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I am submitting herewith a dissertation written by Yifei Zhang entitled “*Ex-situ* Epitaxial YBa₂Cu₃O_{7-δ} Films: Precursor Conversion and Film Characterization”. I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Materials Science and Engineering.

Philip D. Rack

Major Professor

We have read this dissertation
and recommend its acceptance:

Anthony J. Pedraza

Thomas T. Meek

James R. Thompson

David K. Christen

Accepted for the Council:

Linda Painter

Interim Dean of Graduate Studies

(Original signatures are on the file with student records)

Ex-Situ Epitaxial YBa₂Cu₃O_{7-δ} Films: Precursor
Conversion and Film Characterization

A Dissertation
Presented for
the Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Yifei Zhang
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To
my wife, Li Xiang, and my son, Xiaohan Zhang,
for their love, encouragement, and support.

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ABSTRACT

BaF₂-based precursors were deposited on various substrates by electron beam co-evaporation and trifluoroacetates-involved metal organic deposition (TFA-MOD) for fabricating biaxially-textured YBa₂Cu₃O_{7- δ} (YBCO) films. A low-pressure processing system was established for the conversion of the precursors. High critical current densities near 4 MA/cm² (77 K, self field) were obtained for the first time through the *ex-situ* conversion under the total pressures as low as 10 mTorr. The viability of the low-pressure conversion may enable a large-scale, cost-effective batch production of YBCO-based high temperature superconductor (HTS) wires.

The effects of the processing conditions on the film structure and properties were studied. It was found that the structure of YBCO films is very sensitive to the processing parameters. The optimal processing window for making high J_c films from the as-deposited e-beam co-evaporated precursors was relatively small and the conversion rate was limited to less than 1 Å/sec.

The *e*-beam co-evaporated precursor and the TFA-MOD precursor were compared in terms of the precursor characteristics and the conversion behavior. It was found that the precursor crystallinity and chemistry have strong effect on conversion. It was demonstrated that an intermediate heat treatment could drastically change the precursor conversion. The modified *e*-beam co-evaporated precursor can be converted at an effective conversion rate of 12 Å/sec and in a much wider processing window. The result suggested that the precursor structure and chemistry can be further tailored to facilitate fast conversion and high J_c film fabrication.

Conversion of fluorine-free precursors made by pulsed laser deposition (PLD) from an YBCO target was investigated to probe an alternative *ex-situ* route for fabricating biaxially-textured YBCO films. Epitaxial YBCO film with critical temperature T_c of 88 K and critical current density J_c (77 K, self field) of ~ 1 MA/cm² was obtained. Nearly perfect *c*-axis YBCO structure exposed by scanning transmission electron microscopy (STEM) suggested that oxygen deficiency and a lack of defects for flux pinning were the main reasons for the relatively lower T_c and J_c . Therefore, appropriate defects need to be introduced into the films.

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Chapter 1

INTRODUCTION

1.1 Superconductors

1.1.1 Low Temperature Superconductors

A superconducting material exhibits zero dc electrical resistance when it is cooled below its critical temperature T_c . Mercury is the first superconductor that was discovered in 1911 by Heike Kamerlingh Onnes, a Dutch physicist at Leiden University. It has a T_c of about 4 K. The phenomenon, the real disappearance of dc resistivity rather than just a small value below the measuring limit of a voltmeter, was defined as superconductivity. In the following decades, many other superconductors were discovered, however, all those found before 1986 are now classified as low temperature superconductors (LTS), with the highest T_c only 23 K for Nb₃Ge.

The superconductive phenomenon is distinguished not only by the perfect electrical conductivity, but also by the perfect diamagnetism, referred to as the Meissner effect, in presence of small magnetic fields. The perfect diamagnetism means that a magnetic field (*i.e.*, magnetic flux) cannot exist inside the superconductor, or the magnetic susceptibility has the value $\chi = -1$. In general, there are two classes of superconductors, namely Type I and Type II superconductors. For Type I superconductor, there is a temperature dependent critical magnetic field $B_c(T)$ such that when an applied field $B_{app} < B_c(T)$ the material is in the Meissner state, and the material becomes normal when $B_{app} \geq B_c(T)$. According to the theory, $B_c(T)$ can be approximately expressed as $B_c(T) = B_c[1 - (T/T_c)^2]$, where $B_c = B_c(0)$ is the thermodynamic critical field at 0 K.

A Type II superconductor is also a perfect conductor of electricity, but in this case the Meissner state exists only if the applied magnetic field is below the lower critical field B_{c1} . When the applied field is in the range from B_{c1} to B_{c2} , the flux is only partially excluded and the diamagnetism is not perfect, where B_{c2} is the upper critical field. The material is in a mixed state in this range. Only for applied fields greater than B_{c2} (which

can be very large), does the material become normal. Figure 1.1 is a simplified phase diagram showing the magnetic states of a Type II superconductor.

The practical applications of superconductors were pursued immediately after their discoveries. The two classes of superconductors are so different that Type I superconductors have almost no practical value because they cannot support a significant level of supercurrent. Therefore, all power applications of superconductivity are based on Type II materials, and the two basic parameters defining a superconductor's performance are the critical current density J_c (current per cross-sectional area, A/cm²) and the critical temperature T_c . For LTS, the requirement of cryorefrigeration using liquid helium (4.2 K) had confined superconductors to the realm of research laboratories for many years. The first commercial superconducting wires made of NbTi were not adequately developed until 1962, fifty years after the discovery of superconductivity.

Processability is an important factor in addition to superconductive properties when the application of a superconductor is concerned. The superconductor Nb₃Sn ($T_c = 18$ K) has better thermal, electric and magnetic properties (higher B_c , J_c) than NbTi, but

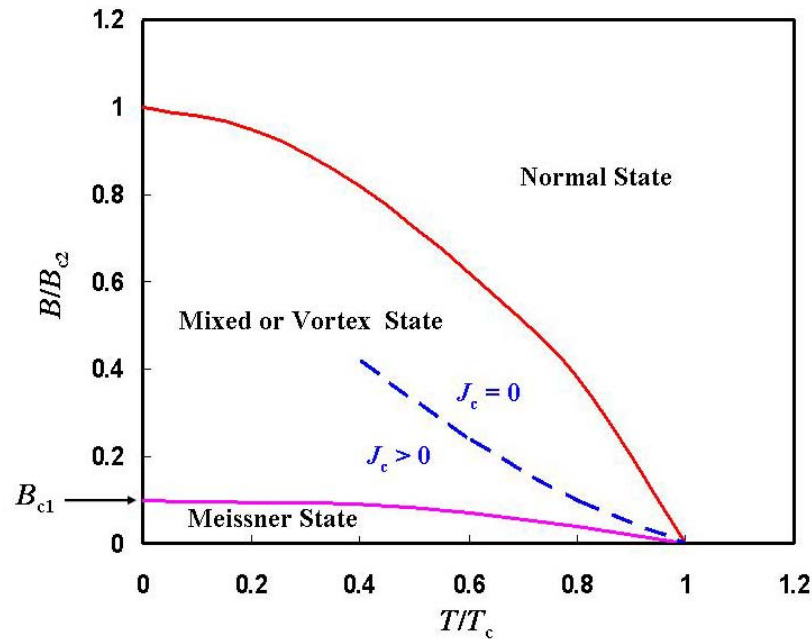


Figure 1.1. Simplified magnetic phase diagram showing the mixed and Meissner states of a Type II superconductor.

Nb₃Sn is an A-15 compound, which is brittle. It is difficult and expensive to form Nb₃Sn into wire. The body-centered cubic structured NbTi, on the other hand, is a metal alloy having typical ductility. Consequently, the material of choice for most LTS wire applications, such as magnets for medical MRI and for large accelerator magnets, continues to be the NbTi (with T_c only 9 K).

1.1.2 High Temperature Superconductors

The discoveries of high temperature superconductors (HTS) in 1986 marked the beginning of a new era in the field of superconductivity. The discovery of the first HTS material, LaBaCuO, set a new record for the critical temperature [1]. Although the 30 K T_c of LaBaCuO is only several degrees higher than that for Nb₃Ge, the essence of this discovery is significant. It broadened the superconductor materials category from elements and alloys to ceramics cuprates. The subsequent discoveries of higher T_c cuprates with T_c from 90 K up to 135 K made this breakthrough even more remarkable because for these cuprates, liquid nitrogen, which has a boiling point of 77 K and is much cheaper than liquid helium, can be used as the cryogen. The critical temperatures of selected high temperature superconductors are listed in Table 1.1 [2]. All HTS are Type II superconductors.

Table 1.1: Critical temperatures and anisotropy parameters of selected high temperature superconductors.

HTS	T_c (K)	Anisotropy Parameter γ
YBa ₂ Cu ₃ O ₇ (YBCO)	92	5
Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀ (Bi2223)	110	50~100
Tl ₂ Ba ₂ Ca ₂ Cu ₃ O ₁₀ (Tl2223)	100	≥ 14
HgBa ₂ Ca ₂ Cu ₃ O ₈ (Hg1223)	133	≥ 27

The crystal structure of Bi2223, one of the important HTS materials is shown in figure 1.2. Generally, all the HTS cuprates have multi-layered, oxygen-deficient structures consisted of conducting layers, separating layers (typically Y or Ca), bridging layers (typically BaO, LaO or SrO) and additional layers (typically BiO, HgO or TlO). The copper-oxygen (CuO_2) layers effectively form the conducting sheets. The layered structure makes the cuprates electronically anisotropic so that the supercurrent basically flows in the conducting sheets (or in the a - b planes) and the conduction perpendicular to the sheets (or along the c -axis) is weak because of the poor coupling between the CuO_2 layers. The anisotropy is characterized by the parameter, γ , such that $\gamma^2 = m_c/m_{ab}$. Here, m_c and m_{ab} are the effective mass of the supercarriers moving in the c direction and in the a - b plane, respectively. The anisotropy parameters of selected HTS materials are also listed in Table 1.1 [2]. Due to the high anisotropy, the structure of a polycrystalline HTS has to be aligned in a way that all the CuO_2 layers are parallel to each other. The textured structure is the key for the HTS to achieve high critical current density.

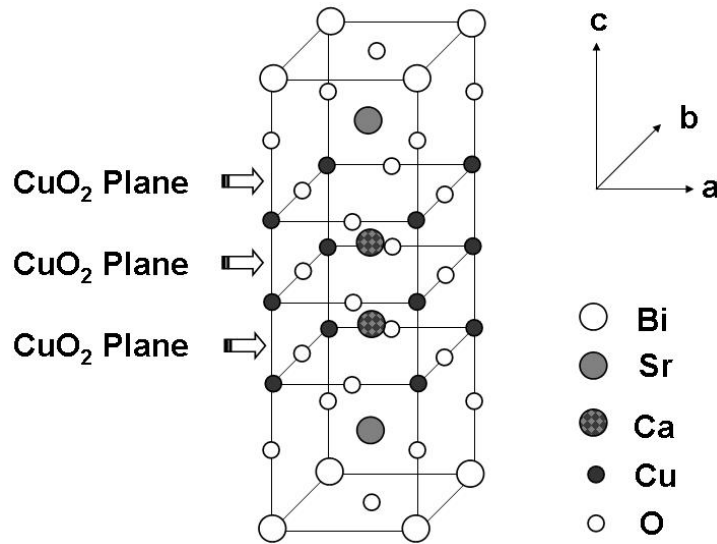


Figure 1.2. The crystal structure of Bi2223. The CuO_2 planes are the conducting sheets where supercurrent flows.

1.1.3 First Generation HTS Wires

The most widely used and successful technique for producing layer-structured HTS wires is the so-called Powder in Tube (PIT) process. The method is almost always used for processing Bi2223 due to its malicious structure and good formability, and it is sometimes used for Bi2212 and Tl1223. A schematic diagram of the PIT process is shown in figure 1.3.

The material of the tube is mostly silver or silver alloy. Silver is permeable to oxygen, is nonreactive with the HTS core material, lowers the melting point of the Bi-based HTS during the heat treatment and forms the template upon which HTS can grow. Typically, the tube is filled with HTS powder, then extruded or drawn into filaments about $1 \sim 2$ mm in diameter. For multifilament wire the filament is drawn into a hexagonal shape, cut into short length, and formed into a stack of 7, 19, 31, 55, 61, 85, or higher numbers of filaments. This stack is then inserted into another tube and the composite is extruded or drawn into wire. During the heat treatment, the HTS is subjected to a partial melt process in which large grains with the crystallographic a - b plane (or the CuO_2 conduction sheets that have high critical current density) oriented parallel to the current flow direction of the wire. The HTS wires made by the PIT process are usually called the first generation HTS wires. Kilometer long PIT Bi2223 wires are commercially available with J_c as high as $40,000 \text{ A/cm}^2$ at 77 K, self field. Unfortunately, YBCO cannot be processed into wires using the PIT technique due to its more isotropic structure and grain morphology.

