [5.17]; (c) the resistivity of overdoped $Tl_2Ba_2CuO_{6+z}$ exhibits a temperature dependence that can be well fitted to $T^2$ [5.18].
The excess conductivity (reduced resistivity) observed in the low temperature region for underdoped cuprates has apparently other origins than the resistivity reduction found in conventional metals mentioned above. This is because the Debye temperatures of the cuprates is unlikely to be influenced so dramatically by the doping level, $x$. Ito et al [5.16] have studied this excess conductivity in the oxygen deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound. By comparing their measurement with the nuclear magnetic resonance (NMR) studies, they concluded that the scattering in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is governed by spin scattering. The excess conductivity in the underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is correlated to the opening of a spin-gap at low temperature. The temperature below which a spin-gap will appear increases when the sample is less doped.

Of particular interest from a Fermi liquid point of view (see later in this Chapter) is the behaviour of overdoped samples. In figure 5.7.b, data for overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ are also presented ($x > 0.15$), adapted from Battlogg et al [5.17]. The resistivity decreases monotonically with increasing $x$, indicating a increasing amount of carriers in the material upon doping. An upturn curvature can be seen in all of the overdoped samples. This curvature is even more obvious in the overdoped $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+z}$ samples, see figure 5.7.c. Tsuei [5.18] has reported that the resistivity goes nearly as $T^2$. Upturn curvature can also be observed in the resistivity data from our overdoped $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ see figure 6.3b of Chapter 6.

5.2.2 The Hall coefficient

The temperature dependence of the Hall coefficient $R_H$ for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is shown in figure 5.8, adapted from Hwang et al [5.19]. It has previously been observed [5.20] that the magnitude and the temperature dependence of the $R_H$ data obtained from polycrystalline cuprate samples have only negligible influence of grain boundaries, and are dominated by the in-plane $R_H$ as measured in a single crystal (i.e., along the CuO$_2$ planes). This indicates that data from samples of different forms such as polycrystalline, thin films and single crystal can be compared directly. Figure 5.8 shows that this is indeed the case. At all doping levels, $R_H$ decreases with increasing doping. This is consistent with the increased carrier concentration in the sample.
We can see temperature dependence in all these samples. For less doped samples \((x < 0.22)\) the temperature dependence of \(R_H\) is stronger. The temperature dependence of \(R_H\), however, is unexpected based on a simple single parabolic band model which predicts a constant \(R_H\) as a function of temperature. From figure 5.8.b, we can see that the temperature dependence becomes weaker at higher temperature. When the doping level is sufficiently high \((x > 0.3)\), the sign of the Hall coefficient changes from positive at low temperature to negative at higher temperature. This indicates that at higher temperature, the carriers in these heavily overdoped \(La_{2-x}Sr_xCuO_4\) change from holes to electrons.

From the examples given above, we can see that the high-\(T_c\) cuprates show anomalous transport properties even in the normal state, \textit{i.e.}, they do not behave like conventional metals. The fact that these materials become insulators with antiferromagnetic ordering of the planar Cu ion moment near \(x = 0\) (left in figure 5.1) may have important consequences. It may suggest that these anomalous properties are caused by a strongly correlated electron system. Based on this assumption, a large number of theories have been developed to describe the normal state behaviours by using the Hubbard model as a starting point. Another theoretical approach uses a more or less independent electron system \textit{i.e.}, the Fermi liquid model as a starting point. By introducing one or other modification to these basic models, theorists hope to unveil the mystery of the 'anomalous' normal state properties. We will look at these two models in the following section.
Figure 5.8. Hall effect of in underdoped (a) and in overdoped (b) regime. (The solid lines are for single crystal thin films, dots are for polycrystalline samples.), adapted from Hwang et al [5.19].
5.3 Two Basic models

5.3.1 The Hubbard model

In the Hubbard model all the electron levels of each ion in a lattice are reduced to a single localised orbital. It thus describes the electron situation in a crystal where each of the lattice sites (ions) can accommodate two electrons and most importantly, where the Coulomb interaction energy of the two electrons located at the same atom cannot be ignored. The state of the model are given by specifying the four possible configuration of each lattice site. Its orbital can be empty, contains one electron with either of the two spins, or two electrons of opposite spin. The Hamiltonian $H$ for the Hubbard model contains three types of term, see equation 5.1

$$H = -t \sum_{\langle i,j \rangle \neq \delta} c_{i,\sigma}^\dagger c_{j,\sigma} + E_0 \sum_i c_{i,\sigma}^\dagger c_{i,\sigma} + U \sum_i c_{i,\uparrow}^\dagger c_{i,\uparrow} c_{i,\downarrow}^\dagger c_{i,\downarrow} \quad (5.1)$$

here $c_{i,\sigma}^\dagger$ and $c_{i,\sigma}$ are the creation and annihilation operators respectively. The first term on the right is diagonal in these states, this is just a positive energy $E_0$ needed to bind a single electron on an isolated ion times the total number of electrons. The second term is also diagonal in these states. This is the positive Coulomb interaction energy $U$ between the two electrons located on the same ion times the number of doubly occupied ionic level. The third term on the right is off-diagonal in these states. It has non-vanishing matrix elements $t$ between just those pairs of states that differ only by a single electron having been moved from a given ion to one of its neighbours (without change in spin). This kinetic energy term is a measure of how easily an electron can jump from one site to its neighbouring site.

In the extreme case, when $t >> U$ (weak correlation between the electrons) the movement of electron will not be hindered by the Coulomb repulsion due to the first electron present on the lattice site. When the ionic orbital is half filled, the holes occupy states up to a Fermi level exactly in the mid-band, i.e., the system should be a metal. See figure 5.9a. In the other extreme case, i.e., when $t << U$ (strongly correlated electron system), the system will favour local magnetic moments, since it
would suppress the possibility of a second electron (with oppositely directed spin) at singly occupied sites. The ionic orbital splits into two subbands, the lower band at energy level $E_0$ and the upper band at energy level $E_0 + U$.

Figure 5.9. (a) In a weakly correlated electron system, a metal can be obtained at half filling (the shaded area). However, (b) the same half filling will lead to an insulator when the electron-electron correlation is strong.

At half filling, the lower subband is completely filled, while the upper subband is completely empty. The material becomes an insulator. One can derive an antiferromagnetic Heisenberg spin hamiltonian to describe the low-lying excitations. When extra holes (electrons) are introduced into the system, they will enter the lower (upper) electron bands. These additional holes (electrons) are mobile and can be measured by Hall-effect measurement. As the number of the mobile holes (electrons) is increased, their motion against the background of interacting spins will destroy long range antiferromagnetic order. However, it is not clear how the model evolves from an antiferromagnetic insulator to a nonmagnetic metal when $t/U$ is varied or more holes are introduced. At higher carrier concentration, this model goes over to a Fermi liquid state.
Soon after the discovery of the high-$T_c$ superconductors, Anderson proposed [5.20] that the essential physical properties of the materials can be described by the above discussed single band Hubbard model. The single band in this case can be identified as the antibonding band of $dx^2-y^2$ mentioned in section 5.1.1.

![Diagram showing hole addition](image)

**Figure 5.10.** When the charge transfer energy $\Delta$ (energy difference between the Cu 3d orbital and the O 2p orbitals) is smaller than the Hubbard gap between the 2 Cu 3d subbands, added holes will mainly go on the oxygen ions in the CuO$_2$ planes.

