SUPERCONDUCTING THIN FILMS OF YBa$_2$Cu$_3$O$_{7-x}$

Jan Hudner

STOCKHOLM 1993
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ABSTRACT

Thin films of the high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) are of significance in fundamental studies of oxide superconductors and for prospected electronic applications based on superconductors operating at liquid nitrogen temperatures ($T = 77 \, \text{K}$). Synthesis of YBCO thin films is complex and a large part of this thesis has been devoted to the elaboration of various techniques in forming YBCO thin films. A general observation was that synthesis of YBCO films exhibiting high zero-resistivity temperatures ($T_c \geq 88 \, \text{K}$) and elevated critical current densities ($J_c \geq 10^6 \, \text{A/cm}^2$ at 77 K) was possible under widely different conditions of film growth. A YBCO film preparation method based on crystallization of an amorphous $\text{Y-BaF}_2-\text{Cu-O}$ layer at $T = 825-900 \, ^\circ\text{C}$, $p_{O_2} = 10^5 \, \text{Pa}$ was investigated. The $\text{Y-BaF}_2-\text{Cu-O}$ films were deposited by coevaporation of $\text{Y}$, $\text{BaF}_2$ and $\text{Cu}$ in a partial pressure of oxygen $p_{O_2} = 10^{-4} \, \text{Pa}$. It was shown that metal composition in the as-deposited film could be accurately controlled by quadrupole mass spectrometer evaporation rate control. Optimization of post-deposition annealing conditions with respect to time and temperature resulted in superconducting YBCO films with $J_c(77 \, \text{K})$ extending from $4 \times 10^5$ to $10^6 \, \text{A/cm}^2$. The mass spectrometer concept has been extended to in situ growth of YBCO at $700 \, ^\circ\text{C}$, $p_{O_2} = 10^{-3} \, \text{Pa}$ by coevaporation of $\text{Y}$, $\text{Ba}$ and $\text{Cu}$. Film oxygenization was accomplished by exposing the growing film to an oxygen plasma, generated by an atomic oxygen radical beam source. Using this method, c-axis oriented thin films have been obtained exhibiting $J_c(77 \, \text{K})$ up to $6 \times 10^6 \, \text{A/cm}^2$. Finally, YBCO films have been prepared by metalorganic chemical vapor deposition (MOCVD) using tetramethylheptanedionate precursors and growth conditions $T=820 \, ^\circ\text{C}, p_{O_2} = 10^{-2} \, \text{Pa}$. Optimized YBCO films displayed $T_c = 90 \, \text{K}$ and $J_c(77 \, \text{K}) = 3 \times 10^6 \, \text{A/cm}^2$.

For the B«-«-ed method, various substrate materials were investigated. Among perovskite-related substrates with low losses in the high frequency regime, $\text{LaAlO}_3$ was found to yield YBCO films exhibiting the highest quality electrical properties. A study of YBCO film interaction with sapphire substrates was performed. A model, based on elemental redistribution and impurity phase formation, was proposed in order to explain YBCO growth on sapphire. It was suggested that the YBCO film on sapphire consists of weakly coupled superconducting grains.

Compositional effects of $\text{Y}$, $\text{Ba}$ and $\text{Cu}$ for MOCVD-YBCO films were examined with respect to morphology, structure, resistivity, ac susceptibility and $J_c(T)$. High $T_c$'s and $J_c$'s were observed for an anomalous large compositional range of $\text{Cu}$ in off-compositional YBCO films. This was shown to be related to the formation of Cu-rich precipitates embedded within a c-axis oriented stoichiometric YBCO film matrix.

Thermal critical current behaviour at zero field in thin films of YBCO fabricated by various methods has been studied by three techniques: transport measurements on patterned microbridges, dc magnetization hysteresis loops using the Bean model and non-linear ac susceptibility analysis. Absolute critical current values obtained from the two former techniques when measured on the same YBCO film were observed to differ about a factor of two. The feasibility of non-linear ac susceptibility analysis in precise determination of the critical current dependence close to $T_c$ was demonstrated.

Key words: $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, YBCO, thin film, coevaporation, ex situ, in situ, post-deposition anneal, partial pressure of oxygen, $\text{BaF}_2$, quadrupole mass spectrometer, evaporation rate control, atomic oxygen, metalorganic chemical vapor deposition, tetramethylheptanedionate, substrate, $\text{LaAlO}_3$, sapphire, redistribution, impurity phase, film composition, critical current density, Bean model, ac susceptibility.
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ROYAL INSTITUTE OF TECHNOLOGY
SOLID STATE ELECTRONICS
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to my parents
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Thin films of the high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7\_x$ (YBCO) are of significance in fundamental studies of oxide superconductors and for prospected electronic applications based on superconductors operating at liquid nitrogen temperatures ($T = 77$ K). Synthesis of YBCO thin films is complex and a large part of this thesis has been devoted to the elaboration of various techniques in forming YBCO thin films. A general observation was that synthesis of YBCO films exhibiting high zero-resistivity temperatures ($T_c \geq 88$ K) and elevated critical current densities ($J_c \geq 10^6$ A/cm$^2$ at 77 K) was possible under widely different conditions of film growth. A YBCO film preparation method based on crystallization of an amorphous $\text{YBaF}_2\text{CuO}_y$ layer at $T = 825-900$ °C, $P_{O_2} = 10^9$ Pa was investigated. The $\text{YBaF}_2\text{CuO}_y$ films were deposited by coevaporation of $\text{Y}$, $\text{BaF}_2$ and $\text{Cu}$ in a partial pressure of oxygen $P_{O_2} = 10^4$ Pa. It was shown that metal composition in the as-deposited film could be accurately controlled by quadrupole mass spectrometer evaporation rate control. Optimization of post-deposition annealing conditions with respect to time and temperature resulted in superconducting YBCO films with $J_c(77$ K) extending from $4 \times 10^5$ to $10^6$ A/cm$^2$. The mass spectrometer concept has been extended to in situ growth of YBCO at 700 °C, $P_{O_2} = 10^{-3}$ Pa by coevaporation of $\text{Y}$, $\text{Ba}$ and $\text{Cu}$. Film oxygenization was accomplished by exposing the growing film to an oxygen plasma, generated by an atomic oxygen radical beam source. Using this method, $c$-axis oriented thin films have been obtained exhibiting $J_c(77$ K) up to $6 \times 10^6$ A/cm$^2$. Finally, YBCO films have been prepared by metalorganic chemical vapor deposition (MOCVD) using tetramethylpentanezionate precursors and growth conditions $T = 820$ °C, $P_{O_2} = 10^2$ Pa. Optimized YBCO films displayed $T_c = 90$ K and $J_c(77$ K) = $3 \times 10^6$ A/cm$^2$.

For the $\text{BaF}_2$-based method, various substrate materials were investigated. Among perovskite-related substrates with low losses in the high frequency regime, $\text{LaAlO}_3$ was found to yield YBCO films exhibiting the highest quality electrical properties. A study of YBCO film interaction with sapphire substrates was performed. A model, based on elemental redistribution and impurity phase formation, was proposed in order to explain YBCO growth on sapphire. It was suggested that the YBCO film on sapphire consists of weakly coupled superconducting grains.

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APPENDED PAPERS
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The author has also contributed to the following papers (not included in the thesis):


PREFACE

This thesis presents results from thin film research of the high temperature superconductor (HTS) YBa$_2$Cu$_3$O$_{7-x}$. When the experimental work for this thesis was initiated in late 1987, the YBa$_2$Cu$_3$O$_{7-x}$ compound had not been known for long time and corresponding thin film synthesis was on a rather primitive level. The field has thereafter developed rapidly and the large progress made in epitaxial growth of YBa$_2$Cu$_3$O$_{7-x}$ layers now constitute a significant achievement in the history of thin film technology. This thesis can be regarded as one historical example of how to gain the mastery of advanced thin film growth of HTS.

The thesis comprises nine papers, being previously published or submitted. The papers demonstrate procedures and optimization schemes elaborated for various thin film techniques and also some in-depth studies concerning physical film properties. In order to fully justify the general nature of the title, the thesis includes a survey of the important thin film techniques for YBa$_2$Cu$_3$O$_{7-x}$ existing today. Such an approach also provides the most efficient way of introducing the new reader to the field rather than referring to a large number of scattered publications. By integrating my own results in the survey, I will show that high quality YBa$_2$Cu$_3$O$_{7-x}$ films can be synthesized under widely different growth conditions. On the other hand, the in-depth studies of substrates, cation stoichiometry and critical currents are gathered in the appended papers and will therefore only be summarized briefly in the thesis part.

The experimental work in this thesis have been carried out at four different laboratories in Sweden and in France. I would like to express my sincere gratitude to all people I have been collaborated with during these years. First of all, I am indebted to Prof. Sture Petersson at the department of Solid State Electronics for creating the opportunities for this thesis. My supervisor Dr. Håkan Ohlsén is greatly acknowledged for a fruitful collaboration. I also highly appreciate discussions with Drs. Mikael Östling and Lars Stolt. Also Mikael Östling together with Nils Lundberg have provided a reliable source of RBS analyses which have constituted an important part of this work. Timo Söderqvist and Erik Rahkolla have always been helpful in solving technical problems in the laboratory. Thank you all others at the department of Solid State Electronics for creating a pleasant working environment.

Numerous magnetical and electrical measurements have been carried out at the Solid State Physics group at Uppsala university and this collaboration is greatly acknowledged. Special thanks to Drs. Per. Norling, Peter Svedlindh, Per Nordblad and Lazslo Kiss. In addition, Mikael Ottosson at Department of Inorganic Chemistry, Uppsala university, is acknowledged for XRD analyses.
I would like to thank Dr. Olivier Thomas for giving me the opportunity to work with metalorganic chemical vapor deposition (MOCVD) of YBa$_2$Cu$_3$O$_{7-x}$ at Institut National Polytechnique de Grenoble. Also I have benefited a lot from Oliviers professional guidance. Thanks are also due to Drs. François Weiss, J.-P. Senateur, Roland Madar, Daniel Boursier, Patrick Chaudouet and Jochen Fick. A special thank to Eric Mossang for all struggling in the MOCVD lab.

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Jan Hudner
1. INTRODUCTION

Superconducting films have for a long time represented a significant field in condensed-matter physics and thin film technology. In experimental research, superconducting films are attractive because they can be prepared in a way which is difficult or impossible to accomplish in the pure bulk material. One example is the fabrication of new material structures, another is the synthesis of specimens with dimensions of the same order as fundamental superconducting parameters. In the development of small-scale electronic applications based on superconductors, superconducting films are of utmost importance. Such films must fulfil high requirements regarding material and electrical properties.

The core of this thesis concerns thin films of the high temperature superconductor \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \). This compound, first reported in 1987, was the first material discovered exhibiting superconductivity above the boiling point of liquid nitrogen. The discovery stands for a breakthrough in superconductivity and was immediately followed by intense activities worldwide aiming for the understanding of the physics of the new superconductor and exploring potential applications. Thin film research has come to play a crucial role in preparation and understanding of the \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) compound and this thesis represents such an effort in the field.

Growing thin films of \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) presents great challenges and the thesis discusses various techniques for preparation of high quality \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) layers. Film quality must be evaluated by a broad range of analytical tools regarding material, structural, electrical and magnetical properties. The thesis intends to give a picture of the physical behaviour of \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) thin films prepared by various techniques. Such studies may yield information about the complicated correlations between superconducting and material properties, the latter directly related to film preparation.

A brief background to the field will be given in chapter 2. Chapter 3 is devoted to thin film growth and the important methods existing today are reviewed. In-depth studies of selected film properties are presented separately in chapter 4, 5 and 6. In chapter 4, various substrates for \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) thin films are discussed. While chapter 5 deals with material properties of \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) (film stoichiometry), chapter 6 treats electrical and magnetical measurements (critical currents). The results are discussed in a technological perspective.
2. BACKGROUND

The background provides a brief introduction to high temperature superconductors and superconducting films. After a short historical introduction, a survey is given of the basic properties of YBa$_2$Cu$_3$O$_{7-x}$. Although electronic applications are not the primary scope of this thesis, they constitute an important driving force for the development of YBa$_2$Cu$_3$O$_{7-x}$ film synthesis and is therefore treated in a separate paragraph. For the basic concepts in superconductivity, the reader is referred to M. Tinkham "Introduction to Superconductivity". For a more extensive review of high temperature superconductors, see e.g. the three volume treatise "Physical Properties of High-Temperature Superconductors" edited by D.M. Ginsberg.

2.1. Traditional superconductors

Superconductivity is a quantum phenomenon which exists below a transition temperature $T_c$ characteristic for the material. The superconducting state gives rise to some remarkable effects observable on a macroscopic scale in the material such as zero dc resistance and exclusion of a magnetic field. Superconductivity was first observed by Kamerlingh Onnes in 1911 when measuring the resistance of mercury at low temperatures. The $T_c$ of mercury was determined to be 4.2 K. Since then, an essential part in the field of superconductivity has been the search for new materials with larger critical temperatures. The maximum $T_c$ among the elements was found 1930 in Nb ($T_c$=9.2 K). An important step was taken when binary alloys and compounds were demonstrated to possess even higher critical transition temperatures. This discovery was reported 1932 for NbO ($T_c$=11 K) followed by NbN ($T_c$=15 K) nine years later. During a long period, Nb remained the favoured base material in search of high critical transition temperatures. In particular, the cubic A15 structures, e.g. Nb$_3$Sn (year of discovery 1960 and a $T_c$=18 K) dominated the scene for many years and were also the materials prospected for applications in high-field superconducting magnets. Nb$_3$Ge, reported on 1973, was for a long time the record-holder with a $T_c$ of 23 K. It is noteworthy that in spite of tremendous progress made meanwhile in theory for superconductors, the search for new superconducting materials was (and still is) more governed on an empirical than theoretical basis.

2.2. High temperature superconductors

In 1986, a new direction was taken in the search for superconducting materials showing high transition temperatures. At that time, Bednorz and Müller reported on a
superconducting transition starting at about 30 K for the oxide system La-Ba-Cu-O.\(^1\) Even though oxide superconductors had been known for a long time before 1986, e.g. BaPb\(_{1-x}\)Bi\(_x\)O\(_3\) with a maximum \(T_c\) of 11.2 K (year of discovery 1975), the observation was totally unexpected because low-carrier density systems such as oxides were generally regarded as very poor candidates for \(T_c\)'s above 25 K. The Bednorz-Müller breakthrough initiated the immediate search for neighbouring materials exhibiting higher \(T_c\)'s. This resulted in the finding of a whole family of multielemental copperoxide based compounds showing similar physical and structural properties. The new materials are referred to as high temperature superconductors (HTS). Today several hundred of HTS are known and several exhibit superconductivity above the boiling point of liquid nitrogen (77 K), the most well-known being YBa\(_2\)Cu\(_3\)O\(_{7-x}\), Bi\(_2Sr_2Ca_2Cu_3O_{10}\) and Tl\(_2Ba_2Ca_2Cu_3O_{10}\), exhibiting zero-resistivity at 93 K, 110 K and 125 K, respectively. Of the HTS listed, YBa\(_2\)Cu\(_3\)O\(_{7-x}\) is by far the most studied. These HTS materials are all hole superconductors with a common parent compound, the antiferromagnetic insulator La\(_2\)CuO\(_4\). In 1989, a new class of copperoxide based HTS was reported showing electron charge carrier transport. In this case, the common parent compound is Nd\(_2\)CuO\(_4\). The \(T_c\)'s, however, are substantially lower for this class of HTS than for the hole superconductors.

### 2.3. Properties of YBCO

YBa\(_2\)Cu\(_3\)O\(_{7-x}\), abbreviated YBCO, was discovered by Wu et al.\(^2\) in February 1987. The YBCO material is classified as a two-layered copperoxide superconductor belonging to a group of HTS denoted 123 compounds represented by the general chemical formula RBa\(_2\)Cu\(_3\)O\(_{7-x}\). Here R stands for rare earth metal, e.g. Y, Dy, La, Nd, Sm, Eu, Gd, Ho, Er, Tm and Lu. All these compounds display very similar physical properties. An important exception is PrBa\(_2\)Cu\(_3\)O\(_7\) (PBCO) where no superconductivity appears. Thin PBCO layers sandwiched between YBCO films have therefore been used in weak link studies of thin films.