1.2 YBCO

1.2.1 Crystal Structure of YBCO

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) was first discovered by M. K. Wu *et al* [3] in 1987. Among all the HTS, YBCO is the most important material and has attracted much more

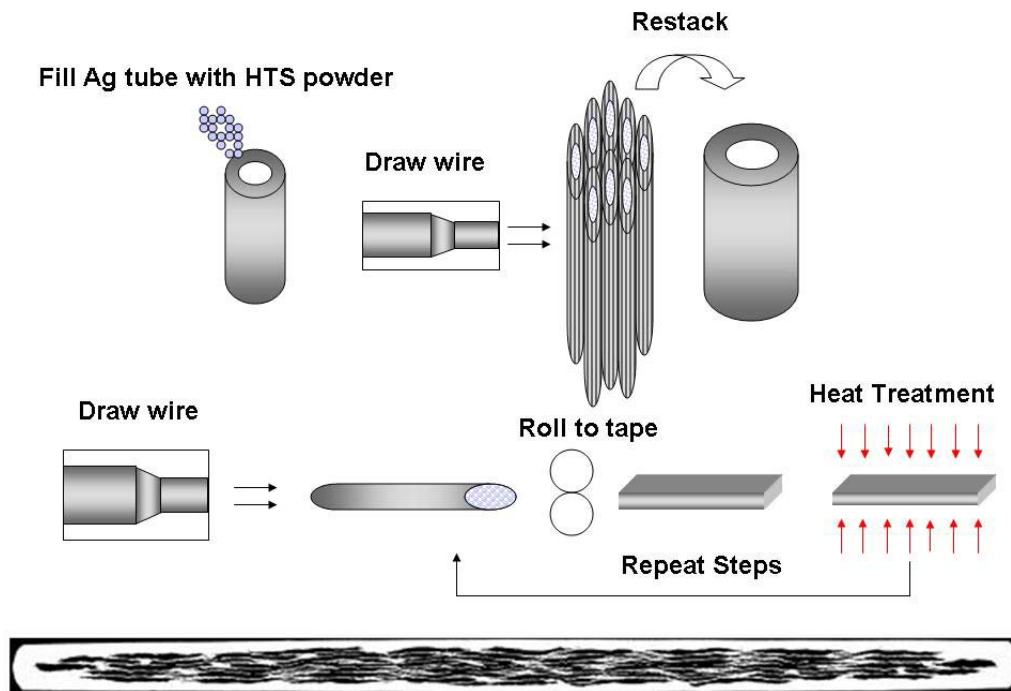


Figure 1.3. Schematic diagram of the Powder in Tube (PIT) process for the fabrication of the first generation HTS wires typically made from Bi2223. Shown at the bottom is the cross section of a 55 filament Bi2223 wire encased in a silver matrix.

investigations. The crystal structure of YBCO is shown in figure 1.4. There are two CuO_2 layers in each unit cell, one on each side of the separation layer of Y. The oxygen occupancy in the conducting layers is relatively constant. The oxygen sites in the Y plane are never occupied, allowing the oxygen in the conducting layers to slightly move towards the separation layer (not shown in the figure). The basal plane at the bottom of the unit cell is also called the CuO chain layer. Oxygen has high mobility in the basal plane and the variation of YBCO oxygen content (δ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$) is mainly due to the change in the oxygen occupancy in the basal plane. Variation of the oxygen content can happen during a low temperature (300 ~ 500 °C) annealing under certain atmosphere, without altering the cation structure. Varying oxygen content results in the lattice constant changes along all the three directions, shown in figure 1.5(a) [4]. Depending on the oxygen concentration, YBCO can have either a tetragonal ($\delta > 0.5$ non-superconducting phase) or an orthorhombic ($\delta < 0.5$, superconducting phase) structure.

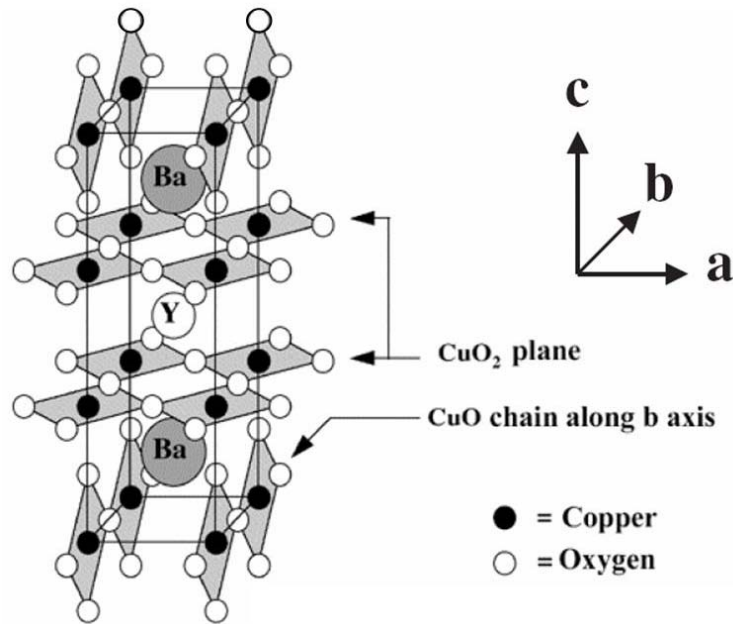


Figure 1.4. The structure of the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($\delta = 0$). The oxygen sites in the b direction on the basal planes are occupied.

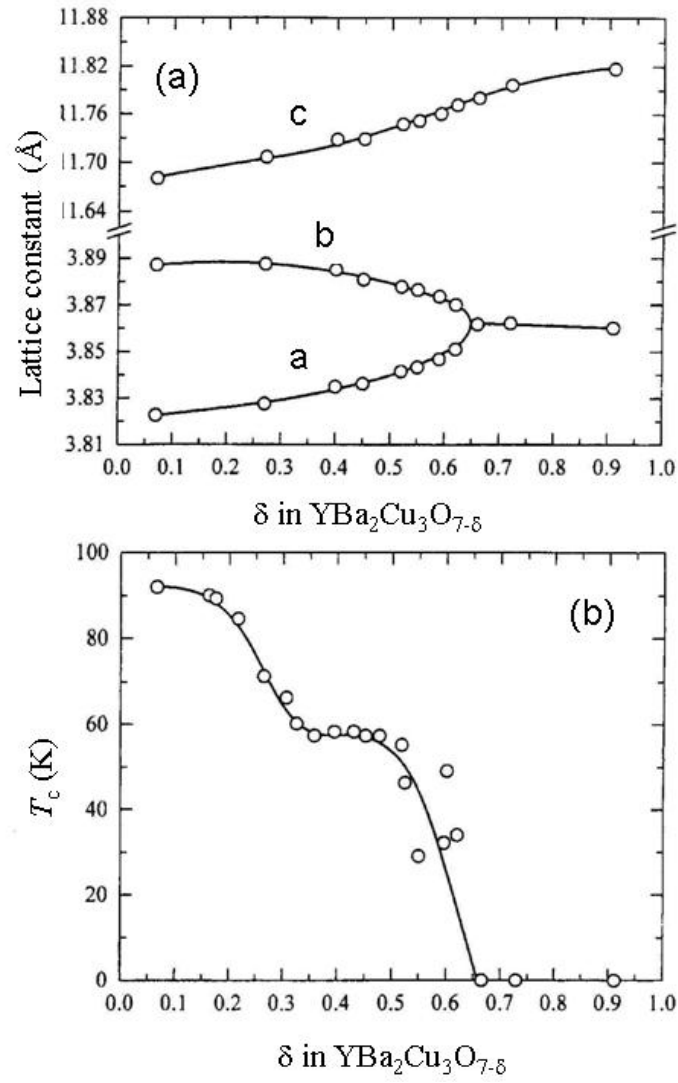


Figure 1.5. The oxygen concentration (δ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$) dependence of (a) the lattice constants, and (b) the critical temperature T_c of YBCO.

YBCO properties are strongly correlated with the oxygen concentration since the CuO chain layers serve as the charge carrier reservoir. The critical temperature basically depends on the oxygen doping level, as shown in figure 1.5(b) [4]. Nearly full oxygen occupancy ($\delta = 0.03$) is necessary to achieve a high critical temperature.

1.2.2 Critical Current Density and Irreversibility Field

The critical current density of HTS cuprates is determined by the combined effects of the coupling strength between the conducting CuO₂ layers and the material defects. The *c*-axis coherence length ξ_c for YBCO is about 0.3 nm, which is much larger than that for Bi2223 (only 0.04 nm). YBCO has much higher critical current density than BSCCO because of the different vortex structure and flux pinning behavior. In fact, due to the rapid decrease of J_c starting from very low magnetic fields, the applications of first generation HTS wires are restricted to temperatures much lower than their critical temperatures. For high current and high field applications, YBCO is a better choice as can be seen clearly from the comparison between the in-field J_c of YBCO and Bi2223 shown in figure 1.6. The LTS Nb₃Sn data are also included in the plot for reference. Figure 1.7 shows the difference in the irreversibility field for these materials. The irreversibility field (B_{irr}) is the magnetic field above which the J_c of a superconductor becomes zero.

Although Tl- and Hg-based materials have relatively higher T_c and comparable B_{irr} , the processing remains a problem due to their toxicity.

1.2.3 Weak Link at Grain Boundaries

YBCO can be made in the forms of polycrystalline bulk ceramics, thin films, or single crystals. Sintered bulk YBCO with polycrystalline randomly-oriented grains has very limited electric current carrying capacity. So does a single crystal YBCO with few defects, especially in magnetic fields. YBCO films show greater potential for practical applications with much higher J_c and B_{irr} . Films also turn out to be the only option for making wires.

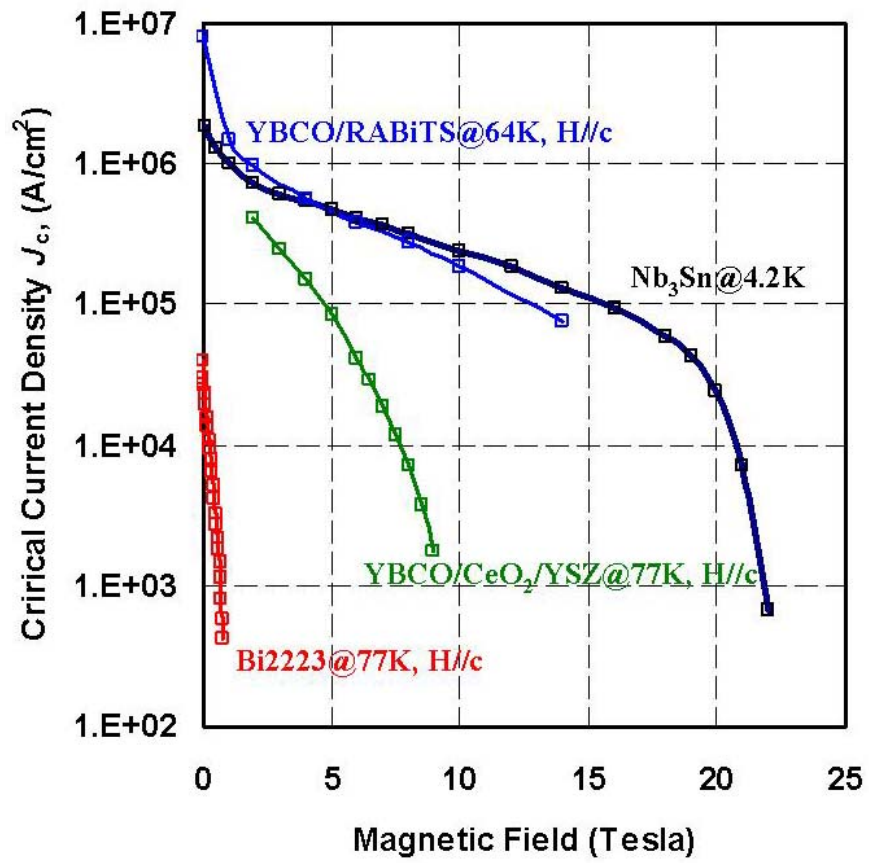


Figure 1.6. Magnetic field dependence of the critical current density for YBCO compared with Bi2223 as well as the LTS Nb₃Sn.

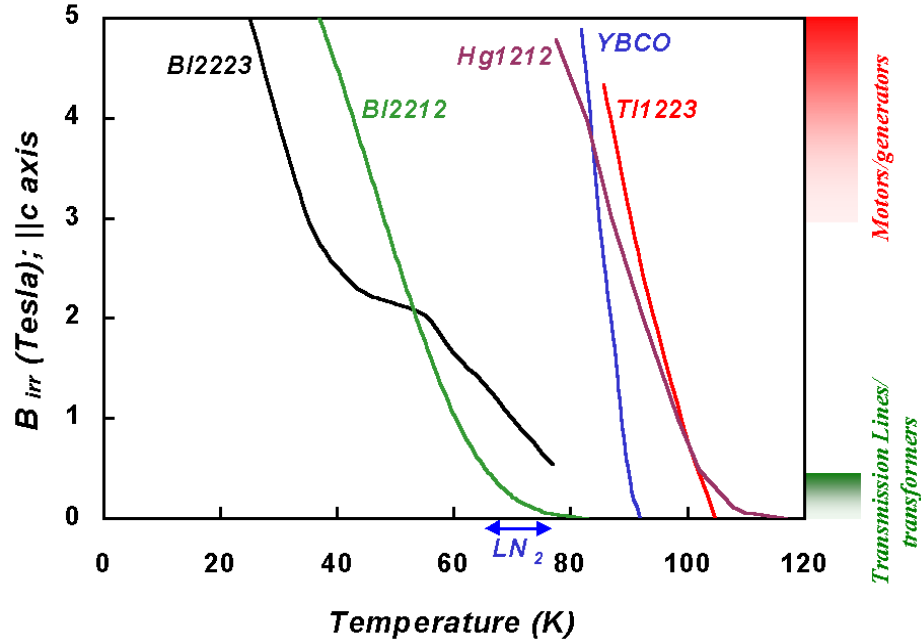


Figure 1.7. Irreversibility field (B_{irr}) versus temperature for YBCO compared with other HTS. The magnetic field requirements for selected applications are also indicated.