Note that the important assumption in the one band model is that the oxygen levels do not introduce extra degrees of freedom in the low energy region of the spectrum, neither do the other Cu d states. However, photoemission and resonant measurements indicated that this is not exactly the case [5.8, 5.21, 5.22]. It was found that the Hubbard gap $U_d$ between the upper and lower Cu 3dx$^2$-y$^2$ subbands is larger than the so-called charger transfer energy. This implies that the oxygen 2p band actually lies in between the two Cu 3d Hubbard subbands. Therefore, the insulating materials are best characterised as charge transfer insulators. At half filling, the holes are primarily situated in the dx$^2$-y$^2$ symmetry states. This is confirmed by polarisation dependent Electron-Energy-Loss spectroscopy and X-ray absorption measurement. When the material is hole doped, however, the added holes
will mainly go on the oxygen. Because of this, Emery[5.23] proposed the 'three band model" (or extended Hubbard model). It contains the two oxygen levels explicitly, i.e., the two pσ orbitals in addition to the Cu dx²-y² orbital; see figure 5.10. Emery proposed initially that the holes on oxygen will destroy the antiferromagnetic ordering of the Cu spin, and feel an attractive interaction via the Cu spin system, which is a possible mechanism for superconductivity.

Zhang and Rice [5.24] argued that the exchange interaction between a hole on the oxygen ion and a particular Cu spin in the CuO₂ plane is so strong that the triplet excitation can be neglected. Extra holes inserted into the CuO₂ planes will form a coherent state on the 4 oxygen atoms around a Cu atom. These two spins will form singlet states (Zhang-Rice singlets). Thus adding holes on oxygen is then equivalent to removing spins from the Cu positions, and these singlets then dilute and propagate in an antiferromagnetic lattice just as in a single band Hubbard system.

5.3.2 The Landau's Fermi liquid theory

The Landau's Fermi liquid theory describes an system of delocalised electrons, in which electron-electron scattering is not ignored. This interaction is taken into account by treating the electron system as a system of independent quasiparticles which obeys Fermi-Dirac statistic. An effective mass \( m^* \) (≠ \( m_e \), the electron mass) is assigned to each quasiparticle.

Based on Pauli exclusion principle and energy conservation, the temperature dependence of the scattering rate \( \frac{1}{\tau} \) between these electrons is found to vary with \( T^2 \), see Ashcroft & Mermin [5.25]. For a single parabolic band electron system where \( \rho = m^*l/(ne\tau) \) and \( R_H = l/(ne) \), this predicts the following temperature dependence for the resistivity and the Hall-coefficient:

\[
\rho \sim T^2 \\
R_H = constant
\]

Note, that the \( T^2 \) temperature dependence of the resistivity is only visible when the relaxation time \( \tau \) due to electron-electron scattering is small (fast enough) compared with other scattering. Typical metallic relaxation times at room temperature are of the order of \( 10^{-14} \) second, while The electron-electron scattering relaxation time is only of the order of \( 10^{-10} \) second. This means that at room
temperature electron-electron scattering proceeds at a rate $10^4$ times slower than the dominant scattering mechanism in metal (electron-phonon scattering). Note that $\rho \sim T^2$ behaviour in metal has been observed at very low temperature.

Anderson has proposed that the electron systems of high-$T_c$ cuprates are in the strong-correlation limit ($U >> t$) of the Hubbard model [5.26, 5.27]. The half-filled $d(x^2 - y^2)$ Cu orbital in La$_2$CuO$_4$ compound leads to an insulator ($x = 0$) because no double occupancy of any site is allowed. The cost in energy $U$ would dominate any gain in kinetic energy. Early Hall experiment on hole-doped La$_{2-x}$Sr$_x$CuO$_4$ showed that as $x$ approaches 0, $R_H$ measured at 100 K diverges as $1/x$. On this basis, it was proposed [5.28] that the behaviour of this material in the range $0 < x < 0.14$ is consistent with a strong correlation viewpoint. This question is still being researched both theoretically and experimentally.

It is interesting to look at high-$T_c$ material in the overdoped region (large $x$). Experiments on heavily overdoped La$_{2-x}$Sr$_x$CuO$_4$ [5.30, 5.31] have shown that the transport properties $R_H$, $\rho$ for $x > 0.3$ are not very different from those of a conventional metal with a low mobility. $\rho$ varies as $T^2$ at low temperature. A temperature independent $R_H$ at $x = 0.5$ gives a Hall number $n_H = 1/(R_H e)$ which corresponds to $2.1 \times 10^{22} \text{cm}^{-3}$. This is equal to 2 holes per planar copper.

While the Hubbard model is able to explain the existence of an antiferromagnetic insulator in the underdoped region, transport properties found at the overdoped end of the generic phase diagram (figure 5.1) seems to favour the Fermi liquid picture. The electron behaviours in region between these two extreme cases is still hard to explain. This situation may change when a more proper tool to deal with strongly correlated electron system is available [5.15].

References


Chapter 6  Scaling of the Hall Coefficient and Resistivity in Underdoped and Overdoped RBa$_2$Cu$_3$O$_y$ Films

N.Y. Chen, V.C. Matijasevic, J.E. Mooij

*Applied Physics, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands*

and

D. van der Marel

*Department of Physics, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

Abstract.

We have studied the normal state transport properties, the resistivity $\rho(T)$ and the Hall coefficient $R_{Hi}(T)$, on two sets of samples of RBa$_2$Cu$_3$O$_y$ compounds (R = Y, Sm) away from optimal doping. In the overdoped regime, $R_{Hi}(T)$ obtained from the Ca-doped SmBa$_2$Cu$_3$O$_y$ shows a saturation at high temperature. While $R_{Hi}(T)$ decreases with $T$ at low temperature, it becomes temperature independent when the temperature exceeds a certain value $T_H^*$. This characteristic $T_H^*$ decreases with doping, and is only visible in our experimental temperature range when the samples are sufficiently doped. By assuming a universal functional form for all doping levels, the temperature dependence of the Hall coefficient can be scaled. Another characteristic temperature $T_P^*$ can be seen from the resistivity data in the underdoped regime, obtained from the oxygen deficient YBa$_2$Cu$_3$O$_y$ samples. Above $T_P^*$, $\rho(T)$ increases almost linearly with $T$, whereas below, it deviates from the linear behavior. We discuss the relationship between these two characteristic temperatures $T_H^*$ and $T_P^*$ for different doping levels. For the underdoped samples, the resistivity is fit well by the relation $\rho(T) = a R_{Hi}(T)T^2 + b$. 
6.1 Introduction

The normal state properties of the cuprate high-$T_c$ superconductors, observable at temperatures above the superconducting transition $T_c$, have enjoyed an increasing amount of attention. This is in addition to the high $T_c$’s found in these materials, which was initially the most fascinating topic for the majority of research. The normal state transport properties, such as the resistivity $\rho(T)$ and the Hall coefficient $R_H(T)$, exhibit anomalous temperature dependencies (i.e. non-Fermi liquid behavior), which by themselves are at least as fascinating as the high superconducting transition temperatures. It may be that the underlying mechanisms for these intriguing properties are related to each other.