#### Structure

The basic crystallographic structure of YBCO is represented in Fig. 1. Depending on the value of \(x\) in the formula YBa\(_2\)Cu\(_3\)O\(_{7-x}\), the structure can be orthorhombic or tetragonal as shown in Fig. 1(a) and 1(b), respectively. The orthorhombic structure consists of CuO\(_2\) planes intercalated by metal-oxygen layers. Such planes, characteristic for all HTS copperoxides, constitute the basal planes of CuO perovskites. Nine oxygen atoms per unit cell would be required to form a perfect perovskite structure. YBCO (\(x=0\)) has seven oxygen atoms per unit cell and is
therefore often referred to as an oxygen deficient perovskite. The additional oxygen in the orthorhombic phase will form one-dimensional chains of CuO along the b-axis, a unique feature among the 123 compounds.

As indicated in the chemical formula of YBCO, oxygen atoms play the role as a dopant. The YBCO material is stable (or metastable) for all values of $x$ between 0 and 1. In conventional YBCO processing, the tetragonal phase is synthesized at relatively high temperatures, typically around 900 °C. This state corresponds to $x$ close to one. During the subsequent cool down, oxygen is incorporated into the tetragonal structure and $x \rightarrow 0$. A phase transition to the orthorhombic structure occurs near $x=0.65$. The final $x$ value reached after processing will have serious consequences for the electrical properties of YBCO, see Fig. 2 which depicts $T_c$ as a function of $x$. While the orthorhombic structure is a superconductor, the tetragonal phase shows an insulating behaviour.

The occurrence of superconductivity in YBCO has been interpreted in terms of a simple charge transfer model where the CuO$_2$ layers play the role as conduction planes and the CuO chains act as charge reservoirs. Superconductivity in YBCO depends on the carriers in the CuO$_2$ layers transferred from the CuO chains. The oxygen incorporation will be responsible for the hole doping of the CuO$_2$ layers. The superconducting CuO$_2$ layers are weakly coupled together by layers of other
elements (see Fig. 1(a)). Thus the YBCO material (and most other HTS) exhibits a two-dimensional character.

The YBCO lattice structure implies highly anisotropic properties. This is reflected in Table I where physical properties of YBCO are listed. Such anisotropic properties may present an obstacle for many future applications. Another highly anisotropic YBCO feature, not shown in Table I, is atomic diffusion. The diffusion of oxygen has been found to be far greater in the ab-plane than in the c-axis direction. This fact may have significant influence on the oxidation of oriented thin YBCO films.

Additional phases and defects
A ternary phase diagram of the system Yo1.5-BaO-CuO has been published by Beyers and Ahn, see Fig. 3. YBCO is a line (point) compound and any deviation from the metal 123 stoichiometry will result in impurity phases. The majority of the non-123 phases are insulating, for example \( \text{Y}_2\text{BaCuO}_5 \) ("green phase") and \( \text{Y}_2\text{Cu}_{2}\text{O}_5 \). However, two other superconducting phases are known, \( \text{Y}_2\text{Ba}_4\text{Cu}_9\text{O}_{16+x} \) (248) and \( \text{Y}_2\text{Ba}_4\text{Cu}_{7}\text{O}_{16+x} \) (247), having \( T_c \)'s of 80 and 70 K, respectively. The 123 phase offers the largest \( T_c \) and in general, this is the desired phase for applications. The 248 phase has generated some interest as an alternative to the 123 material since it does not exhibit the formation of twins (mentioned below) and also is less sensitive to oxygen content.
TABLE I. Physical properties of YBCO.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical temperature ($T_c$)</td>
<td>93 K</td>
</tr>
<tr>
<td>Critical current density ($J_c$) for thin films</td>
<td>$5 \times 10^6$ A/cm$^2$ at 77 K</td>
</tr>
<tr>
<td>Upper critical field ($H_{c2}$)</td>
<td>a-b plane 140 T</td>
</tr>
<tr>
<td></td>
<td>along c-axis 29 T</td>
</tr>
<tr>
<td>Coherence length ($\xi$)</td>
<td>a-b plane 14 Å</td>
</tr>
<tr>
<td></td>
<td>along c-axis 3.5 Å</td>
</tr>
<tr>
<td>Penetration depth ($\lambda$)</td>
<td>a-b plane 1400 Å</td>
</tr>
<tr>
<td></td>
<td>along c-axis 7000 Å</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>a 3.8231 Å</td>
</tr>
<tr>
<td></td>
<td>b 3.8864 Å</td>
</tr>
<tr>
<td></td>
<td>c 11.6807 Å</td>
</tr>
<tr>
<td>Thermal expansion coefficient ($\alpha$)</td>
<td>$11-13 \times 10^{-6}$°C$^{-1}$</td>
</tr>
<tr>
<td>Thermal conductivity ($\kappa$)</td>
<td>20 mW/cmK at 300 K</td>
</tr>
<tr>
<td>Specific heat (C)</td>
<td>2.5 J/cm$^3$ at 300 K</td>
</tr>
<tr>
<td>Melting point</td>
<td>$-1000$ °C</td>
</tr>
<tr>
<td>Density</td>
<td>5.6 g/cm$^3$</td>
</tr>
</tbody>
</table>

Apart from impurity phases, YBCO does in practice contain a broad range of defects such as stacking faults, oxygen vacancies and twins. Among these, the most significant is the [110] twin, a direct result of the tetragonal to orthorhombic distortion. The correlations between defects and physical properties in the HTS are complex and far from clarified.⁶

Electrical and magnetical properties

In the normal state, YBCO displays a relatively high metallic resistivity and a linear $\rho(T)$ characteristic extending from just above the superconducting transition up to several hundreds of °C. Typical $T_c$ values for high quality YBCO films are in the range of 88-91 K which are somewhat lower than the bulk value mentioned above. Films fabricated by an optimized process can now reach critical current densities ($J_c$) at $3-5 \times 10^6$ A/cm$^2$ at 77 K and a factor of ten higher at 4 K (see Table I).

Perhaps the most intriguing superconducting characteristic of the copperoxide superconductors is their extremely small values of the coherence length $\xi$. In YBCO, the value of $\xi$ has been estimated to be about 5 Å in the $c$-direction and 15 Å in the
The superconducting thin films of YBa$_2$Cu$_3$O$_{7-x}$

$T = 950^\circ C$
$P_{O_2} = 0.2$ atm

$YBa_2Cu_3O_{7-x}$, $YBa_2Cu_3O_7$, $YBa_2Cu_3O_{7+y}$

For the new superconductors, however, the irreversibility onset does not occur at the transition temperature but rather at a temperature below $T_c$. As a consequence, the magnetic phase diagram $H(T)$ will be divided into reversible and irreversible regions. The associated flux dynamics in the irreversible regime have been interpreted in various models based on spin-glass analogies, vortex entanglement and the Anderson-Kim theory. The last model predicts very small pinning energies for high temperature superconductors leading to what has been termed giant flux creep. This may have serious consequences on future applications regarding transport and heat dissipation effects.
On the other hand, if the vortices are properly pinned, high critical current densities will be achievable.

2.4. Superconducting thin films

Progress in vacuum technology after World War II made it possible to synthesize materials in the form of pure layers with thicknesses < 1 μm. The first generation of superconducting films, typically metallic elements deposited on substrates like glass, were used in investigations concerning influence of structure, impurities and proximity behaviour. In tunneling experiments, the preparation of superconducting films with smooth and clean surfaces came to play a crucial role. This was first demonstrated by the single-electron tunneling studies of Giaever in 1960, performed on Al/oxide/Pb film configurations. Later, Anderson and Rowell experimentally confirmed the existence of Josephson tunneling (i.e. tunneling of electron-pairs) by the use of thin layers in a superconducting-insulator-superconductor arrangement. The introduction of superconducting binary alloys, notably the A15 compounds, increased complexity in film synthesis. Preparation of A15 alloys in thin film form became interesting because the film growth process made it possible to achieve a metastable composition range. Such layers were found to exhibit enhanced $T_c$:s. The $T_c$ record of Nb$_3$Ge, earlier mentioned, was accomplished using a refined sputtering process for thin films.

Following the discovery of HTS, thin film work was started up rapidly in the spring of 1987. The initial efforts in YBCO were promising: It was shown that high $T_c$:s were attainable, very close to the critical transition temperature found for the bulk material. On the other hand, the Bi- and TI-based HTS turned out to be much more difficult to synthesize in thin-film form. This is connected with difficulties in preparing such structurally complex superconductors in one single phase. Moreover, a very important discovery made relatively early (June 1987) by Chaudhari et al. was that layers of YBCO were capable of sustaining high critical current densities ($10^6$ A/cm$^2$ at 4 K). This was in sharp contrast to all bulk ceramic HTS which already from the beginning suffered from inferior critical currents. The high $J_c$:s observed in YBCO films explain the intense activity which followed in the field. However, initial films were far from ideal and subsequent thin film research have focused on material perfection and optimization of superconducting properties. This has been followed by the fabrication of multi-layers, ultra-thin films and more advanced film structures.

Compared to film preparation of traditional superconductors, the new HTS materials present great challenges to the thin film technologist. Synthesis of thin YBCO films
SUPERCONDUCTING THIN FILMS OF YBa$_2$Cu$_3$O$_{7-x}$

requires the simultaneous deposition of three elements in stoichiometric ratios, one of them (Ba) reacting easily with most other materials. The condensation of film atoms takes place onto a heated substrate in the presence of oxygen, an environment highly incompatible with standard vacuum equipment. Deposition conditions must be carefully adjusted in order to ensure correct YBCO film formation of such a complicated crystal structure. In addition, the YBCO film must undergo a phase transformation involving oxygen incorporation during the subsequent cool-down. This implies special arrangements and solutions in thin film technology, not encountered prior to the HTS era.

The first HTS thin films were fabricated using conventional deposition techniques such as sputtering and evaporation. Later, chemical vapor deposition (CVD) also came in use. While these three methods all had been used for film synthesis of traditional low temperature superconductors, pulsed laser evaporation (PLE) was almost completely unknown in the field before the discovery of HTS. Today, PLE is one of the most significant techniques for HTS thin film preparation. Evaporation, CVD, sputtering, and PLE constitute today the base for preparation of high quality YBCO films. Thick film deposition methods such as metalorganic deposition (MOD) or spray pyrolysis have still not demonstrated high critical current HTS layers.

2.5. Applications of superconducting films

When film technology matured in the 1960's, superconducting layers were first prospected in applications concerning detectors, e.g. infra-red detectors (bolometers). The development of Josephson junction configurations opened the door to the realization of superconducting quantum interference devices (SQUIDs). The SQUID has come to extensive use for ultra-sensitive magnetic flux detection in a large variety of areas. Josephson devices, exhibiting high-speed and low-heat dissipative behaviour, would constitute the basis for an ultra-high performance computer. There exist today large scale integrated microprocessors built up by Josephson elements, e.g. a 4-bit dataprocessor on a single chip operating at 760 MHz clock rate frequency and 25 mW power dissipation. The preferred junction technology for traditional superconducting circuits relies on refractory materials such as Nb and NbN using barrier layers of Al/Al$_2$O$_3$ or MgO.

The common denominator of all devices mentioned above is the requirement of liquid helium (LHe) as the cooling agent. The discovery of HTS made liquid nitrogen (LN$_2$) cooling (77 K) of superconductors possible. Compared to LHe, LN$_2$ is considerably less expensive and, perhaps more important, much more versatile. This
is due to the slow boil-off rate of LN$_2$; Its latent heat of vaporization is about 60 times that of LHe. Closed-cycle one stage refrigerators with low maintenance requirements can therefore be applied in cooling applications of HTS. The majority of prospected electronic applications for HTS has been concentrated on the YBCO. The main advantage with this material is the high film critical currents densities. One disadvantage of YBCO is related to its low temperature margin between $T_c$ and the operating temperature of 77 K. Thin films of the Tl-compound, being structurally less perfect than YBCO layers but having the advantage of a large temperature margin to LN$_2$, have therefore been utilized for certain applications, in particular passive microwave devices.$^{14}$

A high quality YBCO film intended for use in future applications must fulfill several requirements regarding physical properties, see Table II. However, the development of electronic HTS circuits consists not only in mastering thin film synthesis. Of equal importance is the elaboration of film processing techniques compatible with HTS materials. This includes selection of substrate material, techniques in patterning, preparation of low-resistivity contacts and multi-layer design. Such considerations have been extensively studied the last years. One of the key issues concerning applications of HTS is to find a route in combining semiconducting and HTS devices on the same chip. In general, YBCO synthesis on bare semiconductor substrates such as Si and GaAs implies dramatic degradation of the superconducting material. Through the use of buffer layers such as MgO and yttria-stabilized ZrO$_2$ deposited on Si and GaAs, advances have been made in obtaining epitaxial YBCO films exhibiting good superconducting properties.$^{15,16}$

### TABLE II. Characteristics of high quality YBCO films for electronic applications.

<table>
<thead>
<tr>
<th>Film property</th>
<th>Desirable characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance vs temperature</td>
<td>Linear and extrapolating to $R=0$ at $T=0$</td>
</tr>
<tr>
<td>Resistivity at 100 K</td>
<td>&lt;100 $\mu$Ωcm</td>
</tr>
<tr>
<td>$T_c$</td>
<td>88 - 91 K</td>
</tr>
<tr>
<td>$\Delta T_c$</td>
<td>&lt; 1 K</td>
</tr>
<tr>
<td>Critical current density</td>
<td>$&gt; 10^7$ A/cm$^2$ at 4 K, $&gt; 10^6$ A/cm$^2$ at 77 K</td>
</tr>
<tr>
<td>Film morphology</td>
<td>Smooth surfaces</td>
</tr>
<tr>
<td>Surface resistance</td>
<td>$&lt; 1$ mΩ at 77 K and 10 GHz, $&lt; 50$ $\mu$Ω at 4 K and 10 GHz</td>
</tr>
</tbody>
</table>
In 1990/91, the first HTS components appeared on the market. These components are microwave devices such as microstrip resonators and filters, exhibiting competitive surface resistances as compared to existing technology. Recently, an HTS bolometer has also been presented. The above mentioned devices are passive components built up by a single HTS layer. Much more challenging is the fabrication of active HTS devices, e.g. a SQUID magnetometer. The successful fabrication of a SQUID will crucially depend on a reliable Josephson junction technology. Yet no real sandwich tunnel junction built up by HTS materials has been demonstrated. The problems encountered are related to the material characteristics of HTS mentioned above: Short coherence length and strong anisotropic behaviour. Another contributing factor is the loss of oxygen at the surface of YBCO films, reducing the superconducting quality of film interfaces. Alternative approaches for making Josephson devices associated with various weak link configurations have been studied, e.g. edge junctions, step junctions or grain boundary junctions. Films oriented with the $a$-axis perpendicular to the substrate are beneficial since the coherence length is three to four times longer than in the $c$-axis direction. Perhaps the most advanced device structure existing today is given in Fig. 4, showing the cross section of a heteroepitaxial fifteen-layered SQUID with an integrated flux transformer. The weak link is introduced via an artificially created tilt 45° grain boundary in the top YBCO layer. Apart from fabrication processes, much interest have also focused on the 1/f noise properties of HTS-SQUIDs which are important for low-frequency applications in, for example, biomagnetism. This issue has turned out to be particular promising for Tl-based SQUIDs where the noise performance at 77 K is now comparable with commercial dc and rf SQUIDs operating at 4 K. The first commercial YBCO-SQUID for educational purposes has recently been lanced on the market.

![Cross section of an integrated YBCO-SQUID and flux transformer build up by fifteen epitaxial layers.](image-url)
3. THIN FILM GROWTH OF YBCO

An essential part of this thesis covers aspects in preparation and properties of YBCO thin films. A survey is here presented of the various deposition methods and the associated YBCO film characteristics. In order to evaluate a YBCO film, standard methods for material, electrical and magnetical characterization have been applied throughout in this thesis. These methods are presented in Table III.