Although YBCO has a relatively smaller anisotropy parameter (γ), the electrical conduction perpendicular to the conducting CuO_2 planes is still very limited compared with that along the a - b plane. For films of polycrystalline YBCO, a textured structure with the c -axis perpendicular to the substrate surface is necessary. The out-of-plane alignment structure enables a current flowing only in the CuO_2 conducting layers. Moreover, due to the weak links across the grain boundaries (GB), an in-plane alignment of all the grains is also important. Grain boundaries create weak links between superconducting regions. Depending on degree of intergrain misorientation, all grain boundaries more or less act as the barriers to the supercurrent flow. The effects have been widely investigated. Figure 1.8 shows the misorientation angle dependence of J_c of YBCO films deposited on the bicrystal substrates with two different techniques [5]. It can be seen that the J_c decreases rapidly as the misorientation angle increases. The grain boundaries selected were type (001) tilt, (100) tilt, or (100) twist. To minimize the weak link effect from grain boundaries, the grain boundary misorientation angle normally has

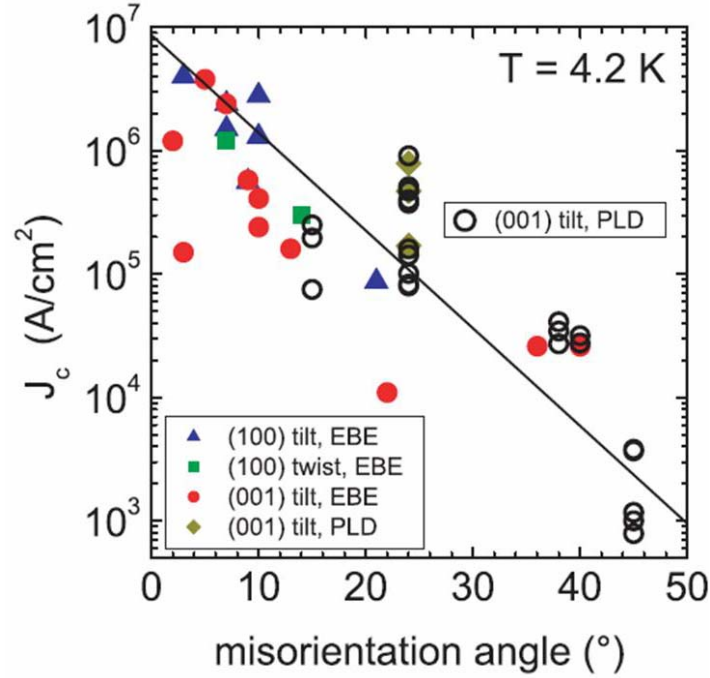


Figure 1.8. Critical current density J_c versus grain boundary misorientation angle for YBCO films deposited by two different techniques on bicrystal substrates with various types of grain boundaries.

to be smaller than $4 \sim 5^\circ$. In other words, a biaxially-textured YBCO film with the alignments of both c -axis and a - (or b -) axis is required to obtain high J_c .

1.3 Coated Conductors

1.3.1 Second Generation HTS Wires

One way to obtain biaxially-textured YBCO is to epitaxially grow the films on biaxially-textured substrate templates. The ideal templates would be single crystal substrates that have certain lattice match and compatibility with the superconductor. Epitaxial YBCO film deposition on many single crystal substrates, such as SrTiO_3 and LaAlO_3 , is relatively straightforward for many deposition techniques. However, single crystal substrates are apparently not practical for long-length wire fabrication. Instead, metallic tape substrates, due to their flexibility and length availability, inevitably become

the best choice. Unfortunately, no metallic substrate has been found that is practically viable for direct YBCO film deposition. The interaction between the metallic substrates and the superconducting films at the high temperatures required for the formation of YBCO appears to be a severe problem. Intermediate barrier layers, which serve as the buffer to protect both the metallic substrate and the superconducting layer, are indispensable. The buffer layers have to be biaxially-textured so that textured YBCO can be grown thereon. During early 1990's, the idea for "coated conductors" emerged. That is depositing superconducting film on a biaxially-textured template consisted of the metallic substrate and the buffer layers. Based on this idea, the so-called second generation (2G) HTS wires that are being intensively pursued could start a new era for the applications of high temperature superconductors. A conceptual configuration of the coated conductor is schematically shown in figure 1.9. Detailed techniques to fabricate the multilayer composite may vary significantly, depending on the metallic substrate structure, buffer materials selection, and the superconducting layer deposition methods.

1.3.2 Biaxially-Textured Templates

Factors that affect the choice of the metallic substrates include lattice mismatch, texture, thermal expansion coefficients, chemical compatibility, oxidation resistance, dielectric properties, magnetic properties, mechanical properties, and cost.

Chemically inert metallic substrates are preferred, as the HTS layer has to be formed at high temperatures and the diffusion of substrate metals up into the film could destroy the superconductivity. The magnetic properties of the substrates could be important in cases where AC losses are of major concern. Metallic substrates of non-magnetic or with small magnetic hysteresis loss are pursued for the application in alternating magnetic fields. The mechanical properties of the substrates are important when the engineering critical current density J_e is of a major concern. J_e is defined as the current per total cross sectional area of the coated conductor. It is preferable to use a thin (but stronger) substrate in order to provide good mechanical support for handling of the tape in various processing steps during and after the deposition. Typically, 50 μm thick

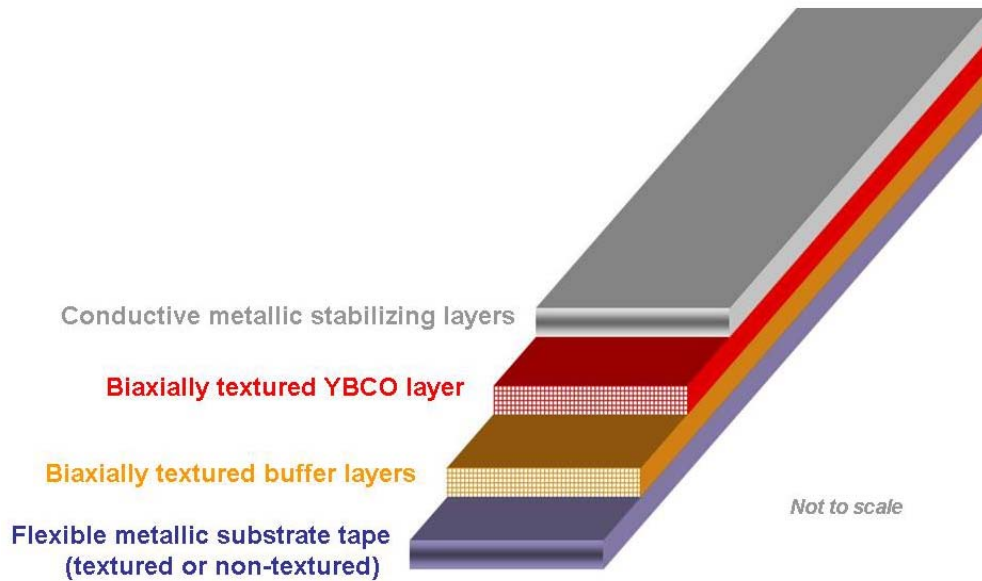


Figure 1.9. Conceptual configuration of the coated conductors, or the second generation HTS wires.

substrates are used. Reasonably high yield strength is necessary because large strain can damage the buffer and the YBCO layer. It is also important to match ($<10\%$) the thermal expansion coefficient of the substrate with the buffer layers and the superconducting film. From a mechanical point of view, the possibility of cracking can be reduced if a slightly compressive stress is generated in the YBCO film as well as in the buffer layer upon cooling from the processing temperature. Thus, an ideal substrate should have a thermal expansion coefficient that is little larger than those of the films.

Among the materials studied, Ni alloys have emerged to be the most promising metallic substrate due to their good stability and oxidation resistance at elevated temperatures. Two major template fabrication techniques, namely RABiTS (Rolling Assisted Biaxially Textured Substrates) and IBAD (Ion Beam Assisted Deposition) are both based on Ni alloy substrates.

The RABiTS template consists of the biaxially-textured Ni alloy substrate and the epitaxially deposited buffer layers. The fabrication of the substrate involves a cold rolling of Ni alloy rod to form the metallic tape followed by a high temperature annealing in

which the desired texture is developed through the recrystallization process. The technique was firstly developed at Oak Ridge National Laboratory (ORNL) in 1996 by A. Goyal *et al* [6]. The basic procedure for this process is shown in figure 1.10. Now, high quality biaxially-textured Ni alloy tapes of hundreds of meters long are readily available. In the RABiTS approach, the biaxial texture of buffer layers originates from the textured metallic substrate through epitaxy.

Since buffer layers function as both the template for texturing and the reaction/diffusion barriers, it is required that the buffer materials have suitable lattice parameters as well as thermal and chemical compatibility with both the substrate and the superconductor layer. Most buffer materials are oxides, either cubic or perovskite type.

IBAD (Ion Beam Assisted Deposition) is a method of depositing biaxially-textured films with an assisting ion beam concurrently bombarding the substrate surface. The use of usually the oxygen or argon ion beam helps control the orientation of the growing texture. The technique generates biaxial texture in a buffer layer on a non-

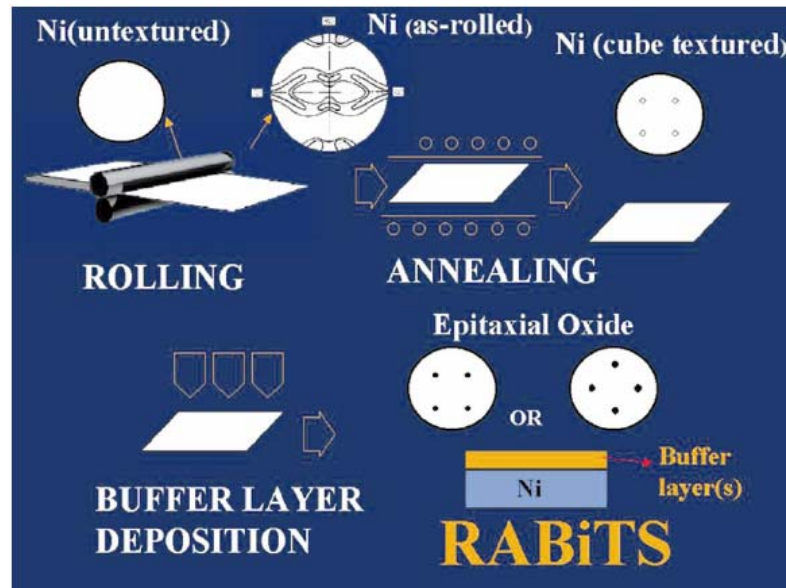


Figure 1.10. Procedure for fabricating biaxially-textured templates using RABiTS technique.

textured polycrystalline metallic substrate. The range of potential substrate materials is large because the substrate itself does not have to be of lattice match and textured. In 1991, Iijima *et al* [7] found that sharp biaxially-textured YSZ (yttria-stabilized zirconia) films can be deposited on a polycrystalline Ni alloy substrate through an off-normal IBAD. YSZ was first selected as the IBAD buffer material because of its good lattice match with YBCO. Later, YSZ was replaced by MgO because MgO can be textured much more efficiently using IBAD. To obtain good in-plane texture only about 10 nm is enough for MgO while for YSZ, film between 500 and 1000 nm thick is required. Similar to RABiTS approach, multi-layer buffers are also necessary for an IBAD template.

1.3.3 YBCO Film Fabrication

Many deposition methods have been used to fabricate YBCO films. Among these techniques, pulsed laser deposition (PLD), sputtering, electron beam co-evaporation (EBE) and pulsed electron deposition (PED) are physical vapor deposition (PVD) processes, and metal organic chemical vapor deposition (MOCVD), sol-gel, metal organic deposition (MOD), liquid phase epitaxy (LPE) and aerosol/spray pyrolysis are chemical deposition processes. PLD, sputtering and MOCVD are generally referred to as *in-situ* methods as these processes produce epitaxial YBCO films simultaneously during the deposition and no additional post heat treatments are necessary, except possibly a lower temperature oxygenation. On the other hand, EBE, PED, sol-gel and MOD belong to *ex-situ* category, since a post-deposition thermal annealing is always necessary in which the pre-deposited precursors are converted into the desired YBCO films. Among all these methods, MOD, MOCVD, EBE and PLD are most popular and promising for the YBCO coated conductor development. Using these techniques, reproducible high quality YBCO films with critical current densities around 2 MA/cm² at 77 K in self field (depending on the film thickness) can be routinely fabricated on both single crystal substrates and buffered metallic templates.

As a typical *in-situ* method, PLD has been widely utilized for fabricating YBCO films. With the high energy of the ablating laser beam, the stoichiometry of a PLD target

can be well retained in the film. Moreover, PLD offers the flexibility that makes it very convenient for doping films or fabricating multi-layer films. I_c as high as 1000 A/cm-width was obtained on small samples with multi-layers of YBCO and CeO_2 [8]. However, there exist some problems for PLD to be scaled up for practical production. First, there is a widespread concern that PLD may not be financially viable, due mainly to its high cost and maintenance of industrial-scale lasers and the associated high vacuum system. Secondly, PLD is a slow-rate process in terms of the throughput of volume deposition, which is due to the relatively smaller deposition area. PLD deposition is often confined to very limited area because of the chamber size and local depositing conditions (T and P_{O_2}). Thirdly, PLD *in-situ* growth requires significant and uniform substrate heating in the oxygen ambient, which proves challenging for large-area or continuous long-length deposition of YBCO films. To obtain a uniform film, more than enough target materials have to be evaporated in the chamber while only a small fraction of the total material is actually deposited onto the substrates. It may result in an over consumption of target materials, and consequently, the change of target can introduce extra problems for a long length tape production. All these can be the difficulties for the scaling-up of the PLD approach.

Ex-situ methods, such as electron beam co-evaporation (EBE) and metal organic deposition (MOD) have attracted more attention in the last ten years. Recent interest originated from the consideration of simpler operation, cost effectiveness and scalability.