The resistivity in these materials when optimally doped (for the highest $T_c$) generally increases linearly with temperature. At the same time, the Hall coefficient has a temperature dependence of approximately $1/T$. Deviation from this behavior becomes increasingly apparent when the materials are further away from optimum doping. Most of the experiments on the RBa$_2$Cu$_3$O$_y$ cuprates ($R = Y$, Lanthanides) were done in the underdoped regime (hole doping less than optimal) on oxygen deficient YBa$_2$Cu$_3$O$_y$ (YBCO) thin films or single crystals. In our work, we try to obtain a more complete picture of this subject by extending our study into the overdoped regime on Ca-doped Sm$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_y$ (SBCO) thin films, and compare them to our oxygen deficient YBCO samples. Recently Ito et al.[6.1], and Hwang et al.[6.2] have shown for different sets of high-$T_c$ cuprates that the normal state properties can be scaled as a function of doping in either the underdoped or the overdoped regimes. We find that the scaling relationship for $R_H(T)$ can be extended to all doping levels of our samples, from the overdoped into the underdoped regime.

6.2 Experiment

We have grown our YBCO thin films on 5 x 5 mm$^2$ (100) SrTiO$_3$ substrates by laser ablation at 750 °C and 1 mbar oxygen pressure. X-ray diffraction measurement showed that they are $c$-axis oriented. No minority phases were observed. The $T_c$’s of the as-made samples were around 91 K with sharp transitions ($\Delta T_c < 2$ K). The resistivity for several samples varies from 180 to 390 $\mu\Omega$cm at 300 K. In order to study the underdoped regime, three samples have been repeatedly annealed at reduced oxygen pressures (1 mbar $< p_{O_2} < 1$ bar) at 450 °C. Two of the samples failed to give reproducible values for $T_c$ and resistivity after annealing back to the original fully oxygenated state. Therefore, we present only the data from one YBCO sample that
survived all anneals, also the one with the lowest resistivity. The $T_c$ of this sample could be restored to its original as-made value after 11 annealing runs with a small increase (0.5 K), accompanied by a slightly increased resistivity (10%). Our Ca-doped Sm$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_y$ thin films were grown by co-evaporation in an MBE deposition system. Films were grown in an ozone beam and at 750 °C. By adjusting the relative evaporation rates for different elements to the desired ratio, samples with three different levels of doping ($x=0.1, 0.2, 0.4$) were made. Ca doping of the structure has been shown to lead to hole overdoping of the plane layers [6.3, 6.4]. Low oxygen pressure annealing of the Ca-doped samples showed us that the $T_c$ increases upon reduction and that therefore the samples are overdoped compared with optimal hole doping. We find a solid solubility regime of Ca-doping for our films up to 0.3-0.4 Ca substitution [6.5].

The in-plane resistivity and Hall coefficient were measured using the van der Pauw technique without patterning. Four Au pads (diameter=0.5 mm) were laser ablated on the corners of the sample through an aluminum foil mask in vacuum at room temperature. This was done to insure good electrical contact between the samples and the contact pins. For each sample, $\rho$ and $R_H$ were measured as a function of temperature in a liquid Helium flow-cryostat during two separate runs. For the Hall measurements a magnetic field of 0.6 T was applied perpendicular to the film.

### 6.3 Results and discussion

In the overdoped regime $R_H$ decreases with increasing temperature, see Fig. 6.1a. At higher doping levels ($x = 0.2, 0.4$) a characteristic temperature $T_H^*$ can be seen. Above the temperature $T_H^*$, which decreases with increasing doping level, $R_H(T)$ becomes almost temperature independent. Hwang et al. reported earlier the existence of $R_H(T)$ saturation in overdoped La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) at high temperatures [6.2]. Here we report this behavior for the RBa$_2$Cu$_3$O$_y$ compound as well.
Figure 6.1 The Hall coefficient ($R_H$) for: (a) overdoped $Sm_{1-x}Ca_xBa_2Cu_3O_y$ samples; (b) underdoped oxygen deficient $YBa_2Cu_3O_y$. The curves in (b) are for various oxygen anneals from 1 bar to 1 mbar going upward.
Figure 6.1b shows the $R_{Hf}(T)$ of the YBCO film measured before and after various low oxygen pressure annealing runs. In most of the underdoped cases, except the ones with the lowest doping (top three lines), $R_H$ decreases with increasing temperature in the whole range of measurement, and follows roughly $1/T$. The deviation from this behavior can be observed for the lowest doping levels at low temperature, where $R_H$ initially increases with temperature (above $T_C$) to a maximum value and subsequently decreases. Ito et al. observed that this deviation followed exactly the excess conductivity found at low temperature in the underdoped samples [6.1]. Our data confirm the observation by Ito et al. It becomes even more obvious when we plot $R_{Hf}(T) T^2$; shown in Fig. 6.2 for the underdoped samples. These curves have the same features as do the resistivity curves for these samples. By choosing corresponding constants $a$ and $b$ for each doping level, the set of $\rho(T)$ and $R_{Hf}(T) T^2$ curves can be fitted onto each other using the relation:

$$\rho_{cal}(T) = a R_{Hf}(T) T^2 + b.$$  

(6.1)

Figure 6.3a compares $\rho(T)$ data (solid lines) and the fitted $\rho_{cal}(T)$ from the $R_{Hf}(T)$ data (circles) for the underdoped samples. The two sets of curves fall well onto each other, if one disregards the differences at higher temperature in the two least doped cases. In the inset of Fig. 6.3a, we show the ratio of this set of curve pairs. At this point, we would like to mention two interesting features concerning the relationship between $\rho(T)$ and $R_{Hf}(T)$. First of all, this relationship which we find for the underdoped regime is similar, but slightly different from the one proposed by Anderson [6.6] for the Hall angle in a Luttinger liquid, $\cot(\theta_H) = \rho/(H R_H) = \alpha T^2 + C$ and first observed by Chien et al.[6.7]. $H$ is the magnetic field and $\alpha$ and $C$ are constants.
Figure 6.2 $R_H(T) T^2$ vs temperature. The Hall data presented in this way are very similar to the resistivity data.

The reason that our data fit better to our Eq. (1) than to the Anderson equation may be due to the fact that our $\rho(T)$ curves do not extrapolate to zero at zero Kelvin [6.8]. The value of $a$, comparable to $\alpha$ in Anderson's relation, decreases monotonically with decreasing doping level in our data. This is in agreement with the results reported by Wuyts et al [6.9] on oxygen deficient YBCO thin films, and other reported experiments on doped LSCO [6.2]. Different behavior has also been reported for YBCO [6.10, 6.11]. Secondly, despite the slight downward curvature in the as-made $\rho(T)$ curve, and the fact that it clearly does not extrapolate to zero at zero temperature, $R_H(T) T^2$ still follows $\rho(T)$ behavior almost exactly.
Figure 6.3 A comparison of ρ(T) data (solid lines) and ρ_{cal}(T) (symbols), fitted from $R_H(T)$ using Eq. (1) for: (a) underdoped YBCO samples, and (b) overdoped SBCO samples. Inset of 3a shows the ratio of the two.
While this relationship is directly obtained by fitting the data from underdoped samples, it is interesting to see whether it is also valid for the samples in the overdoped regime, which show the $R_{Hf}(T)$ saturation ($x=0.2$, $0.4$). In Fig. 6.3b, we plot the temperature dependence of $\rho(T)_{cal}$ calculated from $R_{Hf}(T)$ data using Eq. (1) and fitted with the corresponding values of $a$ and $b$, together with the actually measured $\rho(T)$. Although there is an upward curvature in both sets of curves, these curves do not fall onto each other. Further, the resistivity does not have any characteristic temperature, as does the Hall coefficient. Instead the resistivity curves show an increasing amount of curvature as the doping increases, up to $T^{1.6}$ for the highest doping shown here.