**TABLE III. Basic characterization tools utilized for evaluation of YBCO thin films properties.**

<table>
<thead>
<tr>
<th>Material characterization</th>
<th>Electrical and magnetical characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scanning electron microscopy</td>
<td>Resistivity vs temperature</td>
</tr>
<tr>
<td>Energy dispersive X-ray analysis</td>
<td>Critical current density vs temperature</td>
</tr>
<tr>
<td>Rutherford backscattering spectrometry</td>
<td>AC/DC-susceptibility vs temp. and field</td>
</tr>
<tr>
<td>Structural analysis: 0/2θ, θ-scan</td>
<td>Magnetization loops</td>
</tr>
</tbody>
</table>

The techniques collected in Table III gives a picture of overall YBCO film quality. The most significant analysis tools missing are advanced structural examinations, e.g. pole figures in X-ray diffraction analysis, transmission electron microscopy (TEM) and channeling measurements in backscattering spectrometry. These methods have been applied in singular cases and will be reported on below. Also surface resistance (R_s) measurements at high frequencies have not been applied systematically. Such evaluations, largely depending on material structural perfection, are generally considered as the most stringent quality test for a superconducting film. Nevertheless, correspondences have been reported between R_s values and other film properties such as resistivity, T_c, J_c, and grain alignment, parameters which are covered in the analysis represented in Table III. Also missing in Table III are depth profiling and conductivity noise measurements, to be mentioned below.

3.1. General concepts

There are basically two different approaches in YBCO film synthesis: *ex situ* and *in situ* synthesis. The former constituted the dominating technique in the beginning of the YBCO thin film era. Today, the large majority of all YBCO films are fabricated using the *in situ* approach, although still the highest quality Tl- and Bi- HTS films are
prepared ex situ. The thesis reflects the development in YBCO film synthesis and the appended papers nr 1-6 represents ex situ films while the rest (nr 7-9) concerns YBCO layers grown in situ.

**Ex situ and in situ synthesis**
The difference between ex situ and in situ fabrication of YBCO thin films is visualized in Fig. 5, showing substrate temperature vs time during film processing. In the ex situ method, proper ratios of Y, Ba and Cu are deposited onto a substrate held at a relatively low temperature (100-400 °C). The resulting precursor film is therefore usually in a structurally amorphous state and film crystallization must be performed in a subsequent annealing step taking place at elevated temperatures around 800-900 °C. During this stage, oxygen must also be supplied to obtain the correct film phase. In general, the annealing is performed in a furnace outside the vacuum chamber, thus

![Diagram of ex situ and in situ synthesis](image)

**FIG. 5.** The ex situ and in situ concepts in synthesis of HTS thin films.
explaining the *ex situ* prefix. After the high-temperature step of YBCO, the tetragonal-orthorhombic phase transition is allowed to take place during temperature ramp-down. Different kind of ramp-down procedures, e.g. involving a step in temperature around 400 °C, are sometimes applied.

In contrast, the *in situ* method implies crystallization of tetragonal YBCO already during deposition. Film formation must occur on a hot substrate under strongly oxidizing conditions. As seen in Fig. 5, this step can be performed at substrate temperatures in the interval 650-800 °C, significantly lower than the formation temperatures used for *ex situ* growth. The subsequent temperature ramp-down, permitting oxygen incorporation, is similar to the last step in the *ex situ* method.

The *ex situ* method favors non-complexity and versatility in film deposition. One example is deposition on both sides of a substrate (important for microwave applications), another is YBCO synthesis over large areas. On the other hand, careful selection of post-deposition annealing parameters must be made for optimizing superconducting behaviour. The high temperatures required for the amorphous-to-crystalline transformation is the major disadvantage with the *ex situ* method. Film growth is liable to occur in different directions, resulting in YBCO layers with multiple oriented grains. In addition, enhanced substrate reactions render the fabrication of high quality YBCO layers on substrates such as Al₂O₃ and Si a difficult task. Nevertheless, YBCO films displaying excellent superconducting properties have been made using an *ex situ* approach based on BaF₂ deposition rather than Ba. This method will be considered in section 3.2.

*In situ* growth of YBCO films implies a high degree of complexity in the fabrication process. Very high quality YBCO films can be synthesized using different techniques which are presented in the paragraphs 3.3.-3.6. The lower processing temperature when preparing YBCO *in situ* as compared to *ex situ* is of significance in suppressing film-substrate interactions. In principle, *in situ* formation of YBCO results in layer-by-layer crystallization, yielding epitaxial layers exhibiting smooth surface morphologies. Hence the fabrication of multilayers are possible. One disadvantage with the *in situ* method is the problems in scaling up the process to large areas. This is due to difficulties in controlling substrate temperature and oxygenization over large substrate areas during film growth.
The YBCO stability diagram

Provided a stable substrate material, the final YBCO film properties are essentially dependent on two growth variables: film formation temperature and partial pressure of oxygen (pO_2). This is demonstrated by the YBCO stability diagram shown in Fig. 6. The diagram also depicts lines of constant oxygen stoichiometry, i.e. the value of x in the formula YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-x}. Figure 6 reveals several interesting features crucial for YBCO film synthesis. We consider first the stability limits for YBCO. On the basis of electrochemical reduction experiments, Bormann and Nölting\textsuperscript{23} proposed that the CuO-Cu_2O-O_2 equilibrium line constituted a decomposition line for YBCO. Below this line, YBCO becomes thermodynamically unstable and decomposes into Y_2BaCuO_5, BaCu_2O_2 and Cu_2O. Later, the region for stable YBCO formation has been proved (by thermal gravimetric analysis) to be at least one order of magnitude lower than the CuO-Cu_2O-O_2 line.\textsuperscript{24} There is also a melting line limit for YBCO, indicated to the left in Fig. 6. Off-stoichiometry effects such as excess in Cu or deficiency in Y results in a shift of the melting line towards lower temperatures.

![Diagram](https://via.placeholder.com/150)

**Fig. 6.** The oxygen partial pressure vs temperature diagram for YBCO growth showing stability and melting lines together with lines (dashed) of constant oxygen stoichiometry. Regions I, II and III correspond to different film growth conditions used in preparation of YBCO thin films. (Data in this figure are mainly adopted from ref. 26).
The three regions labelled I, II and III in Fig. 6 represent approximate deposition conditions for the film techniques described here. The spread in oxygen pressure between the various methods is huge, extending from $P_{O_2}=10^3$ mbar to 1 mbar and further down to about $10^{-4}$ mbar for regions I, II and III, respectively. Region I is associated with traditional ex situ film preparation of YBCO and must be performed at high temperatures up to 900 °C. Region II represents in situ synthesis of YBCO films using typical growth parameters: $P_{O_2}$=1 mbar and formation temperatures between 700 °C and 800 °C. Hammond and Bormann suggested that successful in situ synthesis of YBCO was achieved using growth conditions in close proximity to the CuO-Cu$_2$O-O$_2$ line regardless of the film deposition technique applied. Films grown along this line appear to have larger grain sizes and improved surface smoothness in comparison with films prepared off the line. In recent times, it has also been demonstrated that ex situ films of high quality can be prepared in region II. Finally, region III is representative for reactive coevaporated films. According to Fig. 6, this kind of deposition should not be successful but rather lead to decomposition of YBCO. However, the films made in region III are of high quality which is due to the use of atomic rather than molecular oxygen during film growth. Yamamoto et al. have shown via in situ resistivity measurements that the effective (or equivalent) molecular oxygen pressure may be enhanced with up to three orders of magnitude by exposing the film surface to an atomic flux of oxygen of $2 \times 10^{15}$ at/cm$^2$ s. Hence the position of region III in Fig. 6 should be modified with respect to the effective $P_{O_2}$ and film growth would occur above the YBCO stability line.

Comparing regions I and II and the corresponding oxygen stoichiometry lines, it is observed that in situ growth takes place at $x>0.9$ while film preparation made ex situ typically occurs for $x<0.6$. There are clear indications that epitaxial film growth of YBCO is unfavorable for $x<0.9$. One explanation is that the presence of relatively large amounts of oxygen during growth can be responsible for an increased rate of nucleation resulting in small film grains. Also cation mobility might be reduced by a too high oxygen content, e.g. by the formation of metal suboxides on the film surface. Epitaxial growth of YBCO has been proposed to be promoted by distortions of the YBCO lattice associated with $x$ being close to 1, thereby leading to increased cation mobilities.

After in situ growth in region II of Fig. 6, ramp-down in temperature must be properly performed to ensure oxygen incorporation in the Cu-O chains. The conventional technique is backfilling of the chamber with oxygen up to 0.1-1.0 atm. immediately after film deposition and thereafter decreasing of substrate temperature. This route has been shown to be of primary importance for achieving the superconducting phase when preparing YBCO films using molecular oxygen.
contrast, the films prepared in region III can be reduced in temperature under a much lower background pressure than 1 atm. provided that the strongly oxidizing film environment is preserved.

3.2. The BaF$_2$ method

In the past, all HTS thin films were prepared using different kind of ex situ techniques. The most common precursor layers consisted of evaporated films of Y-Ba-Cu-O or multilayers of Y/Ba/Cu (or corresponding oxides) deposited in various sequences. $^{12,29}$ In general, the post-deposition annealing in flowing oxygen resulted in films showing inferior superconducting properties. One example of such a first-generation YBCO film can be found in appended paper 2. More specific, the paper reports on post-annealed Y-Ba-Cu-O films deposited by coevaporation on sapphire and alumina substrates. In spite of correct initial metal composition $^{30}$ and an optimized post-annealing procedure, the films showed broad resistive transitions ending at a final $T_c$ of about 30 K. Similar observations were made using more stable substrate materials such as SrTiO$_3$. $^{31}$ From optical inspection and scanning electron microscopy (SEM), the degradation was proposed to be related to film reactions with the ambient air occurring when removing the film from the vacuum chamber. The degradation showed up as large cracks (10-100 μm) in the as-deposited films.

In late 1987, Mankiewich et al. $^{32}$ suggested a different ex situ approach, here referred to as the BaF$_2$ method. By depositing stoichiometric amounts of Y, BaF$_2$ and Cu and performing a subsequent post-annealing in wet oxygen, YBCO film quality was raised substantially. The incorporation of the stable BaF$_2$ compound rather than Ba strongly reduces the sensitivity of the as-deposited film to the ambient. The F atoms are then substituted against O in the wet oxygen high temperature step by BaF$_2$ dissociation:

$$2\text{BaF}_2(s) + 3\text{CuO}(s) + 0.5\text{Y}_2\text{O}_3(s) + 2\text{H}_2\text{O}(g) \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{6.5}(s) + 4\text{HF}(g)$$  (1)

The presence of H$_2$O rather than O$_2$ strongly promotes the dissociation of BaF$_2$. $^{33}$ Paper 3 demonstrates that shifting from a dry to a wet oxygen process results in a change from semiconducting behaviour in film resistivity vs temperature. The role of BaF$_2$ may also be important in suppressing low-temperature formation of stable Ba-containing oxides or uncontrolled nucleation of YBCO. A careful optimization of the post-annealing procedure must then be performed in order to
achieve films with high quality properties. In contrast, the choice of technique applied in deposition of the amorphous precursor layer appears not to be crucial, although the films exhibiting the best properties have been grown from coevaporated Y-BaF$_2$-Cu-O films.

Reported best physical properties of films fabricated by the BaF$_2$ method are of surprisingly high quality. A well-optimized BaF$_2$-process for perovskite substrates such as SrTiO$_3$ or LaAIO$_3$ produces layers exhibiting T$_c$'s above 90 K, J$_c$(77 K) $> 10^6$ A/cm$^2$ and low channeling yields ($\chi_{\text{min}} < 3\%$). Compared to YBCO films made in situ, however, the "BaF$_2$-films" display in general inferior surface morphologies which in turn are related to the high temperature annealing step during YBCO formation (region I in Fig. 6). By using annealing conditions corresponding to region II in Fig. 6, it has recently been proved that significant improvements of ex situ film properties can be obtained, e.g. in morphology, $c$-axis alignment and surface resistance.

Deposition technique and composition control
In this work, the BaF$_2$ method has been reported in paper 1, 3, 4, 5 and 6. Below, the deposition method and the post-annealing procedure are described. This is followed by a discussion of the resulting superconducting film properties.

Depositions of Y-BaF$_2$-Cu films were performed onto non-intentionally heated substrates by simultaneous evaporation of Y, BaF$_2$ and Cu, see the schematic picture in Fig. 7. The system is described in detail in paper 1. A key issue when preparing multi-elemental films in such a system is in what way and with which precision film composition can be controlled. For YBCO layers synthesized with the BaF$_2$ method, Carlson et al. have shown that film properties such as T$_c$, critical current, and channeling values rapidly deteriorate for minor deviations (>1%) in Y, Ba or Cu stoichiometry in YBCO. Temperature source control similar to that used in traditional molecular beam epitaxy (MBE) is in general not sufficient for accurate composition control. A detecting system for real-time monitoring of the evaporated species is required, thereby permitting modifications of film stoichiometry by closed loop control. A quadrupole mass spectrometer, equipped with an ion beam source and operating in a multiplexed mode, has been utilized in this study for evaporation rate monitoring. Compared with more traditional solutions employed in evaporation rate control such as quartz crystal monitors, the quadrupole concept has certain advantages, e.g. high sensitivity and detection in close proximity to the substrate. Its main disadvantage is associated with space charge effects occurring in the ion source at pressures above $10^{-5}$ mbar.
FIG. 7. Schematic picture of the coevaporator used for deposition of Y-BaF$_2$-Cu-O layers.

The quadrupole mass spectrometer concept has been evaluated in paper 1. For this purpose, Rutherford backscattering spectrometry (RBS) was performed on thin (∼1000 Å) Y-BaF$_2$-Cu films deposited on silicon, see example of a spectrum in Fig. 8. An actual evaporation rate $d(N_t)/dt$ in units of deposited at/cm$^2$s is obtained from the surface energy approximation:

$$\frac{d(N_t)_i}{dt} = \frac{1}{T} \frac{A_i}{H_{Si}} \frac{\sigma_{Si}^{Si}(E_o)}{\sigma_{i}^{Si}(E_o) \left[ E_{o}^{Si}(cos \theta) \right]}$$  \hspace{1cm} i=Y, Ba, Cu \hspace{1cm} (2)$$

where a sticking factor of one is assumed and $\sigma$, $[e_o]$ and $T$ are the scattering cross section, stopping cross section factor and deposition time, respectively (see Fig. 8 for other definitions). The actual evaporating rates calculated from Eq. (2) were related to the ion current of the corresponding detected species in the mass spectrometer. Hence sensitivity factors of the quadrupole could be derived. An important conclusion from this study was that the mass spectrometer system could be utilized for accurate film composition control (±2%). The quadrupole is tuned to the desired 1-2-3 ratio through a calibration procedure, preferably by RBS analysis of thin deposits.
The deposition of the Y, BaF₂ and Cu were performed in a low partial pressure of oxygen, typically $5 \times 10^{-6}$ mbar, held constant by a precision leak servo valve. The presence of oxygen helps stabilizing the films, probably by oxidizing the evaporated Y-species. Indeed, paper 1 gives evidence that the introduction of oxygen mainly affects the evaporation rate of Y. Further on, it was concluded that the mass spectrometer rate control system behaved well up to $p_{O_2}$ pressures of about $10^{-5}$ mbar. For best accuracy of the composition control system, a recalibration of the mass spectrometer becomes necessary for each oxygen pressure.

Immediately after an evaporation run, metal composition for as-deposited films on sapphire was checked by energy dispersive X-ray analysis (EDX) using 15 kV acceleration voltage and a detector angle of 40°. The Y-BaF₂-Cu-O precursor layers synthesized in this study are suitable for this type of analysis since they are thick (~1 μm) and homogeneous (compare with the much more complicated EDX analysis carried out for inhomogeneous MOCVD films in paper 8). Elemental ratios of Cu/Y and Cu/Ba obtained from EDX and RBS measurements are plotted against each other in Fig. 9.
Post-deposition annealing

Transformation to YBCO from the as-deposited Y-BaF<sub>2</sub>-Cu-O layers was performed in a laboratory furnace using flowing wet oxygen during the high temperature step and dry oxygen gas during the subsequent reduction in temperature. The films have been grown using temperatures and pO<sub>2</sub> corresponding to region I in Fig. 6 (800 °C < T < 900 °C, pO<sub>2</sub>=1 atm.). Appended papers number 3, 4 and 5 discuss various aspects of optimizing post-annealing parameters, e.g. temperature and time during the wet oxygen step, partial pressure of H<sub>2</sub>O and the ramp-down procedure. Such an optimization must be performed for a specific substrate material and thereafter related to a selected film property. The most extensive studies have been made for Y-BaF<sub>2</sub>-Cu-O films on sapphire substrates where the zero resistivity temperature (T<sub>c</sub>) was maximized. The maximization was based on the selection of temperature and/or time in the high-temperature annealing step. Results from such optimization studies are summarized in Fig. 10. In the case of Y-BaF<sub>2</sub>-Cu-O layers deposited on perovskite substrates, the T<sub>c</sub>s were observed to be relatively insensitive to variations in the annealing conditions (typically T<sub>c</sub>=90 K). For these samples, measurements of the critical current density gave a more adequate picture of variations in film quality as a function of annealing parameters (paper 6). Typical annealing parameters were 900 °C, 10 min in wet oxygen followed by a temperature ramp-down (-2 °C/min) in dry oxygen.
FIG. 10. Optimal annealing conditions in terms of temperature and time (pO2=1 atm.) for obtaining maximum Tc for the BaF2 films grown on sapphire. Inset shows an example of an optimization procedure.