Ex-situ methods produce YBCO films basically in two separate steps; the deposition of a precursor film and a post-deposition processing that converts the precursor film into YBCO. The precursor film can be deposited by many techniques, either vacuum or non-vacuum approaches. The deposition itself requires no substrate heating. The desired superconducting phase with biaxially-textured structure is formed during the post-deposition processing, which is conducted at elevated temperatures and under certain controlled atmosphere. The quality of the YBCO film made through the solid state epitaxy strongly depends on the characteristics of the precursor, the processing condition for the conversion, and the quality of the biaxially-textured templates.

For various *ex-situ* techniques, the precursor deposition is a relatively easy step to implement. The common difficulty is mostly in the conversion, especially when thicker films are to be made. Thickness becomes an obstacle as the precursor conversion is a complex chemical reaction and solid phase transformation process. The reaction and the epitaxy need to start from the precursor/substrate interface and then proceed towards the precursor surface. During the process the unreacted part of the precursor may suffer chemical and/or structural changes while also exposed to the processing ambient. The reaction product(s) released from the earlier conversion reaction, which needs to be removed by out-diffusion through the precursor, may also have certain effects on the unreacted precursor.

Chapter 2

***EX-SITU* PROCESS OF YBCO FILMS – A REVIEW**

The YBCO superconducting layer is the most important part of the coated conductor composite. The techniques of fabricating YBCO film constitute the core of the coated conductor technology with the template techniques as the basis.

While the mainstream *in-situ* techniques, such as pulsed laser ablation (PLD) and metal organic chemical vapor deposition (MOCVD), have been proven to be promising for practical production, the *ex-situ* processes are equally attractive and competitive. The most prominent advantage of *ex-situ* processes is that the control of the composition and the formation of the phase and structure are separate. In this way, the control and modification of the composition are readily manipulated and during the conversion processing there is basically no concern about the film stoichiometry. For many *ex-situ* techniques, the areas that can be deposited and processed are large, which can effectively increase the throughput in the case of wire production.

In principle, an *ex-situ* precursor can be made using any possible deposition methods. Physical vapor deposition (PVD), chemical solution deposition (CSD) and spray are often utilized. Electron beam co-evaporation has become the most successful PVD method since uniform, stable and thick precursor film can be readily deposited. The co-evaporation method is often referred to as “BaF₂ process” as almost always BaF₂ is involved in the precursor.

The CSD method includes three different approaches: (1) sol-gel process that uses 2-methoxyethanol as a reactant and solvent; (2) hybrid processes using chelating agents such as acetylacetonate or diethanolamine to reduce alkoxide reactivity; and (3) metal-organic decomposition techniques that use high-molecular-weight precursors of water-insensitive carboxylates, 2-ethyl-hexanoates, *etc.* These CSD routes have been used to grow both superconductor films and oxide buffer layers in the development of coated conductors. CSD has been extensively pursued as it does not require a vacuum system for

the precursor deposition and it wastes little of the source materials. For the MOD approach, various metal-organic materials such as citrates, oxalates, neodecanoates, trifluoroacetates, halides, acetates, acetylacetonates and naphthenates have been tried. The metal organic deposition using a solution of trifluoroacetates (TFA-MOD) has been the most successful CSD method.

During the last ten years, great progress has been made in the development of the YBCO fabrication techniques for the production of the coated conductors. However, key issues, such as uniformity, fast processing, thick films with higher critical current density and better in-field behavior are still being intensively investigated.

2.1 Precursor Deposition

2.1.1 Electron Beam Co-Evaporation

Electron beam co-evaporation was first utilized at AT&T Bell Laboratories [9] in 1987 for the fabrication of YBCO films. BaF₂, metallic Y and Cu were used as the source materials for the evaporation. BaF₂, which is basically inert, is used instead of pure Ba or BaO because it does not require special handling and does not contribute much to the outgassing in the deposition system. More importantly, the BaF₂-based precursor is environmentally stable. In contrast, pure barium or BaO-based precursor apparently reacts quickly with CO₂ when exposed to air. The resulting product BaCO₃ is too stable to decompose, which hinders the formation of YBCO.

The *e*-beam co-evaporation chamber usually needs a base pressure at the lower range of 10⁻⁶ Torr. Normally, *e*-beam evaporation is used for Y and Cu while BaF₂ is thermally evaporated. The oxygen partial pressure during the deposition is around 1×10⁻⁵ Torr. The substrate is kept at either room temperature or an intermediate temperature of 300 ~ 400 °C. The deposition rates for the three sources are controlled independently using feedbacks from quartz crystal monitors. The combined gross deposition rate is usually between 0.5 ~ 10 nm/sec. Precursor composition can be calibrated using either Rutherford Backscattering Spectroscopy (RBS) or Inductively Coupled Plasma (ICP) analysis. A stoichiometry better than ± 2 % can be routinely obtained. The as-deposited

films are generally surface featureless, structurally amorphous and electrically insulating. The presence of fluorine in the as-deposited precursor was confirmed by RBS [10], Auger Electron Spectroscopy (AES) depth profiling [11] and X-ray Photoelectron Spectroscopy (XPS) [12]. The result is consistent with the idea that BaF_2 is evaporated and deposited in the molecular state.

Compared to the CSD methods, co-evaporation is relatively straightforward. There has not been much characterization of co-evaporated precursor films except for the various techniques, such as RBS and ICP that have been used for the inspection of the composition. The effects of non-stoichiometry and the deposition parameters, such as oxygen partial pressure and substrate temperature, have been rarely discussed. There is no common agreement on the exact states of the cation components in the precursors.

2.1.2 TFA-MOD

TFA-MOD is the most important approach among all the CSD methods. In 1988, Gupta [13] firstly reported the method using trifluoroacetates (TFA) to generate precursors for making biaxially-textured YBCO films on crystal substrates. McIntyre and Cima [14] further optimized the synthesis parameters and achieved high critical current densities. TFA-MOD is essentially a fluorine-based process. The purpose of using TFA is also to form BaF_2 so as to stabilize the precursor. Similar to the co-evaporated precursor, fluorine can be removed through the later high temperature conversion.

The basic procedure of the TFA-MOD method is described schematically in figure 2.1. In brief, highly purified solution is made and deposited onto a substrate to form the gel film. After a low-temperature calcination, the gel film becomes the precursor film, which is then annealed and converted into YBCO film at higher temperature in a humid oxygen atmosphere. All these processes can be done in an atmospheric pressure ambient.

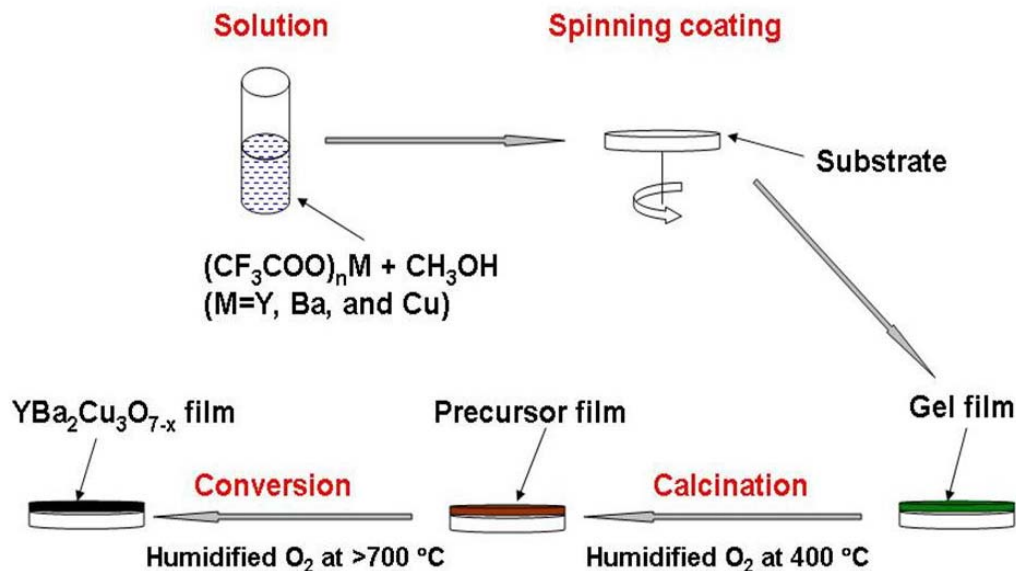


Figure 2.1. Schematic procedure of TFA-MOD process for fabricating YBCO films. Spinning coating is only one example of many available coating methods.

The coating solution preparation is the first and one of the important steps in the TFA-MOD process. Highly purified and stabilized solution is the basis to obtain high quality YBCO films. Normally a metal organic solution is made with stoichiometric Y:Ba:Cu = 1:2:3. The starting materials can be metal salts, such as the acetates or oxides, which dissolve into trifluoroacetic acid to form the trifluoroacetates (TFA). After repeated reflux the extra acid is removed and then the trifluoroacetate gel is redispersed into an organic solvent to form the solution. The cation concentration of the solution is usually below 3 M since higher concentration may result in precipitates because of the limited solubility of the trifluoroacetates. A typical procedure for making TFA-MOD coating solution is shown in figure 2.2.

Highly purified coating solution is difficult to obtain because the impurities in the acids or water (when used) disturb the refining process. Araki *et al* [15] developed a procedure making highly purified solution. It was suggested that by using the purified solution, the sensitivity to the processing conditions is lowered.

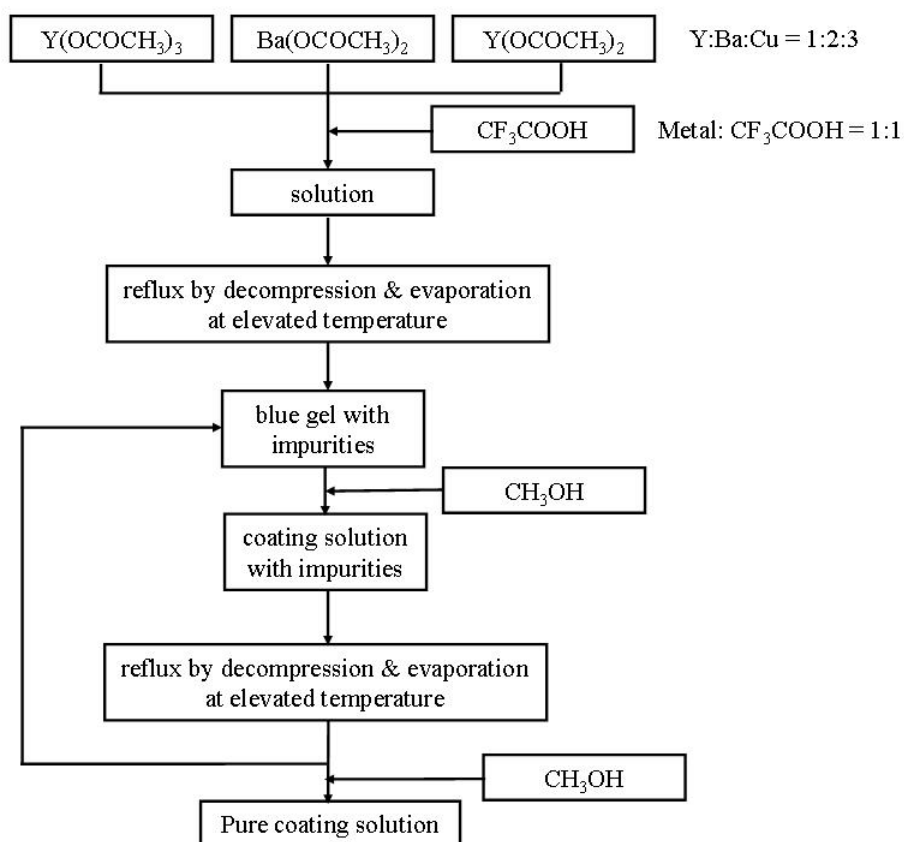
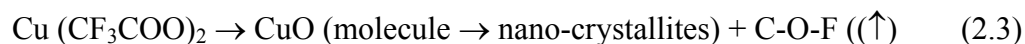
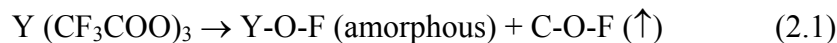


Figure 2.2. Procedure for preparing the coating solution for the TFA-MOD process.

By using spin coating, dip coating, or slot die continuous coating, the solution can be deposited onto a substrate to make a gel film. The thickness and uniformity of the as-coated precursor film are affected by solution viscosity, solution concentration, and coating parameters. It was found that film thickness dramatically increases with the solution concentration [16]. Unfortunately, all the efforts to increase film thickness have been challenged by the cracks resulting from the drying stress, which is an inherent problem with the method. Although the thickness limitation can be relieved by modifying the solution with a crack-preventing additive and/or by using multiple coatings, it is always difficult to obtain crack-free films thicker than 1.5 μm via the TFA-MOD process.

Immediately following the coating, an intermediate calcination up to a modest temperature around 400 $^{\circ}\text{C}$ in controlled water vapor atmosphere is utilized to remove the carbon and the extra organic ingredients from the gel film. The calcination, which is a decarbonization process often called burn-out, usually involves a slow ramp rate and takes a long time. During calcination, the metal trifluoroacetates decompose at 200 ~ 250 $^{\circ}\text{C}$ and the carbon content is expelled. It is believed that the following chemical reactions occur during the calcination [17, 18].



The precursor film produced by TFA-MOD is a partially oxidized version of that obtained by the *e*-beam co-evaporation. The precursor components of the CuO nano-crystallites as well as the Y-Ba-O-F amorphous matrix were confirmed by energy dispersive X-ray spectrometry (EDS) in a dedicated transmission electron microscopy (TEM) [19, 20].