Hwang et al [6.2] suggested, that all overdoped LSCO samples have $R_{Hf}(T)$ that can be put onto one master curve by scaling the temperature axis with the corresponding $T^*$, above which $R_H$ saturates (the same temperature is denoted as $T_H^*$ in this paper), together with an appropriate scaling and offset for $R_{Hf}(T)$. This master curve does not simply follow $1/T$. Following the suggestion of Hwang et al.[6.2] we scaled all of our $R_{Hf}(T)$ curves onto a single master curve by using independent scaling parameters, $T_H^*$ and $R_H^*$, and an offset $R_H$. Here a functional form $R_H^{\infty} + R_H^* f(T/T_H^*)$ is used, where $f(T/T_H^*)$ is the temperature dependent part of $R_H(T)$. Parameters $T_H^*$ and $R_H^*$ are arbitrary to a constant factor. We chose to define them in the same manner as Hwang et al., i.e. we have used the linear extrapolation of the master curve to 0 K for the definition of $R_H^*$; and the intercept of the high temperature $R_H^{\infty}$ with the linear extrapolation of $R_{Hf}(T)$ from low temperature as the definition of $T_H^*$. We find that $T_H^*$ for the RBA$_2$Cu$_3$O$_y$ compound defined in this manner, gives half the value reported by Hwang et al. for the LSCO compound. In our case, the resulting master curve also does not simply follow $1/T$, see Fig. 6.4.
Figure 6.4  The Hall coefficient rescaled as \((R_H(T) - R_H^\infty)/R_H^*\) vs \(T/T_H^*\). The scaling was done in a manner similar to Ref. 2. This master curve seems to follow \(e^{-1.31T/T_H^*}\). Inset: \(1/R_H^*\), as determined from the fit to the master curve, vs the hole number per copper in the copper oxygen planes determined from \(T_C\) as explained in the text. The line is drawn for \(1/R_H^* = p\).

On the other hand, Ito et al.[6.1] and Wuyts et al [6.9] reported that the resistivity curves for the (underdoped) oxygen deficient YBCO can also be appropriately scaled to a master curve by dividing the temperature by a \(T_0\), i.e. the temperature under which the resistivity deviates from linearity (denoted here as \(T_0^*\)). We are also able to scale our \(\rho(T)\) curves onto a single master curve in this manner. Since \(\rho(T)\) and \(R_H(T)\) are approximately related by Eq.(6.1) in the underdoped regime, this implies that \(R_H(T)\) can also be scaled in the underdoped regime. In Fig 4 we show the curves for all doping, scaled as Hwang et al. did for the overdoped case. In addition, because \(\rho(T)\) and \(R_H(T)\) can be fitted onto each other by Eq. (1), then \(T_\rho^*\) should differ from \(T_H^*\) only by a constant factor in the underdoped regime.
In order to plot $T_H^*$ and $T_p^*$ for both overdoped and underdoped RBa$_2$Cu$_3$O$_y$ samples in one figure, we calculated the number of holes per copper in the copper oxygen plane layers using a general relation for the cuprates given by Tallon [6.12] $T_c/T_c^{max} = 1 - 82.6*(p - 0.16)^2$, based on bond valence sums. $T_c$ is the transition temperature measured for each sample, and $T_c^{max}$ is the highest $T_c$ for the sample (at optimal doping, $p = \text{holes}/[\text{Cu-O}_2] = 0.16$). $T_c^{max}$ is chosen as 91.5 K for the YBCO before and after annealing in reduced oxygen pressure. For the Ca-doped SBCO samples, however, we have chosen the respective maximum $T_c$ reached for each composition during successive low oxygen pressure anneals.

We plot $T_p^*$ and $T_H^*$ vs the number of holes per copper in the copper oxygen plane layers $p$ in Figure 6.5. The value of $T_p^*$ has a relatively large uncertainty ($\Delta T_p^* \sim 50$ K) due to the slight curvature in all our $\rho(T)$ curves in the temperature range of our measurement. Both characteristic temperatures decrease with hole concentration and scale with each other well in the underdoped regime. The actual value of $T_H^*$ depends on the manner in which it is defined from the master curve. We have used the same definition as Hwang et al.

$R_{H}(T)$ can be divided into two regions, above and below $T_H^*$. At low temperature ($T_c < T < T_H^*$), the scaling factor $R_{H}^*$ determines the doping dependence of the Hall coefficient. In the high temperature limit, however, $R_H$ sets the value for the Hall coefficient. Both $R_{H}^*$ and $R_H$ decrease with doping. It is tempting to interpret the $R_{H}^*$ as the 'effective' Hall coefficient of the strongly correlated system since $1/R_{H}^*$ follows the hole doping, $p$, rather well; see inset of Fig. 6.4. In fact, the vertical shift between $1/R_{H}^*$ and $p$ may be due to localized holes at low doping. At high doping, we tentatively assign the increase in the Hall number to a contribution from the free carriers in the chains. $T_H^*$ and $T_p^*$ may be related to the spin-gap as suggested by Ito et al [6.1]. In the limit $T \gg T_H^*$, one gradually recovers the usual Fermi-liquid behavior. For the strongly doped samples this is further manifested by a curvature in the resistivity, see Fig. 6.3b, which approaches the $T^2$ behavior predicted for a Fermi liquid.
6.4 Conclusions

In conclusion, we have found that the Hall coefficient of RBa$_2$Cu$_3$O$_y$ films can be scaled onto a single master curve for all doping levels, but that the resistivity scales only in the underdoped regime. The scaling factor for the Hall coefficient is closely related to the actual hole doping of the copper oxygen plane layers. For strongly doped samples, the data show a clear sign of saturation of the Hall coefficient at high temperature, as well as Fermi-liquid like behavior for the resistivity.

We would like to thank Leo Lander, Kitty van Dijk, and Huub Appelboom for assistance. This work is supported in part by FOM and NOP.

![Figure 6.5 Characteristic temperatures $T_H^*$ (full circles) and $T_p^*$ (open circles) derived from the Hall coefficient and resistivity data, respectively.](image-url)
References


[6.8] Even if for the optimally doped sample $\rho(T)$ does extrapolate to 0 at 0K, that may not be the case for the samples away from optimal doping.


Chapter 7  Search for deviations of time-reversal symmetry in YBa$_2$Cu$_3$O$_{7-\delta}$ using transport measurements

H.P. Assink, N.Y. Chen, H.U. Habermeier*, D. van der Marel, P. Hadley
and J.E. Mooij.