Film properties
The physical film properties presented are representative for YBCO layers 3000-10000 Å thick prepared on stable perovskite substrates utilizing the BaF2-method. Post-annealing procedures had been optimized for maximum Tc and Jc. Figure 11 shows structural and morphological features of a 5000 Å thick YBCO film deposited on LaAlO3. The θ/2θ scan from X-ray diffraction analysis (XRD) presented in Fig. 11 (a) gives evidence of a predominantly c-axis film texture oriented perpendicular against the substrate. In thicker films, a mixture between a- and c-axis grains is frequently encountered for YBCO films made by the BaF2 method. This is due to film growth taking place in various directions during the transformation from an amorphous to a crystalline state. Final film orientation will depend on substrate material, initial composition of the precursor film, heat-treatment conditions and film thickness. (See chapter 4 for substrate influence). The SEM micrograph in Fig. 11 (b) reveals YBCO crystallized on LaAlO3 in orthogonal, interconnecting rods. Films become smoother and more dense with decreasing film thickness or increasing annealing temperature.
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Explanations for this type of "basket weave" surface texture, often observed for YBCO films prepared by the BaF$_2$ method, can be found in the literature. The rods have been attributed to rapid nucleation of YBCO along the $a$- and $b$-axis whereas the $c$-axis oriented grains grow perpendicular to the rod axis. The morphology in Fig. 11(b) would therefore be associated with $a$-axis growth. Wang et al. found by TEM analysis that the junctions between the single-crystalline rods were atomically abrupt. The YBCO layer closest to the substrate surface has been proposed to be $c$-axis oriented thus partly explaining the smoother surface morphologies observed for thinner films (< 4000 Å). A further complication in film growth using the BaF$_2$ method is the observed nucleation of the Y$_2$Ba$_4$Cu$_6$O$_{20+y}$ phase (2-4-8). This phase seems to be stabilized by the presence of fluorine during the initial stage of annealing. However, for the films reported about here, the 2-4-8 phase was rarely observed. This is consistent with observations from secondary ion mass spectrometry (SIMS) that the F atoms are efficiently removed by using the annealing conditions described above (paper 6).

Electrical properties of the "BaF$_2$-films" in terms of resistivity ($\rho$) and critical current density ($J_c$) are presented in Fig. 12 (a) and (b), respectively. Resistivity as a function of temperature displays a linear behaviour in the normal state followed by a narrow transition < 1 K down to zero-resistivity which occurs above 90 K. Resistivity is about 300 $\mu\Omega$cm at 300 K and the $\rho$(T) curve extrapolates to $R = 0$ at zero K.
FIG. 12. (a) Resistivity vs temperature for 1 μm thick YBCO on SrTiO$_3$ prepared by the BaF$_2$ method.
(b) Transport critical current density vs temperature for YBCO on NdGaO$_3$. The microbridge was defined by means of Ar ion milling.

Provided proper 1:2:3 composition of the as-deposited film, the type of ρ(T) characteristic shown in Fig. 12 (a) is very reproducible in the BaF$_2$ process for films on SrTiO$_3$ and LaAlO$_3$. In contrast, the critical current densities are more elaborate to maximize. As discussed in paper 6, these are a complicated function of annealing conditions and film thickness. Fig. 12(b) shows a representative $J_c(T)$ curve found from transport measurements performed on an ion-milled bridge 10 μm in width and 2000 Å thick. The $J_c(77 \text{ K})$ is about $4 \times 10^5 \text{ A/cm}^2$. In general, higher critical current values are observed for thinner films ~1000 Å which may be attributed to film homogeneity discussed above. The response in zero-field cooling (ZFC) measurements at 10 Oe is relatively sharp, see Fig. 13 (a). Fig. 13 (b) demonstrates a magnetization hysteresis loop of a 1100 Å YBCO film on LaAlO$_3$ recorded at 20 K. From this plot, the zero-field critical current density was determined to be $10^7 \text{ A/cm}^2$. 
3.3. Evaporation

Fabrication of YBCO thin films in situ by evaporation involves the simultaneous vaporization of Y, Ba and Cu in the presence of oxygen. Both thermal\textsuperscript{43} and electron beam evaporation\textsuperscript{44} methods have been reported (in addition, there is the special case of single target evaporation using a laser, to be discussed separately in section 3.4.) The oxygen gas is often activated by the use of plasma or ozone, thus validating the frequently used term activated reactive evaporation (ARE). Evaporation and molecular beam epitaxy (MBE) are here not distinguished since the latter can be regarded as an evaporation process under controlled conditions. The large impact of the MBE technique in synthesis of semiconductor materials has motivated explorations of in situ evaporation of YBCO. Evaporation systems can be made versatile and a large number of film growth variables can be affected and studied. However, the disadvantage is an increase in complexity for achieving full control over the deposition process. Ultimately, the technique could allow for film growth of the YBCO unit cell layer by layer. Coevaporated superlattice structures of YBCO/PBCO have been reported by Terashima \textit{et al.}\textsuperscript{45}

Evaporation is a film deposition technique associated with high-vacuum conditions. This imposes somewhat of a conflict in YBCO growth since the YBCO stability diagram (Fig. 6) indicates minimal oxygen pressures around $10^{-3}$ mbar for successful in situ formation. Such high pressures make the operation of vital parts in an evaporator, e.g. rate control system and electron beam guns, virtually impossible. One way to overcome this is to supply the O\textsubscript{2} gas in a local, confined region close to the heated substrates.\textsuperscript{46,47} Typically, the oxygen pressure in the vicinity of the substrate region is between $10^{-3}$ and $10^{-2}$ mbar while the rest of the vacuum chamber has $p_{O_2} \sim 10^{-4}$ mbar. Another way is to introduce activated oxygen species, thereby
making it possible to grow YBCO at much lower pressures as discussed under section 3.1. The activated oxygen may consist of ions, atoms or ozone (O\(_3\)). Ionization of O\(_2\) has been proven not to have any real effect on YBCO oxidation during film growth.\(^{48}\) Ozone was early shown by Johnson \textit{et al.}\(^{49}\) for being feasible as an oxidizing agent when preparing YBCO in situ. However, the best results are in general achieved when using atomic oxygen during film growth.\(^{50}\) The first report concerning high quality films of YBCO using atomic oxygen was published in the beginning of 1988 by Terashima \textit{et al.}\(^{44}\)

There are basically three approaches for producing atomic oxygen in YBCO thin film synthesis. First, a remote microwave plasma has been used by several groups, see e.g. Kwo \textit{et al.}\(^{51}\) and Humphreys \textit{et al.}\(^{52}\) According to Ref. 52, the ratio O/O\(_2\) lies typically around 10\%. Second, an electron cyclotron resonance (ECR) oxygen plasma has been proven to be effective in generation of atomic oxygen atoms\(^{48}\) and such sources has been used in low temperature growth of YBCO utilizing evaporation.\(^{53}\) Third, an rf plasma can be utilized for the production of atomic oxygen. Such a plasma is typically introduced between the evaporation sources and the substrates.\(^{44}\)

\textbf{Preparation}

In this thesis, coevaporated YBCO films grown \textit{in situ} using atomic oxygen are presented in paper 7 and 9. The former paper also demonstrates an extension of the technique towards \textit{in situ} synthesis of YBCO/Y\(_2\)O\(_3\)/YBCO multilayers. A combination of electron beam sources (Y and Cu) and a resistively heated source (Ba) is applied similar to the \textit{ex situ} method discussed above. In order to ensure sufficient film oxidation, an atomic oxygen radical beam source situated close to the substrate has been employed, see the schematic picture in Fig. 14. The plasma is created in a small discharge cavity made by quartz and situated close to the substrate. Transport losses associated with recombination of O atoms at the sidewalls can therefore be minimized. When operating the plasma, oxygen species leak out from the aperture to the substrate. Locquet and Mächler have shown that this kind of atomic oxygen beam source is capable of producing high atomic O fluxes while still retaining a relatively low oxygen flow rate.\(^{54}\) In particular, the total oxygen flow rates were 5-10 times less than what was necessary for ECR and microwave oxygen sources working under similar conditions. This makes the atomic oxygen beam source suited for operation under MBE compatible conditions.
Details in fabrication of the evaporated in situ films can be found in appended paper 7 and ref. 55. Briefly, Y, Ba and Cu species were coevaporated under an average oxygen background pressure of $3 \times 10^{-5}$ mbar. Under such conditions, it is still possible to utilize the mass spectrometer for evaporation rate control (see section 3.2.). The substrate was held at 720 °C and the oxygen plasma was operated continuously during evaporation using an rf power of 350 W. Ramp-down in temperature was performed in one hour under an oxygen pressure of $5 \times 10^{-4}$ mbar. The total deposition YBCO rate of 1.5 Å/s implied a required minimum oxygen flux around $6 \times 10^{14}$ atoms/cm$^2$s to ensure proper oxidation. No direct measurements of the atomic oxygen flux, e.g. by a Ag sensor, was carried out here. However, the results reported for an identical oxygen source in ref. 54 indicate that such oxygen flux values would be attainable under the conditions described here.

**Film properties**

The in situ evaporated YBCO films reported about here are grown on LaAlO$_3$ and have thicknesses in the interval 1000-3000 Å. Figure 15 (a) shows the perfect c-axis alignment obtained for this kind of films. The corresponding rocking curve (or $\omega$-scan) recorded for the YBCO (005) peak is given in Fig. 15 (b) and displays a relatively broad full width half maximum (FWHM) value of 0.8°. This may be attributed to the twinned nature of the LaAlO$_3$ substrate which in some cases exhibited rocking curve FWHM values up to 0.5° when scanned over the substrate (012) peak. Preliminary estimations from $\theta/2\theta$-scans of the c-axis lattice parameter
revealed no evidence of c-axis expansion in the evaporated films. Typical c-axis values were 11.67-11.68 Å.

Surface morphology appears to be strongly dependent on metal composition. Baudenbacher et al.\textsuperscript{56} have published a systematical investigation of compositional effects in coevaporated YBCO films on MgO. In the study presented here, no precise film composition could be acquired neither by RBS nor by EDX analysis because of the heavy La element in the substrate material. The SEM micrographs shown in Fig. 16 (a) and (b) are representative of two \textit{in situ} evaporated YBCO films. While the former appears very smooth with no distinct features, the latter reveals the presence of submicron voids. Similar surface morphologies encountered for MOCVD-YBCO layers on LaAlO\textsubscript{3} have been attributed to an Y-rich film composition.\textsuperscript{57} It seems plausible that stringent composition control is necessary for obtaining very smooth surfaces. Tazoh and Miyazawa have recently demonstrated that film surface smoothness with roughness on the order of one unit cell is possible to obtain using

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure15.png}
\caption{(a) 2θ-scan showing perfect c-axis film alignment on LaAlO\textsubscript{3} for an evaporated YBCO film. (b) The φ-scan performed for the YBCO (005) peak.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure16.png}
\caption{(a) SEM micrograph of a very smooth evaporated YBCO film on LaAlO\textsubscript{3}. (b) Evaporated YBCO film on LaAlO\textsubscript{3} showing an morphology exhibiting submicron pinholes.}
\end{figure}
FIG. 17. (a) Resistivity vs temperature for an evaporated film. Observe the non-linear $\rho(T)$ characteristic. (b) Critical current density vs temperature for the pattern shown in Fig. 37.

the same type of system as depicted in Fig. 14 combined with ultralow growth rates (~0.06 Å/s).58

Resistivity vs temperature of the in situ coevaporated films is plotted in Fig. 17 (a). The resistivity at 100 K is only 55 µΩcm and the extrapolated curve intercepts the y-axis at a negative value. Reproducible $T_c$ values in excess of 90 K, a characteristic for the ex situ process discussed in section 3.2, are rarely encountered for the in situ process: Typical zero-resistance values are situated around 88-89 K. Nevertheless, the films display superior superconducting properties in terms of their critical current densities, see Fig. 17 (b) which depicts results from transport measurements carried
out for a 5 μm constriction defined by ion milling. The $J_c(77 \text{ K})$ is above $4 \times 10^6 \text{ A/cm}^2$. In other cases, $J_c$ values up to $6 \times 10^6 \text{ A/cm}^2$ have been observed (paper 7) which are among the highest values reported for thin YBCO films.

Magnetic properties were evaluated by observing fundamental and non-linear response in the AC-susceptibility of the in situ coevaporated films. Figure 18 shows $\rho(T)$ at the transition together with the fundamental and third harmonic response obtained from AC susceptibility measurements close to $T_c$. Resistivity is zero at the onset of AC-susceptibility which demonstrates a rapid fall-down. The single, sharp peak observed in the third harmonic response indicates that the superconducting phase is homogeneous in the film. In Fig. 19 (a) and (b), the ZFC and magnetization

![Graph showing AC susceptibility and third harmonic signal](image-url)
loops are presented. The very sharp transition in the ZFC curve is noteworthy. The magnetic $J_c(39 \text{ K}, H=0)$ from Fig. 19 (b) is $9 \times 10^6 \text{ A/cm}^2$.

The evaporated films have been compared to the BaF$_2$ films by conductance noise measurements in the superconducting transition. This type of analysis constitutes a sensitive probe to the microscopic disorder in the film material. It was found that the detected conductance noise of BaF$_2$ films was three orders of magnitude higher than for the in situ evaporated films, thus indicating a more homogeneous film microstructure for the latter case.

3.4. Pulsed laser evaporation

Laser evaporation was first explored in the late 1960's as a new method for thin film deposition, although it never came to play an important role in the synthesis of low-$T_c$ superconducting films. With the advent of HTS, however, pulsed laser evaporation (PLE) has rapidly established as a film deposition technique for complex oxide superconductors. (Sometimes PLE is also referred to as pulsed laser deposition (PLD) or laser ablation). The PLE technique is based on the evaporation of solid material by pulsed laser light of short duration and high intensity. The spatial variation of film thickness and composition is very different from the distributions found in thermal evaporation. Most importantly, PLE results in congruent evaporation, thereby reproducing the target composition in the growing film. This is due to a forward-directed stoichiometric component of the deposits which is a result of a secondary ejection process. In contrast to electron-beam evaporation discussed above, the PLE system readily works under a partial pressure of oxygen. In addition,
the simultaneous formation of a laser-generated oxygen plasma during PLE highly promotes epitaxial growth of HTS oxide films.

A schematic picture of a PLE equipment for YBCO thin film deposition can be found in Fig. 20. The laser beam is directed through linking and focusing mirrors into the vacuum chamber and impinges onto a stoichiometric YBCO target. The PLE is performed in an oxygen (alternatively N$_2$O) ambient of ~1 mbar corresponding to region II in the YBCO stability diagram of Fig. 6. Venkatesan et al.\textsuperscript{61} have shown by laser ionization mass spectroscopy that the emitted constituents from the YBCO target are primarily composed of binary and ternary suboxides. It was proposed that film stoichiometry reproduces the target composition because of the establishment of a dynamic equilibrium in the ablation process. Apart from $p_{O_2}$ and substrate temperature, the most significant PLE deposition parameters to optimize are laser wavelength, pulse duration, pulse energy density at the target surface and substrate to target distance. The most popular lasers for PLE-HTS fabrication are UV excimer lasers such as ArF ($\lambda=198$ nm), KrF ($\lambda=248$ nm) and XeCl ($\lambda=308$ nm).

![FIG. 20. Schematic picture of a vacuum chamber for pulsed laser evaporation of YBCO.\textsuperscript{62}](image-url)
Dijkkamp et al.\textsuperscript{62} were among the first to demonstrate the high potential in using PLE for reproducible YBCO thin film preparation. Presently, this technique constitutes somewhat of a working horse for HTS thin film fabrication in numerous laboratories worldwide. PLE-YBCO films exhibiting excellent physical properties have been demonstrated by e.g. Roas et al.\textsuperscript{63} and Singh et al.\textsuperscript{64}, the former using very low deposition temperatures (500-550 °C). The utilization of a multiple target sample holder makes PLE extremely versatile in preparation of superlattice structures and it has also become the dominant technique in fabrication of advanced HTS devices such as the one shown earlier in Fig. 4.