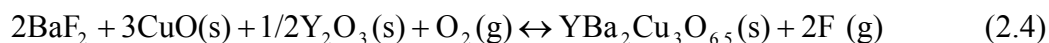
While the main purpose of the calcination is to remove the harmful carbon residuals so as to make a stable precursor film, this long duration step remains as a bottleneck in the entire TFA-MOD process.

2.2 Precursor Conversion

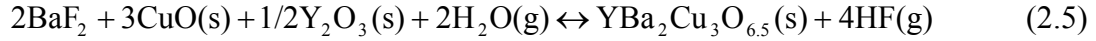
Post-deposition precursor conversion characterizes the *ex-situ* techniques of YBCO film fabrication. The processing, which is often referred to as post-annealing, converts the amorphous precursors into the biaxially-textured crystalline YBCO films. The conversion processing is a chemical reaction and phase transformation process involving complicated thermodynamics and kinetics. Intensive research has been made in understanding and optimizing the process in order to obtain high quality films. A difficulty is that the quality of the annealed film is very sensitive to the processing parameters including temperature, oxygen and water partial pressures, time, ramp and cooling rate, *etc.* These processing parameters have strong effects on the uniformity, phase composition, crystallinity, crystalline orientation, and surface morphology of the film.

The post-deposition processing is almost always conducted at elevated temperatures in a flowing gas mixture containing oxygen and water vapor. The annealing process for the *e*-beam co-evaporated precursors and the TFA-MOD precursors is very similar. To evolve the biaxial YBCO film, the conversion involves at least the following three processes: (1) the decomposition of BaF₂ and any other possible fluorides or oxifluorides, with the release of HF; (2) the epitaxial nucleation of YBCO at the substrate/precursor interface; and (3) the epitaxial film growth of YBCO towards the precursor surface.

Soon after the first report of BaF₂ process, Mankiewich *et al* [11] found that water that was deliberately added into the reaction atmosphere can greatly speed up the conversion. Reduced processing time is always preferred as it leads to reduced substrate/film reaction. In practice, continuous reel-to-reel high yield production relies on a time-efficient processing. Based on thermodynamic calculations, Garzon *et al* [21] gave a rough explanation on why water is necessary. It was proposed that the reaction without the presence of water, which is given by



is possible but only at extremely low fluorine partial pressures at the order of 10^{-23} atm . In the presence of water vapor, however, the thermodynamics is quite different. The reaction



can tolerate HF partial pressures on the order of 10^{-4} atm . Thus, it is evident that the use of water vapor drastically changes the reaction kinetics and drives the conversion reaction to proceed.

YBCO films can only be formed under certain conditions in terms of oxygen partial pressure and temperature. Based on thermodynamics calculations and experimental results, a phase diagram was derived describing the YBCO stability with respect to the oxygen partial pressure and temperature. The film orientation was found also dependent on the two parameters. The correlation for *ex-situ* films systematically studied by Feenstra *et al* [22] is consistent with that for the *in-situ* films obtained by Hammond and Bormann [23]. A typical YBCO phase diagram is shown in figure 2.3, in which the high-temperature YBCO stability region is defined by the melting line *m1* and the decomposition line. The low-temperature tetragonal/orthorhombic transition line indicates oxygen filling of the YBCO chain layer. Along the CuO-Cu₂O equilibrium line (or Hammond Bormann line) is the empirically optimal region for *in-situ* film growth. Annealing conditions yielding films of comparable epitaxial and structural properties are connected by lines denoted as *c1*, *c2*, and *a1*, respectively. Predominantly *c*-oriented films were obtained between *c1* and *c2* and mixed *c*- and *a*-oriented films between *c2* and *a1* lines.

Early conversions were mostly conducted in pure oxygen of one atmosphere pressure. It was found that the *c*-axis oriented YBCO film is only achievable at the annealing temperatures higher than 830 °C [24]. Lower annealing temperatures resulted in significant *a*-axis oriented nucleation for the one atmosphere pressure processing. With oxygen partial pressures varying between 1.0 and $8.0 \times 10^{-5} \text{ atm}$ and temperatures between 890 and 650 °C, a strong dependency of film orientation on the oxygen partial pressure was observed. If the conversion is performed under lower oxygen partial pressure at a compatible lower temperature, *c*-axis oriented films with enhanced properties can be

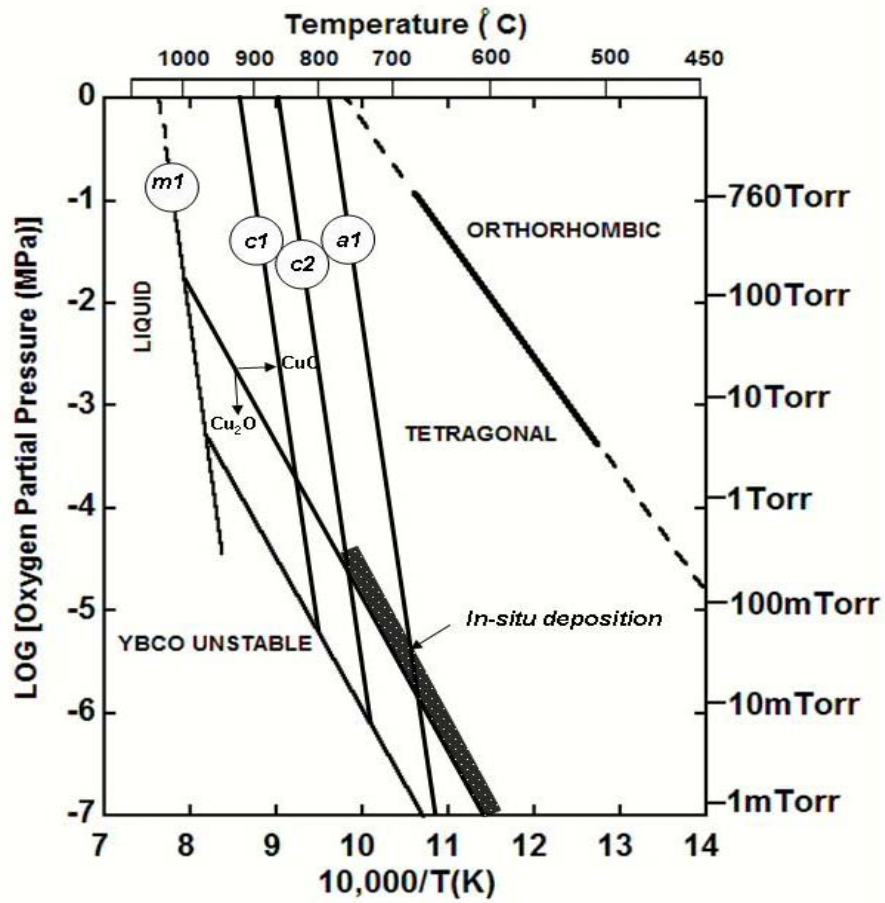


Figure 2.3. YBCO phase diagram showing the oxygen partial pressure and temperature dependences of YBCO stability and film orientation.

obtained [25 - 27]. This implies that the lower annealing temperatures may compensate for the lower oxygen pressures. The improved film epitaxy and smoother morphology at reduced oxygen pressure is suggested to be the result of the enhanced growth kinetics associated with oxygen vacancy concentration and lattice distortions that may promote cation diffusion. Similar results were also reported on TFA-MOD precursors [28]. The best properties were obtained in films annealed at 750 °C under a low oxygen partial pressure.

Film orientation is determined not only by the processing parameters but also by the characteristics of the substrate materials. During the post-deposition processing, water vapor and HF generated from the conversion reaction may cause certain chemical reactions with the substrate and/or buffers. Such reaction can change the substrate/precursor interfacial energy, and therefore change the way that YBCO nucleates. As stated previously, a chemically compatible buffer layer is crucial. Alkaline and alkaline earth oxides (groups IA and IIA in the periodic table) react with HF gas at high temperatures. For example, *ex-situ* YBCO can be grown on LaAlO₃ and SrTiO₃ substrate but not on MgO, due to the reaction with fluorine that forms MgF₂ [16]. Most early successful fabrication of YBCO by the BaF₂-based *ex-situ* processes was on SrTiO₃ substrate. CeO₂, which is inert to HF, has become the best cap layer material on metallic substrates. Although CeO₂ can react with YBCO and the resultant BaCeO₃ is frequently observed using XRD, no evidence has been found that a layer of BaCeO₃ deteriorates the film properties. Lattice mismatch is a fundamental factor that affects film orientation [29]. The *a/b*-axis-oriented component increases in the following order for different substrates: CeO₂ < SrTiO₃ < LaAlO₃ < NdGaO₃. Better lattice matching leads to a larger number of *a/b*-axis-oriented grains. This tendency is consistent with the results for YBCO films prepared by PLD [30, 31].

2.3 Epitaxial Nucleation and Growth

It is generally accepted that the *ex-situ* precursor conversion involves the reaction of BaF₂ with the water vapor present in the processing atmosphere. With the progress of the reaction, epitaxial YBCO film forms simultaneously. The process is delicate since the

biaxially-textured YBCO film first nucleates at the substrate/precursor interface, and the subsequent growth needs to proceed steadily towards the surface without disturbance. To optimize the processing protocol and make high performance films, the nucleation and growth mechanism have to be clearly understood. Although being very important, the following questions have not been well answered.

(1) What are the *typical* structure of the precursor and the status of the cations?

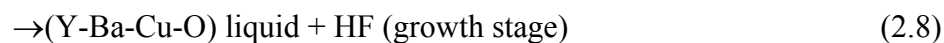
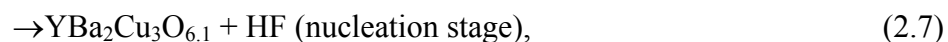
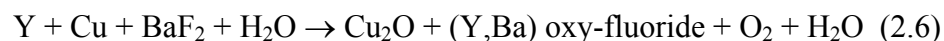
(2) What are the *optimal* structure of the precursor and the *optimal* status of the cations that promote the epitaxial nucleation and growth?

(3) How do the processing parameters affect the nucleation and growth, in terms of the nucleation rate, nucleus density, nucleus orientation, growth mode, and growth rate, *etc.*?

(4) What are the characteristics that qualify a substrate (buffer) structure and the surface as the best to promote the biaxial nucleation and growth?

(5) What are the changes that occur in the upper part of the precursor when the lower part has been converted? What are the effects of these changes on the YBCO growth that happens later during the conversion processing?

Studies of nucleation and growth are difficult since detailed microstructural analysis of the dynamic conversion process is required. A TEM study on a series of quenched samples was done by Wu *et al* [32]. The precursors were deposited using co-evaporation on STO single crystal substrates. It was suggested that the chemical reaction for the formation of YBCO out of the precursor can be written as



The nucleation of YBCO on STO is strongly related to the initial formation of a Y-Ba oxy-fluoride that aligns its (111) planes parallel with the substrate at the initial stage of the reaction. There are two possible mechanisms for the nucleation of YBCO: (i) by the superlattice ordering of the oxy-fluoride along its [111] direction and then releasing of fluorine to form YBCO, or (ii) by the formation of YBCO islands on STO by

the screw dislocation mediated nucleation mechanism from the aligned oxy-fluoride. Once the substrates are covered with the YBCO layer, an amorphous thin layer, approximately 7 nm, which is assumed to be liquid at the reaction temperature, is formed between the YBCO layer and the yet-unreacted precursor. The subsequent YBCO precipitates epitaxially onto the existing YBCO layer out of this liquid. The TEM cross-sectional image in figure 2.4 shows the amorphous (liquid) layer between YBCO and the unreacted precursor, the YBCO layer, and the presence of an interfacial layer (Sr-Ba-Ti-O) between SrTiO_3 and YBCO. The inset is a close-up view of the section containing the liquid layer.

Quenching was also used for the study of the nucleation and growth of YBCO film from TFA-MOD precursors [33, 34]. The quenched film had no obvious grain boundaries in TEM micrographs, implying the involvement of the so-called quasi-liquid in the nucleation and growth process, which is similar to the liquid layer observed in BaF_2 precursors. As previously mentioned, the TFA-MOD precursor has CuO nano-crystallites and an amorphous matrix after the calcination. Araki *et al* [35] found that the size of the CuO nano-crystallites depends on the time of the calcination. In the matrix, there are also Cu-poor regions surrounding the CuO nano-crystallites and Cu-rich regions that turn into the quasi-liquid state at the processing temperature.

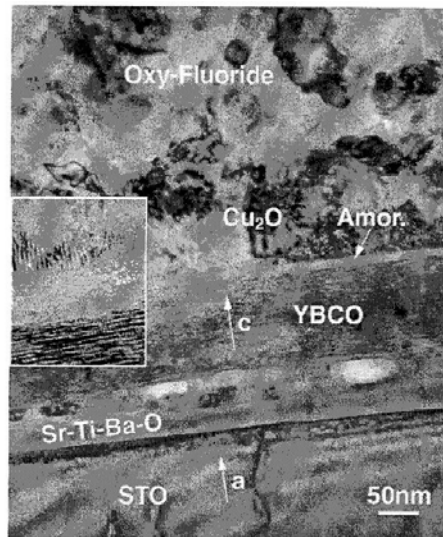


Figure 2.4. Cross-sectional TEM image of a BaF_2 process film quenched after 40 min annealing [32].

Apparently, the quasi-liquid forms everywhere in the TFA-MOD precursor and forms a network. The quasi-liquid network effectively conveys water molecules from the film surface to the growth front and also conveys the generated HF gas from the growth front to the film surface. It is believed that the quasi-liquid only releases YBCO grains on a lattice-matched substrate surface and simultaneously releases HF [36, 18] during the nucleation stage. Subsequently, the quasi-liquid helps the epitaxial YBCO growth by only releasing YBCO grains on the YBCO growth front.