*Delft University of Technology, Faculty of Applied Physics,
Lorentzweg 1, 2628 CJ Delft, The Netherlands

Abstract

One of the observable consequences of the possible breaking Time-reversal symmetry in high-$T_c$ superconductors, as is predicted from anyon models, is anomalous transport property similar to e.g. a Hall conductance. For example, an off-diagonal component in the resistivity tensor would exist in the absence of an external magnetic field. We try to reduce possible cancellation effects due to domain formation, by using thin films with a lithographically defined sample areas of few square microns. The breaking of time-reversal symmetry corresponds to an 'effective' magnetic field, which can be determined by calibrating the zero field off-diagonal resistivity with respect to the Hall voltage in an externally applied magnetic field. Our first experiments indicated that the 'effective' internal field due to time-reversal symmetry breaking is either absent or smaller than 75 Gauss.
7.1 Introduction

If the anyon model [7.1] is valid for high-$T_c$ cuprate superconductors, it is expected that the CuO$_2$ plane layers have an intrinsic orbital magnetic moment perpendicular to these layers [7.2]. If the coupling between the layers is ferromagnetic, there should be a number of observable bulk effects, including anomalous transport properties analogous to a Hall-conductance, which would occur even in the absence of a magnetic field, as indicated by Halperin et al. In the same paper Halperin argues that the apparently unusual properties of the copper-oxide material above $T_c$ suggests that the time-reversal symmetry, $T$, is still present above $T_c$. Indeed, effects of broken $T$ persist above the superconducting transition in the simplest model of weakly interacting anyons.

As from a phenomenological point of view the anomalous properties of a two dimensional system with spontaneously broken $T$ symmetry are similar to the properties of a normal material in an externally applied magnetic field, it seems worthwhile to investigate experimentally the off-diagonal resistivity in the absence of such a field. Usually the Hall voltage is determined by measuring the transverse resistance of two contacts (Hall contacts) connected to opposite sides of a current carrying strip. As it is experimentally difficult to have a perfect alignment of the Hall contacts, one usually finds a non-vanishing voltage over these contacts even in zero magnetic field $H = 0$ due to the presence of a finite longitudinal resistance. It is therefore common experimental practice to repeat the same measurement at a number of different magnetic field values, e.g. by repeating the same measurement at a field $H_{ext}$ and -$H_{ext}$ so that the Hall voltage can be separated from the (assumingly field independent) longitudinal resistance. Obviously in our present investigation, the internal 'effective' field can not be tuned in this way. However, as has been shown by van der Pauw [7.3], the Hall resistance of a singly connected two dimensional sheet can also be determined by measuring the four terminal resistances $R(1,2; 3,4)$ and $R(3,4; 1,2)$ without changing the applied field. Here $R(1,2; 3,4) = (V(3) - V(4))/I(1,2)$ refers to a configuration in which the current $I$ flows from contact 1 to contact 2, and the voltage $V$ is measured between contacts 3 and 4. The latter two contacts have to be on opposite sides of the curve connecting contacts 1 and 2. For a sheet of
homogenous thickness, with sufficiently small contacts connected to the periphery, the off-diagonal sheet resistance $R_{xy}$ then follows from

$$R_{xy} = (R(1,2; 3,4) - R(3,4; 1,2))/2 \quad (7.1)$$

Gijs et al. [7.4] used this method on thin films with a thickness of 100 nm, and with a sample area of about 30 mm$^2$ and found no significant deviation from the Onsager-Casimir symmetry relation [7.5], within a accuracy of 0.02%. As the effect of $T$-breaking may be masked by the presence of many small domains with random orientations, a more definite experimental statement about the presence of $T$-breaking can be given when thinner samples are used with a smaller area.

7.2 Experimental set-up

The measurement were done on a YBCO thin film grown on substrate. The advantage of choosing LaAlO$_3$ as substrate material is that there is relatively a smaller amount of grain boundaries in YBCO films grown on this type of substrates. In this way, we hope to reduce the extrinsic effects in the measurement induced by grain boundaries. The sample thickness was about 254 nm. It was prepared with the pulsed laser deposition technique. The substrate temperature during growth was 775 °C with an oxygen pressure of 1 mbar. The sample was subsequently cooled to room temperature in 40 minutes in 1000 mbar pure oxygen. X-ray diffraction measurement showed only (00$l$)YBCO reflection lines, indicating that the film is $c$-axis oriented with the $a$-$b$ plane along the substrate surface. A microscopic pattern was lithographically defined by means of wet-chemical etching using hydrochloric acid in an aqueous solution. The sample geometry is sketched in figure 7.1. It consists of a crossing of two 6 μm wide lines connected to contact pads. The contact pads were made by evaporating gold onto the YBCO film through a metal mask. Electrical contact to the sample is made by bonding Au wires onto these contact pads.
The resistivity of the sample was measured as a function of temperature using the van der Pauw method [7.3], i.e. by determining \( R(1,3; 2,4) \) and \( R(3,2; 4,1) \) and inverting numerically the following equation

\[
\exp(-\pi R(1,3;2,4)/R_{xx}) + \exp(-\pi R(3,2;4,1)/R_{xy}) = 1
\] (7.2)

The resistivity of the sample varies linearly with temperature in the normal state, see figure 7.2 (inset). The sample become superconducting at \( T_c=89.5 \) K (zero resistance). The superconducting transition width is about 1 K.

High precision measurement of the off-diagonal component \( R_{xy} \) of the 4-terminal resistivity tensor were performed using an AC- technique with a frequency of about 100 Hz. A highly stable current source was used to provide an excitation current of 100 mA. The stability of the current was not effected by the switching of current and voltage contacts, which was necessary for the van der Pauw measuring technique. The signal is amplified by a two phase Lock-In amplifier and subsequently fed into a personal computer. The effect of stray capacitance of the measuring cables was eliminated by means of a numerical calculation. This removes possible effects due to differences in the complex impedance of contacts, sample and stray capacitance for the two current-voltage configuration \( R(1,2; 3,4) \) and \( R(3,4; 1,2) \). Effects due to a

![Figure 7.1. The sample layout](image)
non-perfect common-mode rejection of the signal amplifier were removed by interchanging the two voltage leads, which inverts the differential voltage but leaves the common-mode voltage unaffected. After measuring approximately 90 minutes for $R(1,2; 3,4)$ and $R(3,4; 1,2)$, an accuracy was obtained of 42 μΩ. This corresponds to 0.0004% of the sheet resistance $R_{\text{xx}}$ of 10 Ω. The sample is cooled to 92 K in a flow cryostat. After stabilizing the temperature for more than 8 hours the temperature fluctuation of the sample was less than 0.1 K.

![Graph](image)

*Figure 7.2 Resistivity as a function of temperature measured with the van der Pauw method. The inset shows the total curves, up to room temperature.*

### 7.3 Results and discussion

We show $R(1,2; 3,4)$ and $R(3,4; 1,2)$ versus time in figure 7.3. The first 22 points (left in the figure) were measured without a external magnetic field. The difference in magnitude between $R(1,2; 3,4)$ and $R(3,4; 1,2)$ was very small. This means that the Hall-effect which would have been caused by the 'effective' magnetic field due to T-breaking in the material is very small also. An external magnetic field of 0.6 Tesla was switched on subsequently at the 30-th minute of the measurement. The direction of
the field is perpendicular to the sample surface. A clear Hall effect can be seen from the difference of \( R(1,2 ; 3,4) \) and \( R(3,4 ; 1,2) \). At the 50-th minute of measurement, the external field was switched off, again. We found:

\[
R(1,2 ; 3,4) - R(3,4 ; 1,2) = 10 \text{ m} \Omega
\]  

(7.4)

From the above results, we calculated directly that the measured effect \( (H = 0) \) corresponds to an effective magnetic field of \( 31 \pm 25 \) Gauss, the error being the 95% confidence range. This is of the order of the remnant magnetic field of our magnet (less than 80 Gauss). We can therefore indicate an upper limit of about 75 Gauss on the 'effective' field due to absence of time reversal symmetry as predicted by the anyon model.