Compared to other methods used in YBCO film synthesis, it stands clear that the inherent advantage of PLE resides in its simplicity without the need for composition control or complicated deposition geometries. The feasibility of PLE has also been demonstrated using high deposition rates (~145 Å/s).\textsuperscript{65} On the other hand, a well-known disadvantage with PLE is the frequent appearance of surface irregularities on top of the growing c-axis oriented YBCO. Some of these can be directly attributed to particulates emerging from the target-laser beam interaction. Another kind of surface outgrowth in PLD films, also encountered in sputtered YBCO films, has been identified by Ramesh et al.\textsuperscript{66} as heterogeneous a,b-axis material nucleating at second phase regions.

Preparation and film properties

In this thesis work, c-axis YBCO films prepared by PLE are magnetically and electrically characterized (see paper 9). The layers were grown on MgO substrates by Michel Schwerdtfeger at LETI-CEA, Grenoble.\textsuperscript{67} In brief, layers were deposited at 750 °C in an oxygen pressure of 0.7 mbar using an excimer KrF laser system. The energy density of the laser beam was estimated to be in the range 1.0-4.2 J/cm\textsuperscript{2}. Surface morphology is in general smooth, although a careful optimization of deposition parameters have to be performed in order to avoid surface outgrowths.\textsuperscript{68} For the film reported on in paper 9, structural analysis revealed minor a-axis oriented portions from the XRD spectrum and a fairly wide rocking curve (FWHM=0.48°, MgO substrate).

The PLE film of paper 9 exhibited a normal-state resistivity of 260 μΩcm at 300 K and a slope in ρ(T)=3.1 resulting in a small positive intercept on the resistivity axis in the ρ(T) diagram. Zero resistivity temperature was between 88 and 89 K. Transport critical current density vs temperature is depicted in Fig. 21 showing a high J\textsubscript{c}(77 K) approaching 2 × 10\textsuperscript{6} A/cm\textsuperscript{2}. On the other hand, AC-susceptibility did not in generally yield sharp transitions as compared to evaporated or MOCVD films. This is shown
Pulsed laser evaporation YBCO/MgO 30 μm bridge

\[ J_c(77 \text{ K}) = 2 \times 10^6 \text{ A/cm}^2 \]

FIG. 21. Transport critical current density vs temperature for a PLE film.

in Fig. 22. This points to some inhomogeneity in the superconducting grains, for the moment not fully understood. Interestingly, the behaviour seen in Fig. 22 seems not to be highly detrimental for the \( J_c(T) \) properties of the PLE-film. ZFC and M(H) curves recorded for a PLE-YBCO film is presented in Fig. 23.

FIG. 22. Real-part AC susceptibility \( \chi' \) and third harmonic signal \( |\chi_3| \) for a PLE film, indicating an inhomogeneous superconducting film phase.
3.5. Sputter deposition

Sputter deposition (or sputtering) is a technique frequently applied for synthesis of traditional low $T_c$ superconducting thin films. Consequently, sputtering was quickly adopted in the first efforts to grow YBCO (and other HTS) in situ. Several approaches have been tested including multi-source and single-target sputtering using either an rf or an dc plasma discharge. The preferred concept has come to be single-target YBCO sputtering in a partial pressure of oxygen. If not special precautions are undertaken, such a process may give rise to serious resputtering effects of the growing film. This is due to the formation of negatively charged species, e.g. $O^-$ and $O_2^-$ during sputtering of an oxide target in an oxygen ambient. The ions will be accelerated by the cathode voltage towards the substrate and cause selective resputtering of the YBCO film. The phenomenon results in an inhomogeneous lateral distribution of Y, Ba and Cu which is highly detrimental for epitaxial growth of YBCO.

One way to avoid resputtering effects is to work at high pressures ~10 mbar, thereby reducing the kinetic energy of the bombarding species. The principle of such an on-axis system is demonstrated schematically in Fig. 24 (a). In practice, however, redistribution effects taking place in an on-axis geometry are difficult to fully eliminate. (Very recently, a new on-axis arrangement using an unbalanced magnetron was claimed to be successful in YBCO growth). A different approach is to locate the substrate outside the negative ion impact volume, thereby creating an off-axis arrangement (see Fig. 24 (b)). Such a concept, for example published by Eom et al., was proved to yield high quality YBCO layers in a large range of film thicknesses. One drawback is the difficulties in obtaining high total deposition rates. A more advanced off-axis scheme, introduced by Xi et al., is inverted cylindrical
magnetron sputtering (ICMS). A schematic is depicted in Fig. 24 (c). In ICMS, a cylindrical target is utilized and therefore, this method is often referred to as hollow cathode sputtering. A DC plasma discharge is activated in the cylinder and the substrates, located concentrically on the cylinder axis and below the glow-discharge area, are never exposed to negative ion bombardment. Compared to the off-axis solution in Fig. 24 (b), ICMS can be operated at relatively low pressures (< 1 mbar) and high deposition rates (0.5-1 μm/h).

FIG. 24. Different sputtering deposition geometries used for YBCO film synthesis: (a) on-axis, (b) 90° off-axis and (c) inverted cylindrical magnetron sputtering (ICMS).  

The various sputtering schemes presented above have all been shown capable of producing YBCO films of excellent quality exhibiting $J_c$'s of several million A/cm².
at liquid nitrogen temperature. However, sputtered YBCO films frequently suffer from the surface outgrowth phenomena mentioned above, although the potential for preparation of extremely smooth HTS surfaces exhibiting a film roughness down to the unit cell level has been demonstrated. Sputtering is also more likely to be extended to large area deposition than e.g. PLE.

**Preparation and film properties**

In the present thesis, sputtered YBCO films on MgO are treated in paper 9. The films were prepared by Axel Jäger at LETI-CEA, Grenoble using ICMS in an O₂/Ar mixture of 0.8 mbar and an approximate substrate temperature at 750 °C. Layers were strongly c-axis oriented with a rocking curve width FWHM = 0.69°. Cation composition of such a film (2200 Å thick) was determined by RBS using 5.0 MeV ⁴He ions. The RBS spectrum in Fig. 25 proves that the 1:2:3 stoichiometry in the YBCO target is accurately reproduced in the film material.

![RBS spectrum of an ICMS-YBCO layer.](image)

**FIG. 25.** RBS spectrum of an ICMS-YBCO layer.

Electrical properties of the ICMS film are excellent as demonstrated in paper 9. Normal-state resistivities are low with ρ(300K)=210 μΩcm and a R(300)/R(100)=3.0. It is notable that this particular film exhibited a very high T_c of 90.6 K, a value rarely encountered for in situ films. Figure 26 shows the transport critical current as measured for a 10 μm constriction on MgO, yielding J_c(77 K) in excess of 3 x 10⁶ A/cm². Similarly to laser ablated films, the AC susceptibility characteristics are not as sharp as coevaporated or CVD films (Fig. 27). Also the DC hysteresis loop at 30 K of the sputtered layer shown in Fig. 28 (b) resemble the PLE film characteristic in Fig. 23 (b), suggesting a similar J_c(H) dependence for the two specimens (film geometries and experimental arrangement were similar in the two cases).
3.6. Chemical vapor deposition

Chemical vapor deposition (CVD) or vapor phase epitaxy (VPE) has been in use for synthesis of thin film superconductors since the beginning of the 1960's. Later on, CVD became a significant technique for Nb₃Ge coatings on tapes and single filaments. In general, CVD offers several advantages for preparing multielemental superconducting films such as control over composition, microstructure and film thickness uniformity. There are also strong technological reasons for exploring a technique based on CVD: scale-up potential to large-area deposition, high growth rates and ability to coat complex shapes. With the introduction of HTS, CVD also has an inherent advantage because of its adaptability to a processing environment involving oxygen. Consequently, efforts in CVD of the HTS started not long after the promising prospects reported in physical vapor deposition (PVD) of HTS. The two first papers on the subject appeared in the beginning of 1988 by Berry et al. and
Yamane et al., the latter by an in situ deposition of YBCO. Except for the Yamane group, progress in CVD synthesis of YBCO were rather modest until 1990/1991 when several papers reported on high $J_c$ thin YBCO layers fabricated by CVD. From this time, superconducting properties of YBCO films made by CVD were fully comparable to those reported for PVD layers.

The slower progress in CVD as compared to PVD is connected with the search and development of suitable CVD precursor materials for HTS. Such a precursor material should be of high purity, resistant to ambience and, preferably, non-toxic. Of primary importance is the volatility and stability of the precursor, represented by the vaporizing temperature $T_v$ and decomposition temperature $T_d$, respectively. While a high volatility, i.e. a low $T_v$, is highly desirable in a CVD process, $T_d$ should not be too elevated for proper YBCO film formation around 700-800 °C. On the other hand, it is essential that the condition $T_d > T_v$ is fulfilled in order to avoid decomposition during vapor transport. In addition, the precursor material must be stable in time without any major changes in vapor pressure after prolonged evaporations. Finally, there should be no condensed by-products during decomposition of the precursor in the reactor zone.

The dominating precursor material class used in YBCO-CVD synthesis has been organometallic compounds, although halides have been reported to exhibit a potential in YBCO preparation by CVD. Metalorganic CVD (MOCVD) has been used for long time in epitaxial growth of III-V and II-VI semiconductors. The MOCVD precursors utilized for YBCO thin film synthesis (and other HTS as well) are the $\beta$-diketone metal chelates. The structure and nomenclature of such metal complexes are shown in Fig. 29. Volatilities range in the order (hfa) > (tfa) > (fod) > (thd) > (acac). Even though the fluorocarbon-based metal chelates are the most volatile, an ex situ anneal is in general required in order to remove the fluorine. The (thd):s (tetramethylheptanedionates) have gained the largest acceptance in YBCO synthesis by CVD and the highest quality MOCVD films are today grown using this kind of precursor. However, a large obstacle for reliable MOCVD processing is the poor reproducibility of the $\text{Ba(}\text{thd})_2$. Its volatility is relatively low and evaporation temperatures around 200-250 °C are needed, about 100 °C higher than the temperatures required for the $\text{Y(}\text{thd})_3$ and $\text{Cu(}\text{thd})_2$. Since decomposition of $\text{Ba(}\text{thd})_2$ already starts around 220-230 °C, serious stabilization problems are often encountered for this precursor. In addition, there is a gradual ageing of $\text{Ba(}\text{thd})_2$ taking place at room temperature resulting in decreasing transport rates as demonstrated by Busch et al. Thus control of the film metal composition is therefore an ever-present problem in MOCVD of YBCO using the $\text{Ba(}\text{thd})_2$ and good
A large range of technical solutions in MOCVD-YBCO have been reported, covering hot- and cold-wall reactors as well as horizontal and vertical reactor designs. There is a preponderance for conventional thermally assisted CVD based on multielemental deposition of Y(thd)$_3$, Ba(thd)$_2$ and Cu(thd)$_2$. Attempts to stabilize the long-term behaviour of Ba(thd)$_2$ have been made by saturating the Ar carrier gas with H(thd) (Ref. 84) or using a quadrupole mass-spectrometer for evaporation rate control (compare with the concept used in evaporation above).$^{35}$ Since 1991, low-temperature growth of YBCO using MOCVD has become a significant issue, thereby permitting growth temperatures around 650-750 °C. This can be achieved by (i) plasma-enhanced MOCVD$^{86}$ (PE-MOCVD), (ii) replacing O$_2$ with a more active reactant gas such as N$_2$O (Ref. 87) or O$_3$ (Ref. 88) and (iii) decreasing the pO$_2$ according to the YBCO stability diagram in Fig. 6.$^{89}$ New approaches in YBCO film
synthesis by CVD have recently been explored, e.g. MOCVD from a single-source and YBCO film deposition without carrier gas. Today, high quality MOCVD-YBCO films exhibiting zero-field $J_c: \sim 10^6$ A/cm$^2$ at 77 K have been demonstrated by several groups and in some case, $J_c(77 \text{ K}) > 5 \times 10^6$ A/cm$^2$ has been reported. The high $J_c(77 \text{ K})$: >10$^4$ A/cm$^2$ at magnetic fields of 30 T reported by Matsuno et al. are noteworthy. There are, however, difficulties in combining smooth surface morphologies with high quality superconducting properties for MOCVD-YBCO layers (see paper 8). This is the main explanation for the paucity of publications concerning MOCVD-YBCO multi-layered structures as compared with films fabricated with PVD techniques.

**Preparation**

The MOCVD set-up used for work reported in this thesis is shown schematically in Fig. 30 (a). It consists of a horizontal hot-wall reactor zone heated by rf induction. Each precursor material is loaded in an alumina crucible in a separate furnace. Evaporated species are transported by the Ar carrier gas through a heated zone and subsequently mixed with the two other precursor gases. High purity O$_2$ gas is added before entering the reactor zone. Prior to film deposition, the gas fluxes are allowed to stabilize through the by-pass line, see Fig. 30 (a). The total pressure of the reactor is controlled by a baratron. The substrate temperature was 820 °C and total pressure 5 mbar ($p_{O_2}$=3 mbar). Tetramethylheptanedionates of Y, Ba and Cu were used as precursors. The Y(thd)$_3$ and Cu(thd)$_2$ were of a commercial origin. In contrast, the Ba(thd)$_2$ was synthesized using an alkoxide process developed at Laboratoire de Chimie Moléculaire de Nice. Typical YBCO growth rates were between 0.5-1 Å/s.

The CVD process has been studied by growing single cation layers at different source temperatures (paper 8). The actual deposition rates in at/cm$^2$s obtained from RBS measurements of the cation films were correlated against the corresponding molar mass losses. As seen in Fig. 30 (b) for Y(thd)$_3$, the two measurements yield very similar activation energies when plotted as a function of inverse source temperature. Similar dependencies were observed for the Ba(thd)$_2$ and Cu(thd)$_2$. The behaviour suggests that the film growth rate is controlled by the kinetics of mass transport. The inset of Fig. 30 (b) also shows that actual deposition rates vs molar mass losses scale in the order of Cu, Y and Ba which is the same order as reported volatilities for corresponding chelates. From these results, approximate source temperatures can be derived as a starting point in YBCO synthesis. It was found that the amount of evaporated Y(thd)$_3$, Ba(thd)$_2$ and Cu(thd)$_2$ should be in the proportions 1:4:2 in order to obtain stoichiometric 1:2:3 YBCO in the film.
FIG. 30. (a) MOCVD set-up used in YBCO film synthesis: MFC=mass flow controller, tc=thermocouple. (b) Arrhenius plot showing molar mass losses for Y(thd)₃ and actual film deposition rate for Y as determined by RBS analysis. Inset indicates the actual deposited film rates for Y, Ba and Cu as a function of molar mass losses for Y(thd)₃, Ba(thd)₂ and Cu(thd)₂, respectively.
Film properties
The YBCO properties obtained are typical for MOCVD films with thicknesses between 1000-1500 Å as-grown on MgO. Some results for MOCVD-YBCO on LaAlO$_3$ are also presented.

Figure 31 (a) depicts the $\theta/2\theta$ scan for YBCO/MgO, showing a perfect c-axis alignment of the film. The strong (00$l$) texturing is a characteristic for the MOCVD-YBCO films. Rocking curves or $\omega$-scans, yielding information about the spread of the c-axis distribution, were recorded for the (00$l$) peak of YBCO. Results are shown in Fig. 31 (b) and (c) for YBCO layers on MgO and LaAlO$_3$, respectively. The FWHM are relatively narrow: 0.29° and 0.23° for MgO and LaAlO$_3$, respectively.