2.4 Conversion Rate

Conversion rate is not only an issue of efficiency, but also is of importance when considering thicker films, uniformity and continuous processing. Questions include: How to monitor the conversion rate during the processing? How do the processing parameters affect the conversion rate? How does the film thickness affect the conversion rate? What is the limit of the conversion rate and what are the limiting factors? How can the conversion rate be increased? How does the conversion rate affect the structure of the film, such as the crystallinity and texture?

Conversion rate in the *ex-situ* process, usually given in nm/sec or Å/sec, is defined as the ratio of the YBCO film thickness to the minimum processing time required for a fully conversion. Experimentally the actual conversion rate can be monitored *in-situ* using various diagnostic techniques during the conversion.

Since the amorphous precursor film is an insulator and YBCO is a conductor, measurements of the film conductivity during annealing provide information regarding the conversion kinetics. The film conductivity increases as precursor material is being converted into YBCO, up to the point that the precursor is completely converted where the conductivity becomes a constant [37].

With an X-ray diffraction system based on Bragg-Brentano parafocusing geometry, Energy Dispersive X-ray (EDX) diffraction was used to continuously monitor the development of crystalline phase during the precursor conversion [38]. Full range 2θ spectra were recorded continuously and stored every two minutes throughout the

precursor conversion. BaF₂ (111) and YBCO (002) peak intensities were used for monitoring the decomposition of BaF₂ and the formation of YBCO.

Since the *ex-situ* precursor conversion is a process in which chemical reactions and phase transformation proceed simultaneously, there are two possible rate limiting regimes for consideration: (1) kinetically limited or reaction limited, when the growth rate is determined by compound formation; (2) diffusion limited, when the supply or removal of reactants or products limits the growth rate.

The conductivity measurement results are shown in figure 2.5 [39, 40]. In figure 2.5(a), the coincident linear parts of the 1, 3 and 5 μm film conductivity curves indicate that the conversion rate is thickness independent. From this result, the growth appears to be controlled by the reaction interface, rather than by diffusion within the precursor. Clearly, higher water partial pressure leads to faster conversion. The conductance curves in figure 2.5(b) for films of same thickness suggest that the conversion rate is independent of the oxygen partial pressure as the conversions at different oxygen pressures were completed within the same period of time. Note that the conductance of all three films increases almost linearly and reaches a plateau after a same time of processing.

The conversion rate can be analyzed using reaction kinetics and diffusion theory. A basic assumption is that the chemical reaction that accounts for the conversion is only slightly shifted from the equilibrium. Then, the partial pressure of HF, P_{HF} is related to the water partial pressure $P_{\text{H}_2\text{O}}$ by the equilibrium constant of the reaction. It is obvious that a faster conversion rate can be achieved by increasing water partial pressure and/or reducing HF partial pressure. Further analysis results in a conversion rate r expressed as

$$r = A \frac{\sqrt{P_{\text{H}_2\text{O}}}}{P_{\text{tot}}} \quad (2.10)$$

where A is a constant, P_{tot} is the total pressure of the processing atmosphere. The water partial pressure is an essential factor controlling the conversion rate. The effect of the total pressure on the conversion rate is reasonable, as the HF diffusivity is dependent on

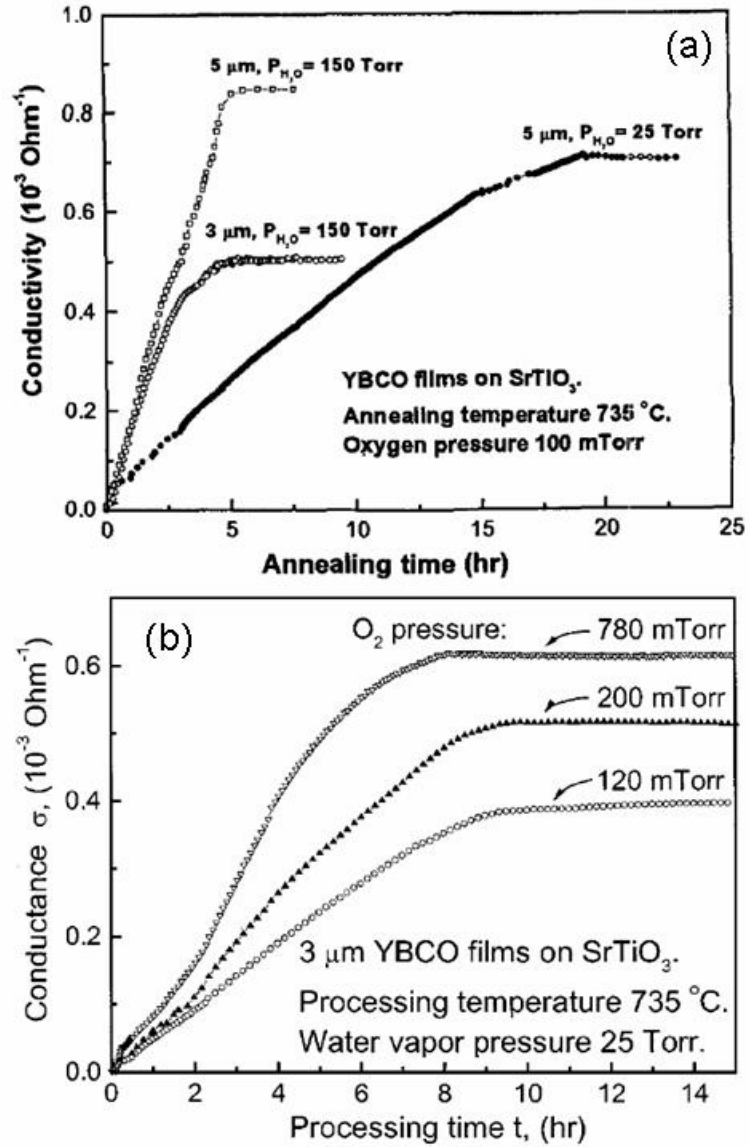


Figure 2.5. (a) Conductivity versus processing time for films of different thickness with various water vapor pressures. (b) Conductance versus processing time for $3 \mu\text{m}$ thick films being converted at different oxygen partial pressures.

P_{tot} . The effects of $P_{\text{H}_2\text{O}}$ and P_{tot} on the conversion rate are shown in the example in figure 2.6 [41].

Water partial pressure is a processing parameter and is relatively easy to monitor and handle. Roughly, $P_{\text{H}_2\text{O}}$ is about the same everywhere in the processing atmosphere. Compared with $P_{\text{H}_2\text{O}}$, the correlation between the conversion rate and the HF partial pressure is more complicated. P_{HF} is difficult to measure and depends not only on the total pressure but also on the gas flow rate. Under atmospheric pressure with low gas diffusivity, the released HF can accumulate and form a stagnant layer built-up on the precursor surface, especially at the downstream region of gas flow. This effect can significantly slow down the conversion with respect to the upstream region, resulting non-uniform films [42]. The problem can be addressed by increasing the gas flow rate, which inevitably will increase the consumption of gases, or by changing the gas flow characteristics (e. g., direction) [43].

Reducing the total pressure should be an effective measure to remove the generated HF, and therefore enhance the uniformity and increase the conversion rate. It has been shown that, for TFA-MOD precursors, effective conversion rates can be as fast

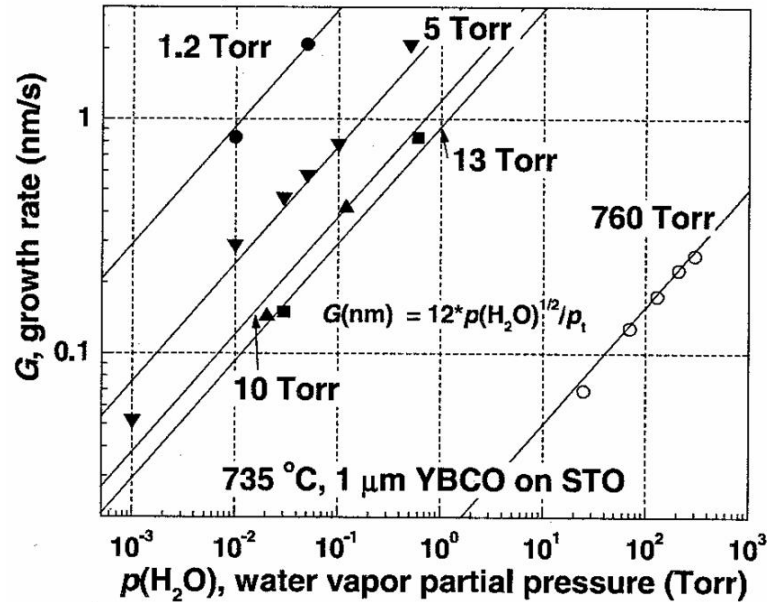


Figure 2.6. The YBCO conversion rates as a function of the water partial pressure at various total pressures for 1-μm-thick films.

as 6 nm/sec when the total pressure is reduced to about 1 Torr [44], while atmospheric pressure processing may have a conversion rate of less than 1 nm/sec. With the assistance of *in-situ* XRD observations during processing, the effect of total pressure on the conversion rate was also confirmed for the BaF₂ precursors [38]. At a total pressure of about 200 mTorr, when the HF removal is no longer a dominating factor, the conversion rate is very sensitive to the water partial pressures ranging from 0.0125 to 5 mTorr.

Although a common understanding has been achieved that lower total pressure and higher water partial pressure can speed up the conversion, there are limitations on implementing the idea. It has been found that the film structure (the orientation) is also affected by the conversion rate. For BaF₂ precursors [45], when the growth rate $r > 0.5$ nm/s, YBCO nucleates as a mixture of *c*-axis and randomly-oriented phases. Stable *c*-axis growth was observed only at $r < 0.2 \sim 0.3$ nm/s with moderate J_c . Higher J_c 's were obtained at even lower rates. The correlation between conversion rate and film structure is still being investigated.

Chapter 3

LOW-PRESSURE CONVERSION

3.1 Motivation

The motivations of applying a low-pressure conversion to the *ex-situ* YBCO film fabrication process are as follows:

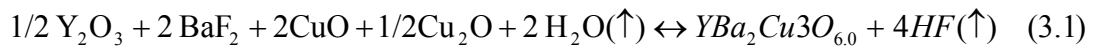
- (1) Improve the uniformity of the YBCO films fabricated using the *ex-situ* process;
- (2) Increase the conversion rate of the *ex-situ* process.

3.1.1 Uniformity

Uniformity of a film is characterized by the consistency in composition, phase, crystallinity, structure, thickness and physical properties between different regions. A YBCO coated conductor fabricated for the electrical efficiency applications should be uniform and homogenous along all the lateral directions. Non-uniformity on a film could significantly degrade its current carrying capacity, and serious inhomogeneity in a wire may compromise the reliability and cause destructive failure in the system.

For *e*-beam evaporation, the precursor film thickness uniformity is affected by the cosine law which determines the geometry of the vapor cloud and the angular distribution of evaporant flux. The effective deposition area with uniform composition is restricted as well, especially in a co-evaporation process using multiple sources. For CSD precursor films, the uniformity depends on the quality of the coating solution and the coating parameters associated with the specific coating method used. A crack-free precursor film of good integrity is the basis for fabrication of high performance superconducting films using the TFA-MOD method. More importantly, the YBCO film uniformity is also strongly determined by the post-deposition conversion.

In the BaF₂-based precursors, the barium source exists as BaF₂. The formation of YBCO during the processing anneal is directly related to the decomposition of BaF₂. An effective conversion reaction can be written as



It is important for the reaction to be fully completed and the precursor totally converted to obtain YBCO film with high phase purity and good performance.

In addition to a certain amount of water vapor, an appropriate amount of oxygen (determined by the YBCO phase diagram) is required in the processing ambient to form YBCO. Normally, the total pressure is balanced to 1 atmosphere with an inert carrying gas, such as argon or nitrogen. As the conversion reaction proceeds, HF is constantly released from the precursor. An HF partial pressure gradient may form on the precursor surface along the gas flow direction; as a result the HF released in the upstream accumulates in the downstream. Under typical atmospheric pressure processing conditions, the removal of the HF relies on the forced convection that is controlled by the gas flow conditions of particular reaction furnace geometry. If the removal of the HF is not efficient enough, the HF concentration gradient within the boundary layer becomes large. A difference in the reaction rate along the gas flow direction will result in an inhomogeneous conversion and consequentially nonuniform films with poor properties. The gas flow rate variation in the stagnant boundary layer in a longitudinal-flow reaction quartz tube furnace is schematically shown in figure 3.1. Also shown in the figure is the surface of a 10-cm-long sample, demonstrating the boundary layer related nonuniformity [46]. Such a nonuniformity problem may be ameliorated by increasing the gas flow rate and/or changing the gas flow direction. In general, it is difficult to produce highly uniform films under atmospheric pressure conditions. For large-scale wire production, atmospheric pressure processing usually consumes huge quantities of gases.