![Graph showing the behavior of four-terminal Hall-resistance](image)

**Figure 7.3.** Four terminal Hall-resistance \( R(1,2 ; 3,4) \) and \( R(3,4 ; 1,2) \) as functions of time. They are measured mostly without an external magnetic field. Between the 30-th minute and the 50-th minute if the measurement, an magnetic field of 0.6 Tesla is switched on. The direction of the field is perpendicular to the substrate surface. The inset shows the drift of the measured points without a magnetic field. The two least-square fits through these points were calculated to have the same slope.
One must keep in mind here, that there are still a large number of differently oriented domains that contribute to the measured results. If one for example assumes an in-plane coherence length for the domain structure of 100 nm and 1 nm in the c-direction, one would have roughly a million domains contributing to the sample we used. If all domains are statistically frozen in random positions the 'effective' internal field is reduced by a factor of 1000. For this particular choice of values for the typical domain size, our experimental results could still be compatible with an 'internal' effective field of (at most) 7.5 Tesla. To make a more definite statement on the existence of the 'internal' magnetic field due to time-reversal symmetry breaking it is therefore important that on the one hand reliable theoretical estimates for the internal field and the domain size are given, and on the other hand smaller and thinner samples are used for the experiment.

References

*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, Stuttgart 80, Federal Republic of Germany


Appendix A  \ Material removal rates by laser

We give here a survey of laser ablated materials. They are listed and divided into four sections: metals, organic polymers, semiconductors and miscellaneous inorganics.

One must consider the following parameters in order to get an idea whether the laser ablation can be used for the processing of an certain material:

1) Matching of laser $\lambda$ to a spectral region of strong absorption in the solid.
2) Reflectivity of the material.
3) Thermal diffusion length in the material.
4) Thickness of material (for thin layers, what type of substrate).
5) Laser pulse parameters: fluence, duration.
6) Chemical reactivity of material with gases or liquids
7) Photoreactivity of etchant gases or liquid at the laser wavelength $\lambda$.

The material removed per laser pulse (regardless of pulse duration) is defined as the volume of substance removed from the target. The unit of ablation rate in the following tables is $10^{-8}$cm$^3$/pulse = 1Å/pulse.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda$ (nm)</th>
<th>Laser fluence (J/cm$^2$)</th>
<th>Ablation rate (Å/pulse)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>308</td>
<td>0.2</td>
<td>1200</td>
<td>[A.1]</td>
</tr>
<tr>
<td>Au</td>
<td>308</td>
<td>0.03</td>
<td>500</td>
<td>[A.2]</td>
</tr>
<tr>
<td>Cu</td>
<td>308</td>
<td>0.08</td>
<td>1000</td>
<td>[A.1]</td>
</tr>
</tbody>
</table>
Table A.2. Ablation rate for organic polymers. The minimum laser fluence for the ablation process to take place (threshold) is also given.

<table>
<thead>
<tr>
<th>Material</th>
<th>λ (nm)</th>
<th>Threshold (J/cm²)</th>
<th>Laser fluence (J/cm²)</th>
<th>Ablation rate (Å/pulse)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymide</td>
<td>248</td>
<td>0.03</td>
<td>0.15</td>
<td>1200</td>
<td>[A.2]</td>
</tr>
<tr>
<td>Polymide</td>
<td>308</td>
<td>0.07</td>
<td>0.15</td>
<td>800</td>
<td>[A.2]</td>
</tr>
<tr>
<td>Polymide</td>
<td>351</td>
<td>0.12</td>
<td>0.15</td>
<td>300</td>
<td>[A.2]</td>
</tr>
<tr>
<td>PMMA</td>
<td>193</td>
<td>0.01</td>
<td>0.2</td>
<td>3000</td>
<td>[A.3]</td>
</tr>
<tr>
<td>PMMA</td>
<td>248</td>
<td>0.5</td>
<td>1</td>
<td>10⁴</td>
<td>[A.4]</td>
</tr>
<tr>
<td>Nitrocel.</td>
<td>193</td>
<td>0.02</td>
<td>0.3</td>
<td>4000</td>
<td>[A.5]</td>
</tr>
<tr>
<td>Polycarb.</td>
<td>248</td>
<td>0.03</td>
<td>0.1</td>
<td>400</td>
<td>[A.6]</td>
</tr>
<tr>
<td>Polystyr.</td>
<td>248</td>
<td>0.03</td>
<td>0.1</td>
<td>150</td>
<td>[A.6]</td>
</tr>
</tbody>
</table>

Table A.3. Ablation rate for semiconductors

<table>
<thead>
<tr>
<th>Material</th>
<th>λ (nm)</th>
<th>Laser fluence (J/cm²)</th>
<th>Ablation rate (Å/pulse)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Si</td>
<td>248</td>
<td>2</td>
<td>2000</td>
<td>[A.7]</td>
</tr>
<tr>
<td>GaAs</td>
<td>248</td>
<td>0.2</td>
<td>5</td>
<td>[A.8]</td>
</tr>
<tr>
<td>GaAs</td>
<td>351</td>
<td>0.2</td>
<td>2</td>
<td>[A.8]</td>
</tr>
</tbody>
</table>

Table A.4. Ablation rate for miscellaneous inorganics

<table>
<thead>
<tr>
<th>Material</th>
<th>λ (nm)</th>
<th>Laser fluence (J/cm²)</th>
<th>Ablation rate (Å/pulse)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrex</td>
<td>153</td>
<td>2</td>
<td>1000</td>
<td>[A.9]</td>
</tr>
<tr>
<td>SiO₂</td>
<td>248</td>
<td>0.6</td>
<td>6000</td>
<td>[A.10]</td>
</tr>
<tr>
<td>Selenium</td>
<td>248</td>
<td>0.1</td>
<td>50</td>
<td>[A.11]</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>308</td>
<td>1.5</td>
<td>1000</td>
<td>[A.12]</td>
</tr>
<tr>
<td>YBCO</td>
<td>248</td>
<td>1</td>
<td>1000</td>
<td>[A.13]</td>
</tr>
</tbody>
</table>

References


Appendix B  Target synthesis

Here I present the different steps we used to make our on composition '123' YBCO target. First of all, ultra fine powder with correct ratio of metal constituents were made using citrate synthesis and pyrolysis technique [2.13]. The powder became superconducting after calcination at 920 °C in flowing oxygen. We have made YBCO target on both Y:Ba:Cu=1:2:3 and 2:4:8 compositions. I will not discuss the making of '248' YBCO target, because the procedures were basically the same as for the '123' YBCO target. The only difference is that different amount of each of the starting materials should be chosen correspondingly to get the desired ratio of the constituents. We performed X-ray diffraction measurements on pressed and sintered pellets to get information about the phase purity of the resulted YBCO powder.

We started with dissolving 19.74 g BaCO₃ powder in 30 ml nitric acid (65%) and 40 ml Q-water in a 100 ml breaker. A clear solution can be obtained after heating the breaker to 60 °C on a heater plate. At the same time, in two other breakers, 5.65 g Y₂O₃ and 11.93 g CuO were solved in 20 ml nitric acid (65%) each (note that CuO can only be solved slightly in 20 ml. The majority of the powder stays on the bottom of the breaker. The mixture of solution and powder has black colour). After putting the three 'solutions' into one single breaker, we neutralised the solution with NH₄OH (25% solution). During the neutralisation, precipitate in the liquid disappeared gradually (the unsolved CuO powders also disappears!). The colour of the liquid turned blue and became increasingly darker when more NH₄OH is added to the solution. We stopped adding NH₄OH to the solution after its pH value reaches 6.8.