MOCVD films have been further studied with respect to in-plane texture. This type of analysis has proven to be very informative about the physical properties of YBCO. For example, small fractions of c-axis mis-aligned grains in YBCO films have been correlated to higher surface resistance values.$^{20}$ In the present study, in-plane texture was analyzed by recording X-ray diffraction pole figures$^{96}$ in the Schulz geometry.$^{97}$ In this method, the Bragg angle $\theta$ is fixed at a certain reflection while two other angles $\chi$ and $\Phi$ are rotated around the surface tilt axis relative to the x-ray beam and
FIG. 32. X-ray pole figures for an MOCVD-YBCO film obtained via a stereographic projection for the density of the normals to the (007), (013) and (113) planes. The projection plane is the film plane.

the surface normal axis, respectively. Three pole figures of a MOCVD-film on (100) MgO are plotted in a stereographic projection given in Fig. 32. The (007) pole figure shows a small extension of about 2°, indicating a high degree of c-axis alignment in the YBCO film. Rotation around the c-axis can be deduced from the (013) and (103) pole figures. The results given in Fig. 32 show a strong in-plane texturing with a small total angular spread in the detected pole figure signals. No reflections from mis-oriented grains can be observed in Fig. 32. The four-fold symmetry indicates a twinned structure, occurring during the tetragonal-orthorhombic transition. The results in Fig. 32 together with pole figure examinations of the MgO substrate
indicate that film-substrate relationship can be written YBCO [100]∥MgO[100] or YBCO [010]∥MgO[100].

A complementary structural analysis of a YBCO film on MgO was made by ion channeling using an incident beam energy of 2 MeV He. The resulting \( \chi_{\min} \) value evaluated behind the Ba surface peak was 10%. This number is much larger than what could be expected from a perfect crystal and therefore other types of defects must be present in the lattice. A TEM study of a similar MOCVD-YBCO film on MgO is reported on in Ref. 99. Planar defects visible in the TEM micrographs are suggested to be due to stacking faults associated with the addition of an extra CuO layer in the YBCO lattice and an \( a/2 \) (or \( b/2 \)) translation. This would then explain one significant contribution to the elevated dechanneling yields.

One example of the surface morphology of an MOCVD film is shown in Fig. 33. The film consists of a relatively smooth film matrix and micron-sized CuO precipitates as identified by EDX and XRD. This type of morphology is frequently encountered in an optimized MOCVD process and is probably due to off-stoichiometric growth of Y, Ba and Cu (the elemental ratios of the film in Fig. 32 is Ba/Y=1.5 and Cu/Ba=1.9). In paper 8, it is argued that the CuO precipitates are buried in a 1:2:3 stoichiometric YBCO film matrix. It appears that the presence of excess Cu promotes the formation of an epitaxial homogeneous YBCO matrix exhibiting strong screening properties. This was observed when systematically altering the metal composition of the MOCVD-YBCO films and studying the resulting physical properties (section 5.2.).

FIG. 33. SEM micrograph showing surface morphology of an MOCVD-YBCO film on MgO with film composition \( Y_{1.3}Ba_{2.0}Cu_{3.3}O_{7-x} \). Cu-rich film grains (identified by EDX) are clearly visible.
Superconducting properties of optimized MOCVD films are presented in Fig. 34-36. Such films are in general relatively rough, displaying numerous CuO precipitates. Resistivity vs temperature for a film on MgO is depicted in Fig. 34 (a). The zero resistivity of the MgO film is 86 K. Films made under identical conditions on LaAlO$_3$ display $T_c=90$ K. There is a clear correlation between high critical currents and low normal state resistivity values. Critical current densities are high for these type of films as shown in Fig. 34 (b): $J_c(77 \text{ K}) = 2 \times 10^6 \text{ A/cm}^2$ for YBCO and $3 \times 10^6 \text{ A/cm}^2$ on LaAlO$_3$.

The $J_c$ properties are corroborated by very sharp AC susceptibility transitions and extremely sharp peaks in the third harmonic signals (Fig. 35 for YBCO/LaAlO$_3$).
FIG. 35. AC-susceptibility characteristic for MOCVD-YBCO on LaAlO$_3$.

FIG. 36. (a) Zero-field cooling curve (10 Oe) and (b) magnetization hysteresis loop (30 K) for MOCVD-YBCO on LaAlO$_3$.

DC-magnetic properties are given in Fig. 36 for a film on LaAlO$_3$. The M(H) loop is different compared to similar films made by other techniques (and measured under the same conditions), possibly suggesting another pinning mechanisms in MOCVD films. (See M(H) diagram comparing different type of films in paper 9).

3.7. Thin film processing

The exploration of suitable thin film processing techniques is a prerequisite for the successful implementation of HTS layers in working electronic devices. Processing of HTS thin films involves patterning, preparation of ohmic contacts, multi-layer
synthesis and integration of HTS with other materials, in particular semiconductors. The experiences from semiconductor technology have been extensively used in processing of HTS films, although the special properties of these materials must be taken into account, e.g. the sensitivity of YBCO to changes in the oxygen content. The present paragraph focus on the two types of processing applied in this work, contact preparation and patterning.

Contacts
Among the first successful efforts in ohmic contact preparation to HTS were the investigations by Ekin and co-workers. They reported about very low contact resistivities in the $10^{-10} \Omega \cdot \text{cm}^2$ range for Ag and Au film contacts deposited on bulk-sintered YBCO. Subsequent research of Ag contacting to YBCO thin films have proved that the contact properties are strongly dependent on film quality and surface conditions. It was also recommended that in order to obtain low resistive contacts to YBCO, electrodes should be deposited immediately after film formation. This observation is closely connected to oxygen loss taking place at YBCO surfaces, rendering the top layer non-superconducting. Clearly, an in situ approach for contact preparation would be the optimum method; However, mostly by practical reasons such as flexibility and alignment considerations, contacts to YBCO are frequently deposited ex situ. A more advanced scheme in ex situ ohmic contact fabrication to YBCO has been reported in Ref. 102.

Here, gold contacts have been deposited ex situ on bare YBCO layers, mainly for the purpose of transport critical current measurements. Contacts have been made on unpatterned as well as patterned films. A typical approach used in Au contact preparation of YBCO films synthesized via the BaF$_2$ route is indicated in paper 4 where also a picture of the mask pattern is given. Gold electrodes, about 1000 Å thick, were prepared by using a lift-off technique involving Au sputter deposition onto a resist pattern made on top of the YBCO film. For the various YBCO films discussed in paper 9, gold contacts were prepared ex situ by Au evaporation through a mechanical mask pressed against the YBCO surface. For both methods, the time between YBCO fabrication and Au deposition was minimized. Elevated contact resistivities seldom presented any problems in $J_c$ measurements for the different films with the possible exception of MOCVD films where CuO precipitates in the YBCO film sometimes imposed a problem in reliable contacting to the superconductor.

Patterning
The basic point concerning patterning of HTS films is that the remaining film must stay unaffected against the patterning process. A number of patterning techniques have been examined for YBCO films such as wet chemical etching, lift-off processes,
ion implantation, laser etching, and ion milling. The most popular wet chemical etchants for YBCO are diluted HNO₃, H₃PO₄, and ethylenediaminetetraacetic acid (EDTA). Regarding dry etching methods, Ar ion milling has gained large acceptance as an efficient tool for high-resolution patterning of YBCO thin films. Fong et al.¹⁰³ have demonstrated fabrication of 0.23 μm wide lines in YBCO using a refined Ar ion milling process, although with a reduction in Jc. A good example of a patterning process of YBCO thin films intended for transport critical current measurements is described by Schomburg et al.¹⁰⁴ A patterning process may present problems if the YBCO films display rough surfaces and/or inhomogeneities. A general experience, however, is that epitaxial high quality layers rarely present any problems in conventional ion beam patterning.

Paper 4 and 6 discuss various patterning strategies of YBCO thin films prepared by the BaF₂ method on sapphire and perovskite substrates. An advantage with the BaF₂ method is that film deposition takes place at low temperatures (<150 °C), thereby enabling lift-off experiments. Otherwise, diluted HNO₃ (1%) or H₃PO₄ (1%) were used as etchants, in some cases prior to the post-annealing, in other cases after the annealing process. However, a general observation is that heat-treatments of the "BaF₂-films" after patterning seriously degrades superconducting properties. On the other hand, layers on SrTiO₃ or LaAlO₃ patterned after YBCO formation were observed to withstand the lithography process with no changes in Tc and Jc.

Papers 7, 8 and 9 all include films patterned by means of dry etching. YBCO layers were patterned by a conventional photolithographic method using S1818 positive photoresist followed by Ar ion milling. The latter was carried out in a system designed by Vide Appareillages Scientifiques de Suresnes. Typical ion milling parameters were an operating Ar pressure of 3 × 10⁻⁴ mbar, acceleration voltage of 500 V and a current beam density of 0.500 mA/cm². In order to obtain maximum etching rates of YBCO (~5 Å/s), it is of significance to optimize the angle between the film normal and the Ar ion beam.¹⁰⁵ Remaining resist on the film surface was removed by exposing the sample to acetone in an ultrasonic bath. No changes in superconducting properties were noticed when carrying out this process for all type of YBCO films discussed in section 3.2-3.6. The most critical step is the exposure of YBCO to acetone¹⁰⁶ which can be avoided by removing remaining resist in an oxygen plasma. Figure 37 (a) gives a visible example of a four-terminal pattern processed in this method. The starting material was a coevaporated YBCO film (2800 Å thick) with evaporated gold contacts on top. The high-resolution capabilities of the Ar ion milling process are clearly demonstrated by the etched 5 μm line in Fig. 37 (b) (magnified view of Fig. 37 (a)). Excellent superconducting properties (Tc=90 K,
$J_c(60 \text{ K})=10^7 \text{ A/cm}^2$) measured for the bridge indicate that the dry etching process does not deteriorate the starting material ($J_c(T)$ curve is given in Fig. 17 (b)).

FIG. 37. (a) Four-terminal pattern used for transport $J_c$ measurements showing film constriction and gold contacts. The film was etched by Ar ion milling. Contact pad area 0.49 mm$^2$. (Evaporated YBCO film, 2800 Å thick).
(b) Magnification of the constriction 5 μm in width demonstrating the excellent resolution in the Ar beam patterning process.
4. SUBSTRATES FOR YBCO THIN FILMS

There are a large number of factors to take into account when selecting a substrate material for YBCO thin films: Lattice match, thermal expansion coefficient, chemical stability, mechanical properties, surface morphology and high frequency electrical characteristics. In addition, cost and availability in large wafers cannot be neglected. No ideal substrate material for YBCO exists and the final choice will always constitute somewhat of a trade-off between the aforementioned properties. Historically, the first substrate used in successful synthesis of YBCO films was SrTiO$_3$. This material displays high chemical stability combined with an excellent lattice match to YBCO, thereby enabling epitaxial growth. A large disadvantage with SrTiO$_3$ is the high dielectric constant and inferior microwave properties rendering this material useless for high frequency applications. Consequently, a large number of substrates have been tested as substitutes for SrTiO$_3$ e.g. MgO, yttria-stabilized Zr (YSZ), LaAlO$_3$, LaGaO$_3$, YbFeO$_3$ and NdGaO$_3$. Also traditional substrates used in semiconductor technology such as Al$_2$O$_3$ (sapphire), Si and GaAs have been explored for YBCO film growth. However, this is a much more delicate task which is due to the large lattice mismatch and chemical reactivity at the high deposition temperatures used when forming YBCO. In general appropriate buffer layers are required between YBCO and the substrate. Large progress have recently been achieved in this area, see e.g. the work by Fork et al. regarding epitaxial growth of YBCO on Si using an intermediate buffer layer of YSZ.

This thesis reports on studies of two substrate materials for YBCO thin films. (In addition, a comparison between LaAlO$_3$ and MgO substrates for MOCVD-YBCO films has been performed in paper 8). The films have been made by the BaF$_2$ method and a brief summary of the results is given here. The first study discusses alternatives to SrTiO$_3$ as a suitable substrate for YBCO, see paper 6 and also ref. 108 and 109. Several substrates are evaluated and LaAlO$_3$ was found to be the most promising substitute for SrTiO$_3$. The second study is about YBCO formation on sapphire and is treated extensively in paper 3, 4 and 5. It is seen that reactions occur between the substrate and YBCO material during the post-deposition annealing. A model has been proposed for the degradation mechanisms occurring during the post-deposition heat treatment.

4.1. Perovskite-related substrates

The motivation for this work was to explore potential alternatives to the SrTiO$_3$ substrate in YBCO preparation using the BaF$_2$ method. Even though films exhibiting
superior electrical properties had previously been synthesized on SrTiO$_3$\textsuperscript{110} the high rf losses associated with this ferroelectric strongly called for another substrate material showing improved behaviour in the high frequency regime. A natural route is to investigate other perovskite systems with close lattice match to YBCO. The perovskite family, structurally based on CaTiO$_3$, is very large and some materials which have been tested for YBCO thin film growth include LaAlO$_3$, NdGaO$_3$, LaGaO$_3$, YbFeO$_3$, PrGaO$_3$ and KTaO$_3$. In the present study, LaAlO$_3$, NdGaO$_3$ and LaGaO$_3$ were selected as promising candidates for SrTiO$_3$. These substrates show good lattice match to YBCO combined with low losses in the high frequency regime. A summary of the substrate properties in terms of structure and rf characteristic, and lattice match as a function of temperature are given in Table IV and Fig. 38, respectively. In particular, Fig. 38 shows that the gallates have an excellent lattice match to YBCO\textsuperscript{111} However, a large drawback with perovskites are structural phase transitions occurring at elevated temperatures. This explains why LaAlO$_3$ and LaGaO$_3$ are strongly twinned and consequently, surface quality for these substrates are questionable. In contrast, NdGaO$_3$ does not exhibit any structural transitions below 1000 °C. Another twin-free substrate included in the study was CaNdAlO$_4$ which also exhibits low microwave losses. The CaNdAlO$_4$ is however not a perovskite; It is based on the K$_2$NiF$_4$ structure. As shown in Fig. 38, the CaNdAlO$_4$ lattice match to YBCO is therefore inferior as compared with the perovskites.

TABLE IV. Structural and rf properties of perovskite-related substrates for YBCO.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Crystal structure</th>
<th>Crystal symmetry\textsuperscript{a}</th>
<th>Dielectric constant\textsuperscript{b}</th>
<th>Loss tangent\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$</td>
<td>Perovskite</td>
<td>Cubic</td>
<td>&gt;300</td>
<td>0.1</td>
</tr>
<tr>
<td>LaAlO$_3$</td>
<td>Perovskite</td>
<td>Rhombohedral</td>
<td>24</td>
<td>3 x 10$^{-5}$</td>
</tr>
<tr>
<td>NdGaO$_3$</td>
<td>Perovskite</td>
<td>Orthorhombic</td>
<td>22</td>
<td>3 x 10$^{-4}$</td>
</tr>
<tr>
<td>LaGaO$_3$</td>
<td>Perovskite</td>
<td>Orthorhombic</td>
<td>26$^c$</td>
<td>1 x 10$^{-4}$</td>
</tr>
<tr>
<td>CaNdAlO$_4$</td>
<td>K$_2$NiF$_4$</td>
<td>K$_2$NiF$_4$</td>
<td>19</td>
<td>1 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}At room temperature.
\textsuperscript{b}At 1 GHz and 77 K.
\textsuperscript{c}At 1 MHz and 300 K.
The results from resistivity measurements on optimized "BaF$_2$-films" prepared on the various substrates are summarized in Table V. Best results are obtained for LaAlO$_3$ which display identical features in resistivity as SrTiO$_3$. On the other hand, films on LaGaO$_3$ and CaNdAlO$_4$ display inferior $T_c$'s than the other substrates. The film on LaGaO$_3$ indicated low critical current densities $\sim 10^{3}$ A/cm$^2$ at 77 K. Similar observations have been made by Koren et al.$^{112}$ and were proposed to be due to the heavy twinning of LaGaO$_3$. The reason for the inferior superconducting properties of untwinned CaNdAlO$_4$ might be a combination of large lattice mismatch and reactions occurring with the substrate. It was observed that the $T_c$ of YBCO films on CaNdAlO$_4$ depended critically on the annealing conditions in the BaF$_2$ process, a well-known trademark for chemically unstable substrates such as sapphire. Indeed, chemical instability at high formation temperatures was suggested by Young et al.$^{113}$
TABLE V. ρ(T) measurements for YBCO films prepared by the BaF$_2$ method on perovskite-related substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$T_c$ (K)</th>
<th>$ΔT$ (K)</th>
<th>ρ(300 K) (μΩcm)</th>
<th>$ρ(300 K)/ρ(100 K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$</td>
<td>91.0</td>
<td>1.2</td>
<td>300</td>
<td>3.0</td>
</tr>
<tr>
<td>LaAlO$_3$</td>
<td>91.0</td>
<td>1.2</td>
<td>300</td>
<td>3.0</td>
</tr>
<tr>
<td>NdGaO$_3$</td>
<td>89.9</td>
<td>1.7</td>
<td>450</td>
<td>2.6</td>
</tr>
<tr>
<td>LaGaO$_3$</td>
<td>87.0</td>
<td>2.3</td>
<td>270</td>
<td>2.0</td>
</tr>
<tr>
<td>CaNdAlO$_4$</td>
<td>85.5</td>
<td>2.9</td>
<td>660</td>
<td>2.1</td>
</tr>
</tbody>
</table>

for being partly responsible for inferior microwave performance observed in the YBCO/CaNdAlO$_4$ system.