According to gas kinetics theory [47], gas flow can occur in three different regimes, which are primarily dependent on the geometry of the system and the total pressure. With different Knudsen numbers, which is defined as the ratio of the gas molecule mean free path to the characteristic dimension of the system, or $K_n = \lambda/D$, gas flow can be in the viscous regime, molecular regime, or an intermediate regime. When the Knudsen number is smaller than ~ 0.01 , the gas flow is in the viscous regime. This is the case for the atmospheric pressure processing of the *ex-situ* precursors,

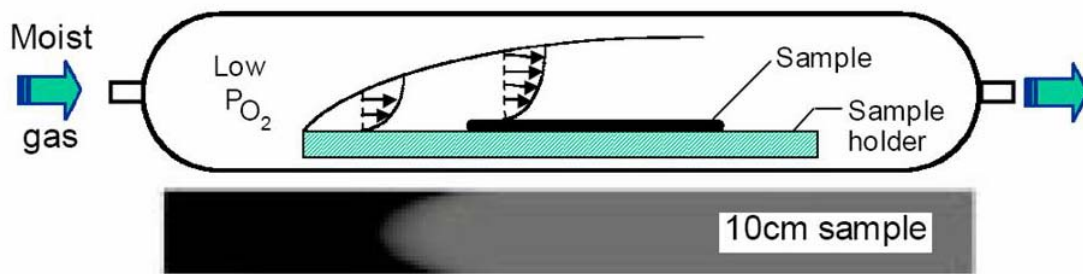


Figure 3.1. The gas flow rate distribution in the boundary layer in a longitudinal-flow quartz tube reactor. Bottom is the surface view of a 10-cm-long sample showing the nonuniform conversion.

as indicated in blue in figure 3.2. If the gas velocity is also small the flow is laminar and the flow velocity at the surface is zero. The mean free path and the gas diffusivity are small, so the transport of gas in the direction perpendicular to the gas flow is very slow. Gas flow will be in the molecular regime when the Knudsen number is larger than ~ 1 . In this case, with large mean free path the gas molecules can efficiently diffuse away from the surface. It may not be practical to convert the precursor in the molecular regime (which requires a total pressure less than 1 mTorr) due to the restriction of the oxygen pressure on YBCO stability. However, for total pressures ranging from 10 mTorr to hundreds of mTorr, indicated in green in figure 3.2, the gas flow will be in an intermediate regime ($0.01 < K_n < 1$). It is expected that under this condition, the gas diffusion will be greatly enhanced and the removal of HF is much faster.

3.1.2 Conversion Rate

The effect of total pressure on the conversion rate is analyzed in the following model based on the gas kinetics, diffusion and thermodynamics principles [48].

According to chemical reaction kinetics theory, the rate of the chemical reaction (3.1), thus the precursor conversion rate, strongly depends on the value of the ratio P_{HF}^2/P_{H_2O} . The concentrations of HF and H_2O at the reaction front between the precursor

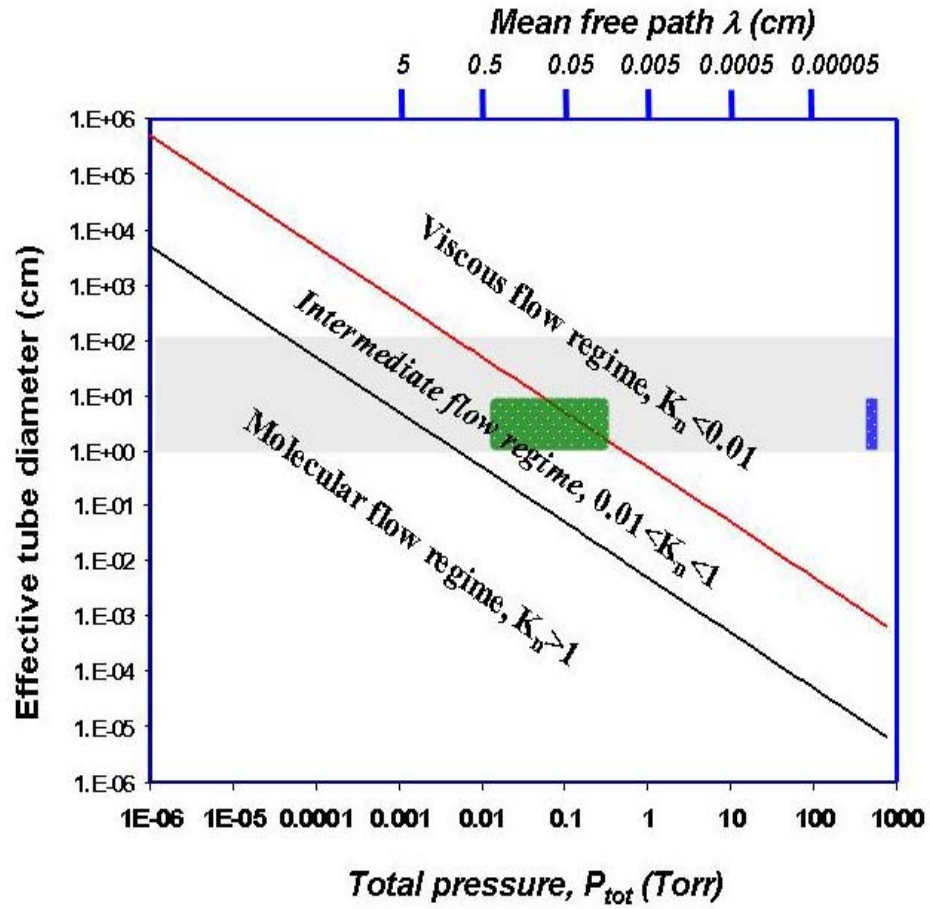


Figure 3.2. Gas flow regimes defined by the value of the Knudsen number K_n , which varies with the effective reactor dimension and the total pressure P_{tot} .

and YBCO can be approximated by the partial pressures P_{HF} and P_{H_2O} at the precursor surface (provided the diffusion rates within the precursor are sufficiently rapid) [49]. In this approximation, the removal of HF determines the conversion rate when the water partial pressure is maintained constant. As pointed out earlier, when the total pressure is high, *e.g.* at 1 atmospheric pressure, the removal of HF at the surface is mainly implemented by gas flow (forced convection). At lower pressures, however, when HF can diffuse away from the surface more effectively, the effect of HF removal on YBCO conversion rate can be evaluated in the absence of flow related effects due to a large mean free path of gaseous molecules.

For an assumed constant YBCO growth-front rate, r (cm/s), the steady-state HF molecular out-flux, Φ (molecules/cm²-sec) is

$$\Phi = \frac{4r}{V_{cell}} \quad (3.2)$$

where $V_{cell} \approx 1.74 \times 10^{-22} \text{ cm}^3$, is the volume of YBCO unit cell. For a planar geometry, the molecular flux of HF can be expressed as

$$\Phi = -D \frac{dC(z)}{dz} \quad (3.3)$$

where D is the diffusivity of HF and $C(z)$ is the HF concentration, which can be related to P_{HF} as $C(0) = P_{HF}/kT$ at the sample surface.

From kinetic gas theory [50], the diffusivity D is inversely proportional to the total gas pressure, and for a binary gas system with HF as one component and the other gases (O_2 and H_2O) as the second component,

$$D \approx \frac{kT \sqrt{\frac{8kT}{\pi} \left(\frac{1}{M_{HF}} + \frac{1}{M_{O_2}} \right)}}{3\pi\delta^2 P_{tot}} \quad (3.4)$$

where M_{HF} and M_{O_2} are the molecular weight of HF and O_2 , and $\delta = (\delta_{HF} + \delta_{O_2})/2$ is the average molecular diameter. For simplicity, suppose that the HF is absorbed at the wall of the quartz furnace tube a distance z_0 away from the sample surface, so that $C(z_0) \approx 0$. Then, from equations (3.2) - (3.4), we obtain P_{HF} at the sample surface,

$$P_{HF} = \frac{12\pi\delta^2 z_0 P_{tot}}{V_{cell} \sqrt{\frac{8kT}{\pi} \left(\frac{1}{M_{HF}} + \frac{1}{M_{O_2}} \right)}} \quad (3.5)$$

Figure 3.3 gives the relationship between the ratio P_{HF}/P_{H_2O} and the assumed YBCO growth rate r based on equation (3.5). The results are given for total pressures and specific water partial pressures under typical atmospheric pressure processing and for certain low-pressure processing conditions. It can be seen that, in the absence of convection, the required ratio P_{HF}/P_{H_2O} for atmospheric pressure processing is lower than that for low-pressure processing at a given YBCO growth rate. However, the assumed growth rates r are only possible provided the ratio P_{HF}/P_{H_2O} is far below that defined by the thermodynamic equilibrium condition, when the Gibbs free energy of reaction (3.1) approaches zero. At equilibrium, $\Delta G = 0$, that is

$$\Delta G = \Delta G^\circ + 2RT \ln \frac{P_{HF}^2}{P_{H_2O}} = 0 \quad (3.6)$$

where $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Therefore, P_{HF} is calculated as

$$P_{HF} = \sqrt{P_{H_2O} \exp\left[-\frac{\Delta H^\circ - T\Delta S^\circ}{2RT}\right]} \quad (3.7)$$

For reaction (3.1), the standard enthalpy $\Delta H^\circ \approx 634$ kJ/mole and standard entropy $\Delta S^\circ \approx 293$ J/mole-K, based on the data from references [51] and [52]. At the temperature of 730 °C, the calculated equilibrium ratios of P_{HF}/P_{H_2O} , which are also indicated in figure 3.3, are 2.35×10^{-4} and 1.05×10^{-1} for $P_{H_2O} = 0.1$ mTorr and $P_{H_2O} = 20$ Torr, respectively. These ratios actually limit the validity of any assumed YBCO growth rates. It can be seen that without the forced gas flow, which should further decrease the ratio P_{HF}/P_{H_2O} , YBCO film growth is limited to a slower rate under atmospheric pressure processing conditions than for the low-pressure regime. In other words, low-pressure processing should be effective in increasing the conversion rate. The experimentally observed rates $r \geq 0.2$ nm/sec for 1 atm processing is presumably only possible with forced-flow convection.

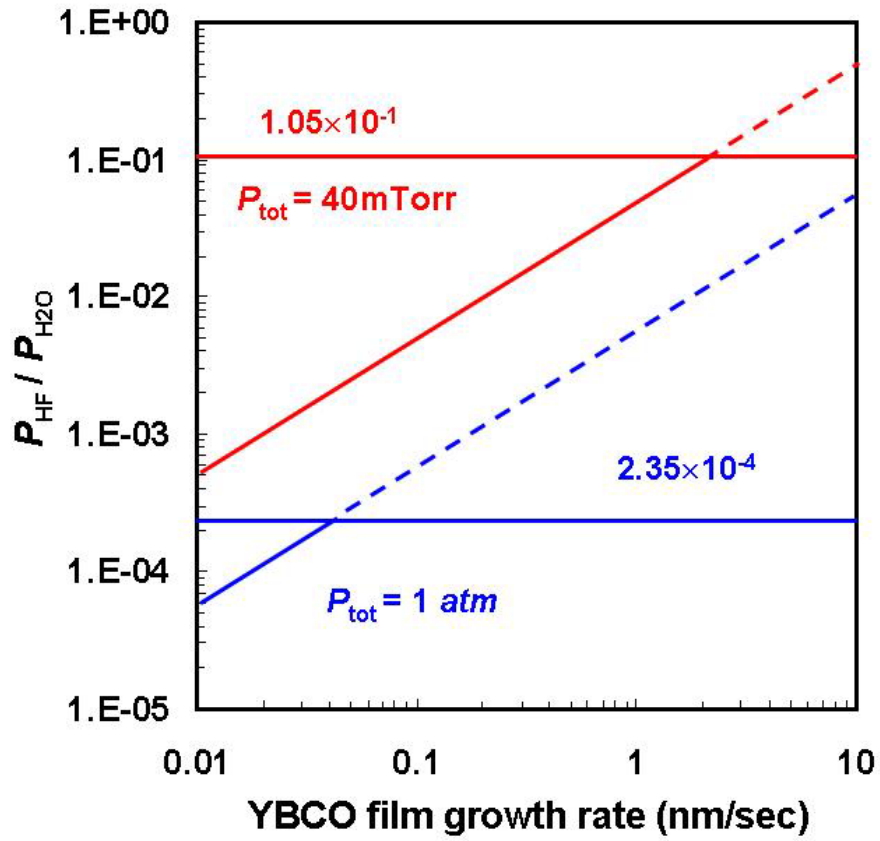


Figure 3.3. Relationship between $P_{\text{HF}}/P_{\text{H}_2\text{O}}$ and assumed conversion rate at the given conditions of $P_{\text{tot}} = 1 \text{ atm}$ for atmospheric pressure processing, and $P_{\text{tot}} = 40 \text{ mTorr}$ for low-pressure processing. At an assumed processing temperature of 730°C , the horizontal lines represent the equilibrium thermodynamic conditions, where the conversion ceases.

3.2 Precursor Deposition

3.2.1 Substrates

Several substrate templates were used for the deposition of the precursors, including single crystal SrTiO_3 and LaAlO_3 , ceria (cerium oxide, CeO_2) buffered single crystal yttria-stabilized zirconia (YSZ) and RABiTS.

Precursors were deposited directly on single crystal SrTiO_3 (strontium titanium oxide, STO) and LaAlO_3 (lanthanum aluminum oxide, LAO) substrates. These (100) oriented single crystal substrates were selected because they have a good lattice match with YBCO. The one side polished single crystal substrates, the products of Princeton Scientific Corp, were used in the as-delivered state.

CeO_2 was deposited on the (100) oriented single crystal YSZ using RF sputtering. The YSZ substrates were ordered from Crystal GmbH. Before the deposition, YSZ were first ultrasonically cleaned in acetone for at least 10 min, then rinsed in methanol, and finally dried with blowing argon. Using a ceria target from Plasmaterials, Inc, the RF sputtering was conducted in an AJA RP3 sputtering system having a base pressure of $\sim 10^{-7}$ Torr. A sputter gas of Ar - 4% H_2 was used for generating the plasma, and water vapor, maintained at a partial pressure of $\sim 8 \times 10^{-6}$ Torr, was introduced into the deposition chamber as the oxygen source for assured stability of CeO_2 . During the deposition, the total pressure in the chamber was about 5 mTorr. The substrate temperature was kept at 740 °C, and the deposition was usually conducted at an RF power of about 120 watts. The CeO_2 -buffered YSZ was inspected using XRD diffraction and atomic force microscopy (AFM) for the crystalline structure and the surface morphology. It can be seen in figure 3.4 that the (200) oriented CeO_2 layer is epitaxially grown on YSZ and its surface is very smooth with an average roughness R_a around 0.2 nm.