We pour 100 ml of the solution in a Pyrex 2 litre breaker each time and heated it up on a heater plate. The temperature of the heater plate is set and kept at 150 °C during the whole heating process. During the heating a viscous mass started to form on the surface and gradually extended to the whole volume of the liquid. This was followed by a large swelling of the viscous mass and spontaneous combustion (the top of the flame can reach as high as 1 meter). The resultant black colour (slightly brown) foam filled the whole breaker, a large amount of flakes even flied over the whole working space. Each of the heating runs, from placing the breaker onto the
heater plate to the spontaneous combustion of the viscous mass, took at least 45 minutes.

We ground the resultant foam (consists of particles with 100 nm diameter) into powder in an Al₂O₃ grinder. The powder was then placed into an oven with flowing oxygen. The oven was heated up to 920 °C in 4 hours. After annealing the powder at this temperature for more 12 hours, we slowly cooled the oven to room temperature in 24 hours. The powder retreated from the oven was completely black. The brown colour tint in the powder observable before the annealing disappeared completely. We pressed 3 to 5 mm thick pellets with 15 mm diameter in a stainless steel form, and reannealed the pellets in flowing oxygen at 920 °C for another 12 hours followed by the same slow cooling.

In figure B.1 we show the X-ray diffraction data from one of our target. It is measured with a powder diffractometer using a Cu Kα source. In addition, we also show the expected position of diffraction peaks of the fully oxygenated orthorhombic YBCO. These were calculated from the X-ray wavelength and the YBCO crystal lattice parameters (open square). Except two peaks in the figure (as indicated), each of the other peaks can be attributed to the orthorhombic YBCO crystal.

![Figure B.1. X-ray diffraction data from one of our self made target which has a 1:2:3 composition.](image)

*Figure B.1. X-ray diffraction data from one of our self made target which has a 1:2:3 composition.*
Summary

The subjects in this thesis can be divided in two parts. Part one describes the implementation and applications of a laser deposition system to grow high Tc cuprate superconductor thin films. It consists of the first three chapters (Chapter 1 to Chapter 3). In part two we describe our studies on normal state properties of the YBCO compound. Normal state resistance noise (Chapter 4), the temperature dependencies of the normal state resistivity and the Hall-coefficient (Chapter 5 and 6), and a test for possible deviation from time-reversal symmetry in YBCO (Chapter 7).

**Chapter 1.** A thorough discussion is given about issues such as the crystal structure and the phase stability of the YBa$_2$Cu$_3$O$_{7.8}$ (YBCO) compound.

**Chapter 2.** After optimizing the growth parameters, we were able to produce, on a routine basis, single phase YBCO films with typical $T_c$ of 90 K and a sharp transition ($\Delta T_c < 2$ K). X-ray diffraction and Fourier Transform Infrared measurements showed that the films prepared by this system are highly aligned, with c-axis oriented perpendicular to the substrate surface. By incorporating a multi-target holder in the deposition chamber, targets made of different materials can be ablated in sequence without breaking vacuum. We have also examined the possibilities to grow in situ thin films of the chemically more stable Y$_2$Ba$_4$Cu$_6$O$_y$ using our laser deposition system.

**Chapter 3.** Due to the anisotropic properties of the YBCO compound, for some applications, it is required to have YBCO thin films with their c-axis along the substrate surface. One way to grow this type of films is to use (110) substrates. In most cases, the YBCO film grows with both (103) and (110) orientations. The substrate temperature during deposition is one of the major factors that determines the crystal orientation. In our experiment, effort was made to examine the influence of the initial substrate temperature on the relative amount of (110) and (103) oriented grains. The amount of (103) oriented YBCO is reduced systematically with decreasing substrate temperature. At the lowest deposition temperatures we find only (110) oriented growth.

**Chapter 4.** We have measured the $1/f$ normal state resistance noise at room temperature in laser ablated YBCO thin films of various qualities. After normalising the measured noise using the Hooge formula in a conventional manner, the high
resistivity samples give lower noise levels than the low resistivity films. The lowest noise is 100 times lower than any previously reported for the YBCO compound and is comparable to the lowest noise found in the cuprates. Upon oxygen reduction, noise in the high resistivity films increases monotonically, whereas it decreases in the low resistivity films. Our experiment suggests that the high level of measured noise in YBCO maybe intrinsic to the structure due to conduction along the Cu-O chains. The low noise in the high resistivity films indicates that their chain conductivity is degraded.

Chapter 5. A short overview of the experimental results of the normal-state transport properties of high-Tc superconductors is given. A brief description of the Hubbard model and the Landau Fermi liquid theory is also included. This chapter is meant as an introduction chapter for Chapter 6.

Chapter 6. We have studied the normal state transport properties, i.e., the resistivity $\rho(T)$ and the Hall-coefficient $R_H(T)$ on two sets of samples of RBa$_2$Cu$_3$O$_{7-\delta}$ compounds (R=Y, Sm) away from the optimal doping. In the overdoped regime, $R_H(T)$ obtained from the Ca-doped SmBa$_2$Cu$_3$O$_{7-\delta}$ shows a saturation at high temperature. While $R_H(T)$ decreases with $T$ at low temperature, it becomes temperature independent when the temperature exceeds a certain value $T_H^*$. This characteristic $T_H^*$ decreases with doping, and is only visible in our experimental temperature range when the samples are sufficiently doped. By assuming a universal functional form for all doping levels, the temperature dependence of the Hall coefficient can be scaled. Another characteristic temperature $T_\rho^*$ can been seen from the resistivity data in the underdoped regime, obtained from the oxygen deficient YBCO samples. Above $T_\rho^*$, $\rho(T)$ increases almost linearly with $T$, whereas below, it deviates from the linear behavior. We discuss the relationship between the two characteristic temperatures $T_H^*$ and $T_\rho^*$ for different doping levels. For the underdoped samples, the resistivity is fit well by the relationship $\rho(T)= aR_H(T)T^2 + b$.

Chapter 7. One of the observable consequences of the possible breaking of the time-reversal symmetry in high-Tc superconductors, as is predicted from anyon models, is an anomalous transport property similar to a Hall-conductance. For example, an off-diagonal component in the resistivity tensor would exist in the absence of an external magnetic field. We tried to reduce possible cancellation
effects due to domain formation by using thin films with a lithographically defined sample area of a few square microns. The breaking of time reversal symmetry corresponds to an 'effective' magnetic field, which can be determined by calibrating the zero field off-diagonal resistivity with respect to the Hall resistance in an externally applied magnetic field. Our experiments indicate that the 'effective' internal field due to time reversal symmetry breaking is either absent or smaller than 75 gauss.
Samenvatting

Eigenschappen in de normale toestand en laserdepositie van dunne films van YBa$_2$Cu$_3$O$_7$-d supergeleiders

Bij de in dit proefschrift behandelde onderwerpen kunnen twee delen onderscheiden worden. Deel 1 beschrijft de implementatie en de toepassingen van een laserdepositie system voor het groeien van dunne lagen van hoge-$T_c$ supergeleiders. Het bestaat uit de eerste drie hoofdstukken (Hoofdstuk 1 t/m 3). In het tweede deel beschrijf ik onze studies van de eigenschappen van YBa$_2$Cu$_3$O$_{7.8}$ (YBCO) in de normale toestand: De weerstandstwees (Hoofdstuk 4), de temperatuurafhankelijkheid van de soortelijke weerstand en de Hall-coëfficiënt van dit materiaal (Hoofdstuk 5 en 6) en een test voor het mogelijk ontbreken van tijdsomkeer-symmetrie in YBCO.