The films on SrTiO$_3$, LaAlO$_3$ and NdGaO$_3$ were further evaluated by their transport critical current properties. Results from measurements on ion-milled bridges 40 μm in width and 1.0 μm thick, are depicted in Fig. 39. Maximum $J_c$(77 K) = $4 \times 10^5$ A/cm$^2$ are found for NdGaO$_3$ and LaAlO$_3$. Further on, YBCO films on LaAlO$_3$ were studied as a function of film thickness and annealing conditions by means of recording magnetization loops (paper 6). (Observe that NdGaO$_3$ is not suitable for this type of analysis because of its magnetical properties). A significant observation was that thinner films (1000 Å) on LaAlO$_3$ displayed higher magnetical $J_c$'s (H=0) than thicker films (3000-5000 Å). The reason for this is not fully clear; It might be due to a more homogeneous c-axis film texture developed in a 1000 Å film as compared with thicker films which typically display mixed a- and c-axis growth resulting in a porous basket weave structure earlier mentioned. The highest $J_c$'s achieved for the 1000 Å films on LaAlO$_3$ were $10^6$ A/cm$^2$ at 77 K and $10^7$ A/cm$^2$ at 20 K. These $J_c$-values are in the same order as the highest reported for "BaF$_2$-films".

Although this investigation is far from complete (examinations of film structural and rf properties should preferably be added), some general statements can be made. For microwave applications of YBCO, LaAlO$_3$ seems to be the most favorable substrate as shown in Table IV. Even though YBCO on NdGaO$_3$ exhibits similar $J_c$ properties as on LaAlO$_3$, the former has a loss tangent that is ten times greater than LaAlO$_3$, see Table IV. Microwave performance has indeed been proven to be superior for YBCO on LaAlO$_3$ as compared to NdGaO$_3$. In addition, direct comparisons carried out by Phillips et al. between "BaF$_2$-films" prepared on these two substrate materials.
revealed worse structural properties for NdGaO$_3$ than for LaAlO$_3$ as seen by channeling analysis. (This was attributed to the formation of YGa$_6$ in the YBCO/NdGaO$_3$ system.) In summary, LaAlO$_3$ appears as the best choice for the process described, although twinning and lattice mismatch may present future obstacles in preparing ultrathin films or multilayers.

From paper 6, it is seen that the investigation discussed above also included traditional substrates used in microwave applications, i.e. sapphire, MgO and LiNbO$_3$. Compared with the perovskites in Table IV, such substrates display relatively large mismatch relations to the YBCO unit cell. In the study reported on in paper 6, T$_c$:s were all above 77 K for the YBCO films prepared on sapphire, LiNbO$_3$ and MgO. However, SIMS analysis showed that for the two former materials, substantial film-substrate intermixing occurred. MgO appeared stable in the SIMS spectrum. Nevertheless, the film was highly degraded exhibiting very high resistivities and depressed T$_c$:s < 80 K. This is probably due to the hygroscopic nature of the MgO material, being highly unadaptable for the wet oxygen process associated with the BaF$_2$ method.
4.2. Sapphire

The preparation of YBCO thin films on sapphire using the BaF\(_2\) method was studied extensively during the first part of this thesis work. In this thesis, the results are summarized in paper 5. Direct comparisons with the perovskite substrates LaAlO\(_3\) and SrTiO\(_3\) are also presented therein. Papers 3 and 4 add details about post-annealing optimization studies and patterning experiments for the system YBCO/sapphire. Paper 5 gives a comprehensive study of the current knowledge in the field and this paragraph provides the significant conclusions from this paper.

For future HTS thin film applications, the sapphire substrate is of interest because of its outstanding high frequency properties: Its dielectric constant is 9.9 (room-temperature value) and the loss tangent below 10\(^{-6}\) at 1 GHz and 77 K (compare with values quoted in Table IV). Sapphire displays a hexagonal structure (a=4.763 Å, c=13.0 Å) and a thermal expansion coefficient less than that of YBCO (8 and 13 \(\times\) 10\(^{-6}\) °C\(^{-1}\), respectively). For sapphire cut in the r-plane, the lattice mismatch to YBCO is between 5 and 10% combined with an angular misfit of about 4°. Highly c-axis oriented films grown directly on sapphire, although with poor in-plane epitaxy, have been demonstrated by Char \textit{et al.}\(^{117}\) using PLE at low substrate temperatures < 700 °C.

The primary problem when forming YBCO on sapphire is chemical reactions occurring above 700 °C. In this study, the investigations of the system YBCO/sapphire intended to elucidate electrical and material degradation mechanisms occurring in "BaF\(_2\) films" fabricated on sapphire substrates. Layers of about 1 \(\mu\)m thickness were prepared using the BaF\(_2\)-route described in section 3.2. The zero-resistivity temperatures are typically in the range 80-85 K depending on initial composition of the precursor film and annealing conditions (see Fig. 10). Normal-state resistivities are relatively large with typical room-temperature values in the order of mΩcm. Resistivity curves vs temperature display a very different behaviour compared to the \(\rho(T)\)-curves found from corresponding films on SrTiO\(_3\). After an onset around 90 K followed by a rapid decrease in resistivity, the \(\rho(T)\) curves of YBCO/sapphire exhibit a characteristic tail towards zero resistance. Further on, inhomogeneities in the superconducting phase are clearly observed by DC susceptibility analysis, showing a very broad response as a function of temperature. The transport critical current densities are order of magnitudes lower than the numbers observed for films on perovskite substrates.

The observations above are consistent with different superconducting on-sets between the grains (intergrain) and within the grains (intragrain). More specific, zero
resistance is a result of percolation, i.e. dc conduction along filamentary paths of least resistance. The films are probably made up of weakly coupled superconducting grains. This is to be contrasted to films made exactly in the same manner on perovskite substrates where the films, although polycrystalline, consist of grains strongly coupled through the "basket weave" structure.

![Graph](image)

**FIG. 40.** 2θ-scan of a YBCO film synthesized by the BaF$_2$ method on sapphire indicating the formation of poly-crystalline YBCO and impurity phases such as 211 (o), CuO(+) and BaAl$_2$O$_4$ (*).

A major reason for the degraded superconducting behaviour of YBCO films on sapphire can be seen from Fig. 40. The XRD spectrum shows the formation of a polycrystalline YBCO film together with impurity phases, mainly BaAl$_2$O$_4$. Also CuO, Y$_2$BaCuO$_5$ and Y$_2$O$_3$ can be found from XRD spectra of the system YBCO/sapphire. The chemical reaction

$$2YBa_2Cu_3O_{6.5} + 4Al_2O_3 \rightarrow Y_2O_3 + 6CuO + 4BaAl_2O_4$$ (3)

has been proven to be thermodynamically favorable when forming YBCO on sapphire.$^{118}$ Paper 6 (and 5) presents a model of the degradation occurring when forming Y-BaF$_2$-Cu-O precursor films on sapphire, see Fig. 41. The model is based
FIG. 41. Simple model for the degradation of YBCO during the post-anneal of a Y-BaF$_2$-Cu-O layer on sapphire.

on XRD, SIMS and RBS measurements performed on identical precursor films heat-treated at different times and/or temperatures. In this way, various levels of degradation in the system YBCO/sapphire can be discerned. The observations were corroborated by preparation and analysis of YBCO/X/Al$_2$O$_3$ structures where X=Y$_2$O$_3$, BaAl$_2$O$_4$ or CuO. A formation of BaAl$_2$O$_4$ is proposed to take place in the interfacial region of the film, see Fig. 41. Excess Cu and Y will transform into CuO, Y$_2$BaCuO$_5$ and Y$_2$O$_3$ (the various layers indicated in Fig. 41 are not considered as distinct and should be regarded as more or less intermixed with each other). It is also possible that Al originating from the substrate diffuses through the film grain boundaries to the top layer. In particular, Keim et al.$^{119}$ have pointed out the existence of BaAl$_2$O$_4$ in the grain boundaries of YBCO layers reacted on sapphire. Such a formation would be detrimental for the establishment of high critical currents in a YBCO film made on sapphire. Prolonged annealings of the YBCO/sapphire samples will totally consume the YBCO phase and result in BaAl$_2$O$_4$, CuO and Y$_2$Cu$_2$O$_3$. 
5. YBCO FILM STOICHIOMETRY

5.1. Oxygen stoichiometry

The oxygen content in a YBa$_2$Cu$_3$O$_{7-x}$ thin film is largely determined by the ramp-down procedure applied after film growth at elevated temperatures. During this stage, the variable $x$ approaches zero because of filling up non-occupied oxygen sites in the tetragonal YBCO lattice structure, see Fig. 1. As already mentioned, the oxygen content is crucial for the final superconducting film properties ($T_c$ decreases with increasing value of $x$). In this thesis work, however, oxygen stoichiometry has not been subject to study. This is due to the large difficulties in precise determination of the oxygen content in a YBCO thin film sample. Raman spectroscopy and X-ray diffraction have been applied for oxygen determination in thin films. The former encounters difficulties associated with anisotropic Raman intensities for $c$-axis oriented thin films. Determinations of the $c$-axis lattice parameter from XRD data have been correlated to the oxygen content in YBCO powder samples. However, this method also presents problems which is due to measurement uncertainties and/or possible $c$-axis expansion effects in YBCO thin films.

Figure 42 illustrates the effect of oxygen annealings at low temperatures on the transport critical current of a patterned MOCVD-film on MgO. In (a), the $J_c(T)$ measurement was suffering from high Au contact resistances thus giving rise to a poor critical current characteristic. In order to improve the contact properties, an annealing at 300°C for 1 hour was accomplished in flowing O$_2$ kept at 1 atm. As can be seen in Fig. 42 (b), this treatment was successful with respect to the contacts. However, the YBCO superconducting properties were seriously degraded, now exhibiting a $T_c$ around 50 K and $J_c(4 K) \sim 10^6$ A/cm$^2$. This degradation in superconductivity can be attributed to removal of oxygen atoms from the CuO chains in the YBCO lattice, thereby strongly affecting $T_c$. By performing a second annealing under identical oxygen conditions but this time at 400°C for 24 hours, oxygen can be incorporated in the MOCVD film and the superconducting properties fully recovered, see Fig. 42 (c). Observe that the curves in (c) and (a) superimpose nicely. Figure 42 provides a good illustration of the reversible electrical properties of YBCO thin films considering the oxygen content.
FIG. 4. Changes in \( J_c(T) \) behavior of an MOCVD film when exposed to low temperature.

(a) 400°C, 24 h oxygen anneal

(b) 300°C, 1 hour oxygen anneal

(c) YBCO/MgO 30 μm bridge MOCVD
5.2. Cation stoichiometry

The cation composition of YBCO corresponds to the ratio Y:Ba:Cu which nominally equals 1:2:3. However, in YBCO thin film synthesis, deviations from cation stoichiometry are always likely to occur, in particular for multi-source deposition systems such as CVD and coevaporation. For the latter case, a system for cation composition control based on a quadrupole mass-spectrometer was presented in section 3.2. (and paper 1). In this paragraph, compositional effects of MOCVD-YBCO films are considered. The investigation can be found in paper 8.

The objective of this work was to map a region of the cation compositional diagram and look to changes in physical properties of MOCVD-YBCO thin films. A large number of samples ~1000-1400 Å were grown on MgO substrates using the method described under paragraph 3.6. The cation composition was varied by changing the source temperatures of the precursor furnaces for each deposition. By performing high energy RBS analysis (4.3 MeV), the cation elemental peaks could be separated in the RBS spectra and thus cation film ratios could accurately be determined. The films covered a large range of compositions: 1.1< Ba/Y <2.3 and 1.5< Cu/Ba <4.6, see compositional diagram in paper 8. All samples were then subjected to structural, microscopical, electrical and magnetical characterization.

One key point of paper 8 is that several important physical quantities of the layers remain relatively unaffected by large variations in cation compositions. One example is the strong (00\ell) film texture revealed by XRD analysis, another is the zero resistivity temperature. Figure 43 shows the resistive transitions and the c-axis lattice parameter as a function of Ba/Y. In contrast to results reported for coevaporated layers by Matijasevic et al.,\textsuperscript{121} neither a maximum in T\textsubscript{c} nor any c-axis expansion is observed for the MOCVD films. On the other hand, morphology is largely affected by the changes in cation composition, clearly demonstrated in paper 8 for variations in the Cu content of the YBCO film. The smoothest film is the one closest to 1:2:3 composition, see Fig. 4 in paper 8.

One significant explanation of the above observations is that the MOCVD films consist of a superconducting matrix with embedded grains (or precipitates), mainly consisting of CuO. It was shown in paper 8 that the composition of the matrix was approximately 1:2:3, thereby accounting for the anomalous large compositional regions exhibiting large T\textsubscript{c}:s. The strong screening capabilities of the MOCVD films, however, show a more limited compositional range in the Cu/Ba ratio. Surprisingly, sharp transitions are absent for the sample being closest to proper 1:2:3 ratio. A discussion regarding these observations is given in paper 8.
The best superconducting properties for the MOCVD-YBCO films on MgO were found from Ba-deficient samples (Ba/Y=1.6 and Cu/Ba=3.5) with $T_c=85$ K and $J_c(77 \text{ K}) = 1.2 \times 10^6 \text{ A/cm}^2$. A trade-off between smooth film surfaces and high quality electrical film properties were observed for Ba/Y=1.5 and Cu/Ba=1.9 resulting in $T_c=81$ K and $J_c(77 \text{ K})=3 \times 10^5 \text{ A/cm}^2$. Almost the same optimum cation ratios were found by Li et al.\textsuperscript{122} but in this case for an PE-MOCVD process and LaAlO$_3$ substrates.

FIG. 43. (a) Superconducting resistive transition ($T_c - T_{onset}$) and (b) $c$-axis lattice parameter as a function of the Ba/Y ratio in MOCVD thin films.
6. CRITICAL CURRENTS IN YBCO THIN FILMS

One of the most significant parameters of a superconductor is its DC critical current density ($J_c$). In technology, future applications of new superconducting materials will largely rely on their critical current capabilities, no matter how large $T_c$. In understanding the electromagnetic properties of type II superconductors, $J_c$ measurements as a function of field and/or temperature may provide valuable information about the flux dynamics in the material. Hence appropriate estimations of $J_c$ have long been regarded as an essential part in experimental superconductivity research and this fact has even become further accentuated for the HTS. This is due to their unconventional physical properties which strongly affect the critical current behaviour, e.g. short coherence length, large anisotropy and granular character.

In this thesis, the critical current density vs temperature of YBCO thin layers has been studied extensively. The major work is collected in paper 9, although $J_c(T)$ curves also can be found in papers 5, 6, 7 and 8. In paper 9, however, the $J_c(T)$ properties of YBCO thin films constitute the central issue: The paper reports on a comparative study of different $J_c$ measurements applied on various YBCO layers. In this section, a short summary is given of the main results obtained in paper 9, starting with a brief recapitulation over theoretical models describing the thermal critical current behaviour in type II superconductors.

6.1. Theoretical models

The models presented below are well established and the associated terminology is frequently used in the literature. The focus is put on the functional dependence of $J_c(T)$; The various experimental tools for determining the $J_c(T)$ behaviour are given in section 6.2.