Hoofdstuk 1. Een discussie over onder meer de kristalstructuur en de fase-stabiliteit van YBa$_2$Cu$_3$O$_{7.8}$.

Hoofdstuk 2. Na het optimaliseren van de groeiparameters waren wij in staat, op een routinebasis, dunne films van enkel-fase YBCO te vervaardigen met een $T_c$ van ca. 90 K ($\Delta < 2K$). Röntgen diffractie en Fourier transform infrarood meting tonen aan dat de films goed georiënteerd zijn met de c-as loodrecht op de substraatoppervlakken. Door een multi-target houder in de depositiekamer in te bouwen is het mogelijk om targets van verschillende materialen achter elkaar te ableren. Wij hebben bovendien de mogelijkheden bestudeerd om het chemisch stabielere Y$_2$Ba$_4$Cu$_8$O$_{16}$ in-situ te groeien.

Hoofdstuk 3. Vanwege de anisotropische eigenschappen van de YBCO is het voor sommige toepassingen aantrekkelijker om dunne films te vervaardigen met de c-as langs het substraatoppervlak. Een van de manieren om dit type films te vervaardigen maakt gebruik van (110) georiënteerde substraten. In de meeste gevallen worden er in de films naast de (110) georiënteerde groei, ook kristallen met (103) oriëntatie gevonden. De substraattemperatuur tijdens de filmgroei is één van de belangrijkste factoren die de kristaloriëntatie bepalen. Tijdens ons experiment hebben wij de invloed van de substraattemperatuur op de relatieve hoeveelheden van (110) en (103) georiënteerde groei in de film bestudeerd. De hoeveelheid (103) georiënteerd YBCO is op een systematische wijze verminderd door middel van temperatuurverlaging. In de
films die gegroeid zijn op de laagste temperaturen kunnen wij alleen (110) georiënteerde YBCO waarnemen.

**Hoofdstuk 4.** Wij hebben de 1/f-weerstandsruis in lasergeableerde YBCO films van verschillende kwaliteit bij kamertemperatuur gemeten. Na het normaliseren van de weerstandsruis op een conventionele wijze met de formule van Hooge, blijkt dat de samples met een grotere soortelijke weerstand een lager ruisniveau hebben dan de samples met een kleinere soortelijke weerstand. De laagste genormaliseerde ruis van onze samples is 100 maal lager dan alle tot nu toe gemeten weerstandsruis in YBCO en is vergelijkbaar met het laagste ruisniveau dat ooit in de cupraat hoge-T_c supergeleiders is gemeten. Na het verminderen van het zuurstofgehalte in de films stijgt het ruisniveau in samples met een grotere soortelijke weerstand, terwijl een daling van ruisniveau is te zien in samples met een kleinere soortelijke weerstand. Ons onderzoek toont aan dat het algemeen waargenomen hoge ruisniveau in YBCO een intrinsiek verschijnsel kan zijn als gevolg van de elektrische geleiding langs de Cu-O ketens. Het lagere ruisniveau in de films met een grotere soortelijke weerstand zou kunnen wijzen op een gedegradeerde geleiding langs de ketens in die films.

**Hoofdstuk 5.** Een kort overzicht wordt gepresenteerd van experimentele resultaten van de transporteigenschappen van hoge-T_c supergeleiders in de normale toestand. Tevens wordt in dit hoofdstuk een korte beschrijving gegeven van het Hubbard model en de Landau Fermi liquid theorie. Dit hoofdstuk is bedoeld als een inleiding voor Hoofdstuk 6.

**Hoofdstuk 6.** Wij hebben de soortelijke weerstand \( \rho(T) \) en de Hall coëfficiënt \( R_H(T) \), in de normale toestand van twee series \( \text{RBA}_2\text{Cu}_3\text{O}_{\gamma_\delta} \) (R = Y of Sm) met verschillende doteringen bestudeerd. In het overgedoeterde regime, gemeten aan Ca-gedoeteerde \( \text{SmBA}_2\text{Cu}_3\text{O}_{\gamma_\delta} \) films, vertoont \( R_H(T) \) een verzadiging bij hoge temperatuur. Terwijl \( R_H(T) \) daalt met toenemende temperatuur in het lage-temperatuur gebied, is hij temperatuuronafhankelijk als de temperatuur een bepaalde waarde \( T_H^* \) overschrijdt. Deze karakteristieke \( T_H^* \) wordt lager naarmate het sample zwaarder gedoteerd wordt en is alleen dan in het meetgebied zichtbaar als het sample met een voldoende percentage met Ca gedoteerd is. Door een universele functionele vorm aan te nemen voor alle doteringen, kan de temperatuuronafhankelijkheid van de Hall-coefficient geschaald worden. Een andere karakteristieke temperatuur \( T_p^* \) is te zien in de zuurstof-deficiente YBCO samples. Bij een temperatuur hoger dan \( T_p^* \) stijgt \( \rho(T) \) nagenoeg lineair met \( T \), terwijl \( \rho(T) \) afwijkt van deze lineariteit bij \( T < T_p^* \). Wij bespreken de relatie tussen de twee karakteristieke temperaturen \( T_H^* \) en \( T_p^* \) voor verschillende dotering. Voor ondergedoetede samples kan de soortelijke weerstand geschreven worden als \( \rho(T) = aR_H(T) T^2 + b \).
Hoofdstuk 7. Een van de waarneembare gevolgen van het ontbreken van de tijdsomkeer-symmetrie in hoge-$T_c$ supergeleiders, zoals voorspeld is op basis van het anyon model, is een anomalie transport eigenschap die vergelijkbaar is met een Hallweerstand. Bijvoorbeeld zal er een niet-diagonale component in de soortelijke weerstand tensor aanwezig zijn, zelfs zonder een uitwendig aangelegd magnetisch veld. Wij trachten het uitdovingseffect als gevolg van domeinvorming te reduceren door lithografisch gedefinieerde samples van enkele μm² te gebruiken. Het onbreken van tijdsomkeer symmetrie komt overeen met een 'effectief' magnetisch veld. Deze kan bepaald worden door de niet-diagonale component van de soortelijke weerstand tensor, gemeten zonder veld, te calibreren t.o.v de Hall-weerstand gemeten in een uitwendig magnetisch veld. Uit onze experiment blijkt dat het 'effectieve' magnetische veld als gevolg van het ontbreken van tijdsomkeer-symmetrie niet aanwezig is of kleiner moet zijn dan 75 gauss.
Curriculum Vitae

Neng-Yu Chen

1962    Geboren op 12 januari te WuHan, China.
1973-1976 HongSan middelbare school, WuHan.
          Afstudeer vakgroep: Delft Centre for Submicron Technoloty (CST).
1990-    Promotie onderzoek aan de Technische Universiteit Delft in de
          vakgroep Vaste Stof/Supergeleiding o. l. v. Prof. dr. ir. J. E. Mooij.