**Anderson-Kim flux creep model**

The flux-creep model yields an expression for the critical current dependence in a homogeneous type II superconductor. Consider a superconducting film at $T>0$ sustaining a transport current in zero field. Upon increasing the current, vortices will enter into the film ($H>H_{c1}$) and a critical state will establish in the material. The Anderson-Kim theory accounts for dynamical effects of the flux lines attributed to thermally assisted jumps of vortices from one pinning site to another. The drift velocity $v$ of the flux lines will then be:
where \( U(t) \) is the pinning barrier, \( v_0 \) is the drift velocity in the absence of a pinning barrier and \( W(t) \) represents the minimum energy for moving a flux bundle on a characteristic length scale.\(^{124}\) (Here \( t = T/T_c \) is the reduced temperature). The transport current enters into Eq. (4) through \( v \) and \( W(t) \). The former quantity is evaluated from the induced electrical field \( E = v \times B \) acting on the vortices which in this case (no external field and EIU) simply will be \( E = v \beta J(t) \) (\( \beta \) is a temperature-independent constant). \( W(t) \) can be related to \( J(t) \) through the thermodynamical critical field \( H_c \) and the coherence length \( \xi \) giving an implicit expression for \( J(t) \):\(^{125}\)

\[
\frac{E}{v_0 \beta J(t)} = e^{-(U(0)/k_B T)} \sinh \left[ \frac{J(t) \Phi_0 \xi^2}{k_B T} \right]
\]

\( \Phi_0 \) is the flux quantum. What remains to elucidate is the temperature dependent terms in Eq. (5). Tinkham\(^{126}\) has shown that the pinning barrier can be expressed as:

\[
U(t) = U(0)(1 + t^2)^{3/2}(1 - t^2)^{1/2}
\]

where \( U(0) \) is the vortex pinning potential at zero temperature. Further on, \( \xi(T) \) is easily derived from the Ginzburg-Landau theory and empirical relations for \( H_c \) and \( \lambda \):

\[
\xi \sim \sqrt{\frac{1}{H_c \lambda^2}} \sim \sqrt{\frac{1 + t^2}{1 - t^2}}
\]

Equations (5), (6) and (7) can be utilized in performing experimental curve fitting to the theory of flux creep. The Anderson-Kim model results in an approximately linear \( J_c(T) \) dependence for \( t < 1 \). This can be seen in the fit made over a large temperature interval in Fig. 6, paper 9 for transport data obtained from a coevaporated YBCO film. The fitting parameter with most straightforward physical interpretation is \( U(0) \).
In the case of the coevaporated film, the optimal fitting resulted in a vortex pinning potential of 50 meV. This value can be compared to U(0) numbers of 60 meV calculated from remanent magnetization measurements vs temperature for MOCVD-YBCO films on SrTiO$_3$.\textsuperscript{127}

Granular superconductors

In the theory for granular superconductors, the material is modelled as a collection of superconducting grains connected through weak links. Such weak links can be either grain boundaries, poor superconducting regions, normal conducting or insulating barriers. The two latter cases will be considered below. This kind of modelling is particularly interesting for HTS which often display an inhomogeneous granular character.

SIS model

In the superconductor-insulator-superconductor (SIS) picture, the barriers are considered as insulating. Here the model of Clem is outlined for determination of the $J_c(T)$ dependence.\textsuperscript{128} In this model, the superconductor is divided into a cubic array with lattice parameter $a_o$ and grain size $V_G$. The grains are weakly coupled via the Josephson current $I_o$. The core of the theory is to consider the relationship $\varepsilon$ between the intergranular coupling energy $E_J$ and the intragranular condensation energy $E_G$: $\varepsilon = E_J/2E_G$, where $E_J = \hbar I_o / 2e$ and $E_G = H^2V_G / 8\pi$. Clem showed that the parameter $\varepsilon$ could be expressed as $2\xi^2/a_o^2$. Now, consider the limit $\varepsilon \ll 1$. In this regime, the intergranular currents are small and suppression of the superconducting gap parameter is negligible. For a thin film with thickness $d$, the critical current will simply equal $J_c(T)$.

$$I_o(T) = \frac{\pi \Delta(T)}{2eR_n} \tanh \frac{\Delta(T)}{2k_BT}$$  \hspace{1cm} (8)

Equation (8) is the Ambegaokar-Baratoff expression for the maximum tunnel junction current.\textsuperscript{129} In Eq. (8), $\Delta(T)$ stands for the BCS superconducting gap parameter and $R_n$ corresponds to the tunneling resistance of the junction in the normal state. For $T \rightarrow T_c$, $J_c$ will be proportional to $\Delta^2(T)$ and

$$J_c \sim (1-T)$$  \hspace{1cm} (9)
For $\varepsilon >> 1$, the Josephson coupling energy is much larger than the condensation energy of a grain and the gap suppression becomes significant. In this limit, the critical current reduces to the Ginzburg-Landau expression in the dirty limit:

$$J_c \sim (1-t)^{3/2}$$  \hspace{1cm} (10)

which is valid near $T_c$. For $\varepsilon < 1$, the theory by Clem predicts a crossover from Ambegaokar-Baratoff dependence at low temperatures to Ginzburg-Lindau dependence when $T$ approaches $T_c$.

**SNS model**

When the barriers consist of normal conducting material such as a metal, the superconductor is built up by an array of superconducting-normal conducting-superconducting (SNS) junctions. Such junctions cannot be described by the Ambegaokar-Baratoff theory. In this case, the granular SNS material is invoked in a proximity-effect junction model. This modelling has been elaborated by e.g. de Gennes\textsuperscript{130} and Clarke\textsuperscript{131}, resulting in the following expression for the maximum SNS current:

$$I_o(t) \sim (1-t)^2 \exp \left[ -\frac{a_n\sqrt{t}}{\xi_n(T_c)} \right]$$  \hspace{1cm} (11)

The parameter $a_n$ stands for the width of the normal conducting barrier and $\xi_n$ is the penetration distance of the Cooper pairs into the normal conducting layer. The critical current will largely depend on the ratio $a_n/\xi_n$.\textsuperscript{125} In the limit $t \to 0$, the exponential term dominates. However, when $t \to 1$, another $J_c$ dependence is found:

$$J_c \sim (1-t)^2$$  \hspace{1cm} (12)

The various functional behaviours of $J_c(t)$ found near $T_c$ can be used in curve fittings for a granular superconductor. Such fittings were performed in paper 9 where $J_c(T)$ data close to $T_c$ measured on various YBCO films were found to be well described by $J_c \sim (1-t)^n$. The values of $n$ differed for films prepared by different techniques. However, great care should be taken when interpreting the nature of weak links in a film on the basis of fittings from the $J_c(T)$ curves in this temperature regime. This is due to uncertainties in $J_c$ measurements near $T_c$ and relatively small differences...
between the models. Nevertheless, almost identical \( J_c \) dependencies (close to \( T_c \)) were observed both in transport measurements and AC susceptibility analysis. It would probably be advantageous to extend the measurements in paper 9 to the field dependence of the critical current density.

6.2. Measurements of critical currents

The three different methods of measuring \( J_c(T) \) used in paper 9 are transport measurements, non-linear AC susceptibility measurements and DC remanent magnetization. The principles of the measurements are given below.

**Transport measurements**

Direct transport measurements allow the most easy interpretation of the critical current: It is the zero-voltage current within the accuracy of a predetermined electrical field criterion. Here, measurements have been performed on patterned samples as shown in Fig. 37 using an AC method where the current was swept at a frequency of about 10 Hz. Figure 44 illustrates an I-V characteristic obtained by this method. The straight line on the ordinate (I-axis) corresponds to twice the critical current.

**FIG. 44. Typical I-V curve of a superconducting microbridge in transport measurements using an AC current technique.**
Non-linear AC susceptibility analysis was applied in determination of the critical current behaviour close to $T_c$. This type of $J_c(T)$ determination is simple, fast, highly sensitive and non-destructive. However, interpretation of measurements and derivation of absolute $J_c$-values are not straightforward. The detection of non-linear harmonics reflects the movement of vortices when passing the superconducting transition. This type of measurement is therefore closely connected to the transition from a flux flow to a flux pinning state in the superconductor. Indeed, non-linear AC susceptibility analysis has been utilized in determinations of the irreversibility line in HTS.

The film was sandwiched between an excitation coil and a single detection coil and the response of the third harmonic signal $|X_3|$ was recorded as a function of temperature. (No DC field was used in these experiments). A single peak in $|X_3|$ appears near $T_c$ for a homogeneous superconducting layer as predicted in the Bean model. This type of response is associated to dissipative losses occurring in the film prior to establishment of a sufficiently strong screening current. In paper 9, the $J_c(T)$ behaviour was found from several measurements of the $|X_3|$ signal against temperature for various excitation fields. The critical current is then considered to be linearly dependent on the excitation coil current. This can be understood in the framework of the Bean model. The temperature value of the peak in $|X_3|$ corresponds to the full penetration field $H_p$. By performing many measurements at various external fields, the temperature dependence of $H_p$ will be mapped. Since the Bean model states $J_c \propto H_p$, the $J_c$ can in a first-order approximation be regarded as linear dependent on the excitation coil current. The proportionality factor will be a function of film geometry and a coupling factor between coil and film. In paper 8 and 9, the proportionality factor was experimentally determined by means of calibration against transport measurements. Films with different $J_c$ capabilities and characteristics resulted in the same calibration constant.

DC remanent magnetization

The final method in determination of $J_c(T)$ is based on the recording of magnetical hysteresis cycles at constant temperatures with the applied field perpendicular to the film surface. This detection represents a static type of measurement; It assigns the trapped flux in the film to loss-free currents circulating in the sample. $J_c$ is determined through the well-known Bean equation in a cylindrical geometry: $J_c = 30 \times M_{\text{rem}}(H=0)/R$ where $M_{\text{rem}}$ is the remanent magnetization in emu/cm$^3$ and $R$ represents an effective radius in cm for the sample. This equation has also been proven to be approximately valid in a thin film geometry where the current is
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described by the more realistic Kim-Anderson form \( J_c = \alpha/(H+H_o) \).\(^{135}\) The Bean equation relies on a number of assumptions, e.g. that no strong-weak link behaviour is present in the sample. Such aspects are discussed in paper 9.

6.3. Comparative studies

Figure 45 shows one example of the three different \( J_c \) methods performed on the same specimen. Observe that the results from AC susceptibility covers only a small temperature interval near \( T_c \) (0.9<\( t \)<1) and that the values have been calibrated against the transport measurements. One important observation is that the magnetic \( J_c \) is lower than the transport \( J_c \), typically with a factor of 2. Paper 9 discusses potential reasons; possible explanations might be different critical current criteria, ill-defined sample geometries and an oversimplified Bean equation. Also seen in Fig. 45 is that results from transport measurements and AC susceptibility analysis yield approximately the same functional behaviour. This is substantiated by fitting \( J_c \sim(1-t)^n \) where the same value of \( n \) is found for the two critical current measuring techniques. Thus the non-linear AC susceptibility measurement would offer a rapid examination of the \( J_c \) properties near \( T_c \) and absolute values are obtainable via a calibration procedure. Further on, the various \( J_c \) methods applied on different high quality YBCO films grown by different techniques give a consistent picture as demonstrated in paper 9. A conclusive remark is that none of the three \( J_c \) methods rarely can account for the full \( J_c(T) \) dependence; In general, more than one measurement technique will be required for detailed studies of the thermal critical current behaviour.
FIG. 45. $J_c(T)$ of an evaporated film on LaAlO$_3$ measured by three different methods: AC-susceptibility, DC magnetization loops and transport measurements.
7. CONCLUDING REMARKS

This thesis has demonstrated various techniques for preparation of YBCO thin films. The films have been characterized regarding their physical properties. Special attention has been paid to the substrate (BaF$_2$-films) and the cation stoichiometry (MOCVD films). Critical current densities vs temperature have been measured and evaluated for all type of YBCO films. In this section, some concluding remarks will be made and future work suggested.

One ex situ method and four in situ methods in YBCO thin film preparation have been presented. Regarding dc electrical properties, all the methods have proven to be capable of producing high quality films. However, the epitaxial growth process attainable when growing films in situ yields the highest overall quality, see the film properties collected in Table II. At the present stage, the BaF$_2$ method therefore appears obsolete. Nevertheless, the BaF$_2$ method has inherent advantages in simplicity and versatility and is extremely adaptable for single layer depositions over large areas. The recently proposed approaches using low oxygen partial pressures during film crystallization$^{26}$ might also stimulate further activities for the BaF$_2$ method. The stabilizing role of BaF$_2$ during film crystallization is still not clear and should be paid special attention in future studies.

Clearly, the selection of an in situ deposition technique for YBCO will be a trade-off between a factors of which several have been mentioned in chapter 3. In application-minded work requiring reproducible fabrication of YBCO in multilayered structures, PLE and sputtering seems to be the preferred choices today. In the long run, however, it is highly possible that CVD will emerge as an important competitor. This is due to its potential manufacturing capabilities, allowing scaled-up deposition areas and high throughput. For applications not requiring atomically smooth surfaces, e.g. screening of electromagnetic fields, the CVD technique should be prospected in the near future. The intricate connections between homogeneous film morphologies and superconducting properties for MOCVD-YBCO films have been demonstrated in the thesis and similar studies will be needed in order to elucidate optimum growth conditions. Rapid improvements might evolve with new types of precursors and/or modified CVD approaches such as single-source systems. It is not impossible that development of CVD synthesis of YBCO will become similar to that one encountered in MOCVD epitaxial growth of III-V semiconductors where inferior precursor materials hampered advancement in the past.

Evaporation using an atomic oxygen beam source was shown to yield high quality YBCO films in situ. The highest $J_c$ numbers at 77 K for all films treated in this thesis
were found in evaporated films. The large advantage of an evaporation/MBE approach resides in its flexibility, permitting investigations of a large number of growth parameters. Reflected high-energy electron diffraction (RHEED) during YBCO growth might yield valuable information about film formation. However, it is not likely that evaporation will have any larger impact on applications involving YBCO thin films, let alone on a laboratory scale. Rather, the advantages can be found for investigations concerning basic thin film growth studies. On the other hand, it is possible that evaporation allows lower substrate temperatures than other methods for proper formation of the YBCO structure which may be related to atomic mobilities during film growth. This would be highly advantageous in epitaxial growth of YBCO on semiconductor substrates.

Various substrates of importance for HTS applications have been investigated and LaAlO$_3$ was found to be the most suitable replacement for SrTiO$_3$ regarding films made by the BaF$_2$ method. The conclusion was made on the basis of electrical and magnetical measurements. However, such studies must be followed up by structural and microwave examinations. New generations of untwinned lattice matched substrates in large size wafers are needed in the future. In applications not relying on low RF losses, SrTiO$_3$ is still a very good choice.

From a physics point of view, the thesis indicates several advantages in using thin films of YBCO in basic research of HTS. Probably, the highest degree of material perfection in HTS is today achieved in YBCO thin films. Thin films can be fabricated in a relatively controlled manner and the technology offers a large number of variables to be altered, thereby affecting superconductivity. The critical current measurements reported on here call upon the necessity in understanding the origin of pinning in HTS thin films. These materials show a broad range of defects and it is by no means clear which of them act as effective pinning centers. Also one cannot exclude the possibility of an intrinsic pinning mechanism associated with the layered structure. It would be highly desirable in the future with a more unified approach involving material, structural, electrical and magnetical measurements. It is a striking fact that films made under totally different growth conditions all can yield high critical current densities above $10^6$ A/cm$^2$ at 77 K. What type of pinning mechanisms which are responsible for such critical currents will constitute a key issue in future research.

Considering the very unusual properties of the YBCO compound, the large progress made in the field of thin film growth during the recent years are remarkable. Even though many properties in the YBCO remains to be understood, the present mastery of a thin film technology gives an optimistic picture for future applications. Without
doubt, the HTS revolution resulting in $J_c:s > 10^6$ A/cm$^2$ at liquid nitrogen temperatures has meant that the market potential for superconductors is now orders of magnitude higher as compared with the time before the discovery of Bednorz and Müller. Microwave components are now already on the market. For active circuits, much work remains in processing and integration of the HTS films in multilayers and microstructures. Increased control and understanding of film orientation, ultrathin layers and grain boundary properties will probably be studied. Certain application niches may evolve, utilizing the unique properties of superconductors. Hybrid technologies based on HTS and other materials, e.g. semiconductors, are likely to be developed. If HTS applications based on active circuits will have any greater impact on the electronics market in the future, a reliable Josephson junction technology must be developed. From experiences in low-$T_c$ superconducting materials, we know that this will be a challenging task.
REFERENCES

7. See e.g. A.P. Malozemoff, MRS Bulletin June 1990, p. 50.
13. Superconductor Technologies Inc., 460 Ward Drive, Suite F, Santa Barbara, Ca 93111-2310, USA.
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38Another way to calculate $d(N_l)/dt$ is based on the amount of collected charge during the measurement. Since the RBS system used here was not absolutely calibrated, this calculation was not possible, ibid., p 125.
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96Pole figure analyses were carried out at Université de Metz.
105M. Vabre, (private communication).
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