RABiTS templates were provided either by Oak Ridge National Laboratory (ORNL) or by American Superconductor Corporation (AMSC). The configurations of the

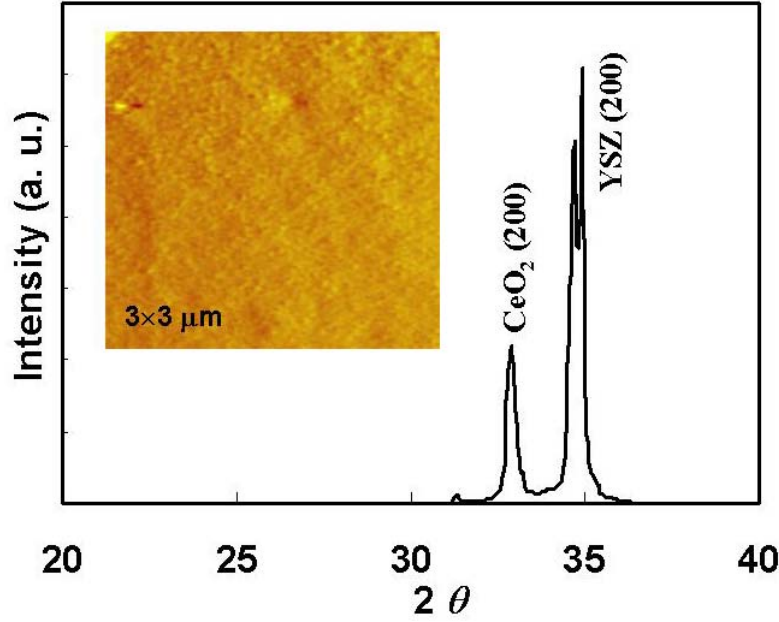


Figure 3.4. XRD $\theta \sim 2\theta$ Scan Pattern of the CeO_2 buffer layer deposited on the YSZ substrate using the RF sputtering. The insert is an AFM micrograph of the CeO_2 surface.

templates are basically the same. For ORNL RABiTS, it is $\text{CeO}_2(20 \text{ nm})/\text{YSZ}(200 \text{ nm})/\text{Y}_2\text{O}_3(20 \text{ nm})/\text{Ni-W}$. For AMSC RABiTS, it is $\text{CeO}_2(75 \text{ nm})/\text{YSZ}(75 \text{ nm})/\text{Y}_2\text{O}_3(75 \text{ nm})/\text{Ni-W}$. All the buffer layers were deposited by PVD methods, either sputtering or e -beam evaporation. Some of the characteristics of the above single crystal substrates and buffer materials are listed in table 3.1.

3.2.2 Electron Beam Co-Evaporation

The electron beam co-evaporation system used for the YBCO precursor deposition is schematically shown in figure 3.5. The system has a base pressure of about 1×10^{-6} Torr. BaF_2 , and the metallic pure Y and Cu are used as the source materials. During the deposition, small amount of oxygen was dosed into the vacuum chamber to partially oxidize the precursor. The oxygen pressure was controlled at a level of $(5 \sim 9) \times 10^{-6}$ Torr and the substrate temperature was maintained at approximately 100 °C.

Table 3.1: Characteristics of selected single crystal substrates, buffer materials and YBCO.

Material	Crystal Structure	Lattice Constant (Å)	Misfit to YBCO (% RT)	Thermal Expansion Coefficient α ($10^{-6}/^{\circ}\text{C}$)
SrTiO ₃	pervoskite	3.905	+1.43	10.4
LaAlO ₃	pervoskite	3.789	-1.51	10
CeO ₂	cubic (CaF ₂)	5.411	+0.14	8.9
YSZ	cubic	5.139	-5.56	8.8
Y ₂ O ₃	cubic (Mn ₂ O ₃)	3.723	-3.30	8.5
YBCO	orthorhombic	a = 3.8227 b = 3.8872 c = 11.6802		11.4

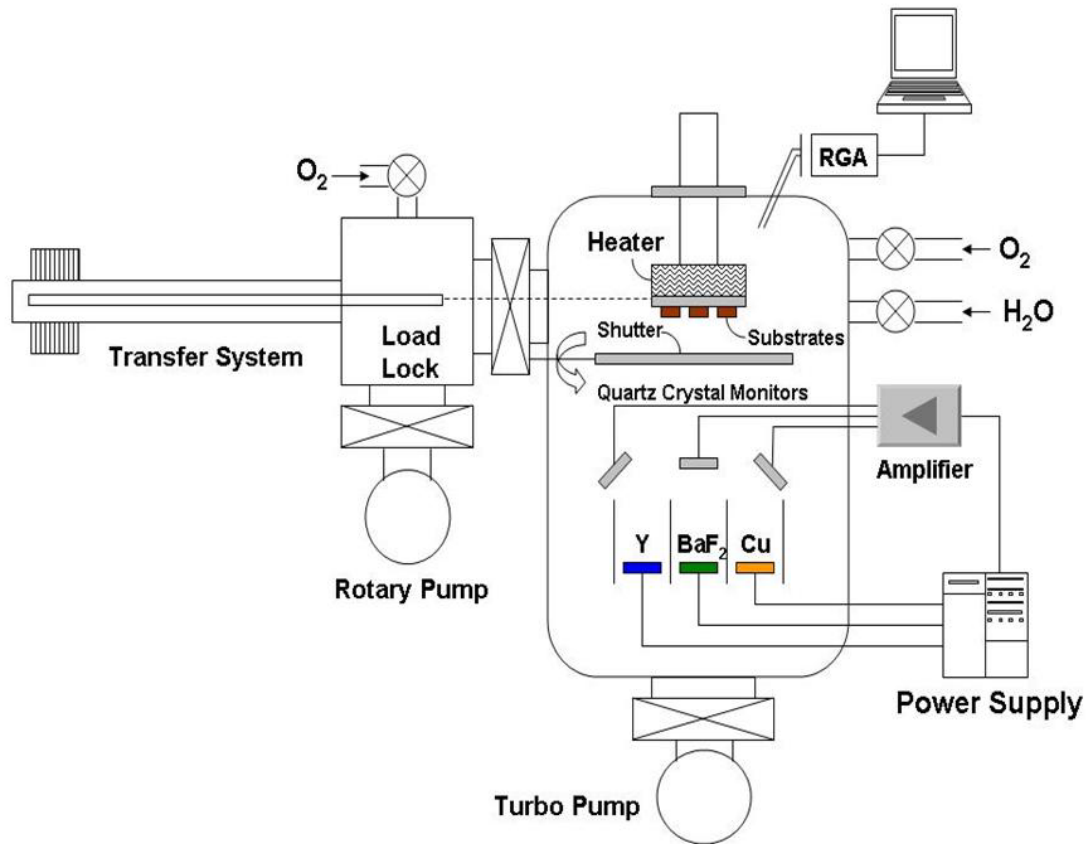


Figure 3.5. Schematic diagram of the electron beam co-evaporation system.

To obtain a stoichiometric composition of the precursors, the evaporation rates of the materials were independently controlled using three individual quartz crystal thickness monitors (QCMs). The composition of the precursors was frequently calibrated using the Rutherford backscattering spectroscopy (RBS) or the inductively coupled plasma (ICP) analysis after the deposition. Precursor thickness was inferred from the combined QCM readings, which was also calibrated against the RBS result or a profilometry measurement.

3.2.3 TFA-MOD

The YBCO precursors were deposited using the TFA-MOD method based on the procedure described in figure 2.1.

The coating solution was prepared according to the method given in figure 2.2. In brief, starting materials of $\text{Y}(\text{OCOCH}_3)_3$, $\text{Ba}(\text{OCOH}_3)_2$ and $\text{Cu}(\text{OCOCH}_3)_2$ powder with cation ratio $\text{Y}:\text{Ba}:\text{Cu} = 1:2:3$ were fully mixed and then reacted with trifluoroacetic acid (TFA). The resultant was then refluxed at 70 °C water bath in a reducing atmosphere into a glassy state. The blue residue was redissolved in methanol. The reflux and redispersion were repeated several times in order to remove the extra acid from the solution. The final solution usually has a total cation concentration of about 1 mol/l. Spin coating was used to coat the substrates with the solution. Speeds ranging from 2,000 to 3,000 rpm and time ranging from 30 ~ 120 sec were utilized for the coating.

The as-coated precursors were calcinated by a slow heating to 400 °C in a humidified oxygen atmosphere to become the precursors. The calcination was conducted in a quartz tube furnace. The furnace contains three heat zones in a horizontal configuration with the temperature controlled by three K-type thermocouples. Humidified atmosphere is obtained by bubbling the oxygen through a water bath, the temperature of which ranges from 0 to 65 °C. A humidified atmosphere is important because it is believed that the copper in the precursor has high vapor pressure at the calcining temperature and its evaporation can be suppressed with the presence of water vapor [53]. The temperature protocol for the calcinations is shown in figure 3.6.

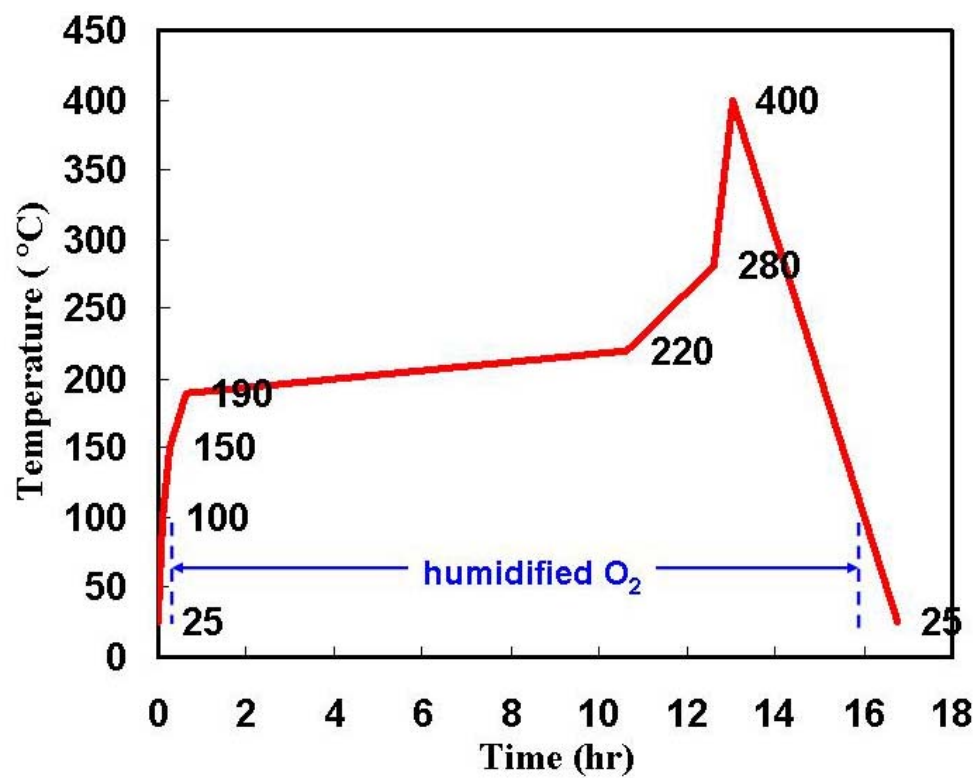


Figure 3.6. The temperature versus time profile used in the TFA-MOD process to calcinate the as-coated gel film into the precursor.

3.3 Low-Pressure Conversion and Film Characterization

3.3.1 Precursor Conversion

The low-pressure conversion was conducted in an induction vacuum heating system [54]. The configuration of the system is schematically shown in figure 3.7.

The sample is located at the center of the quartz tube in which the base pressure is about 2×10^{-6} Torr and is 4×10^{-6} Torr at the functional conductance. To maintain a small gas flow that is consistent with the controlled pressure in the quartz tube, the mini valve connecting the main vacuum chamber and the quartz tube is set first before the introduction of any gas. Water vapor is introduced from a deionized water source and its partial pressure (P_{H_2O}) is adjusted by a variable leak valve. P_{H_2O} is monitored by an ionization vacuum gauge for pressures lower than 2 mTorr, and by a convectron gauge when higher than 2 mTorr. A MicropoleTM model MPA6-7-2/65C RGA (Residual Gas Analysis) detector was also used to check the water partial pressure. Values of P_{H_2O} can be adjusted in a range from 2×10^{-5} Torr to more than 100 mTorr. After the stabilization of P_{H_2O} , high purity oxygen is introduced by adjusting another variable leak valve. The total pressure in the quartz tube (P_{tot}) is set as indicated by the two convectron vacuum gauges, which are located upstream and downstream from the sample position. No carrier gas is used in the system for typical low-pressure processing. Therefore, P_{O_2} is obtained as $P_{O_2} \approx P_{tot}$ when $P_{H_2O} \ll P_{O_2}$, and $P_{O_2} = P_{tot} - P_{H_2O}$ when P_{H_2O} is comparable to P_{O_2} . During processing, a typical gas flow rate is about 0.3 ~ 1 sccm in this particular system based on a gas kinetics calculation. The small gas flow rate indicates that the processing in this system is in a quasi-static state.

Sample temperature was determined by measuring the temperature of the induction tube using a two-color optical pyrometer. The relationship between the two temperatures was calibrated against a type-K thermocouple introduced at the sample position before a sample is loaded. The heat-up ramp rate for the annealing can be varied from a very low value up to ~ 300 °C/min by adjusting the power supply for the induction coil. Annealing times varied depending on film thickness. About 5 min before

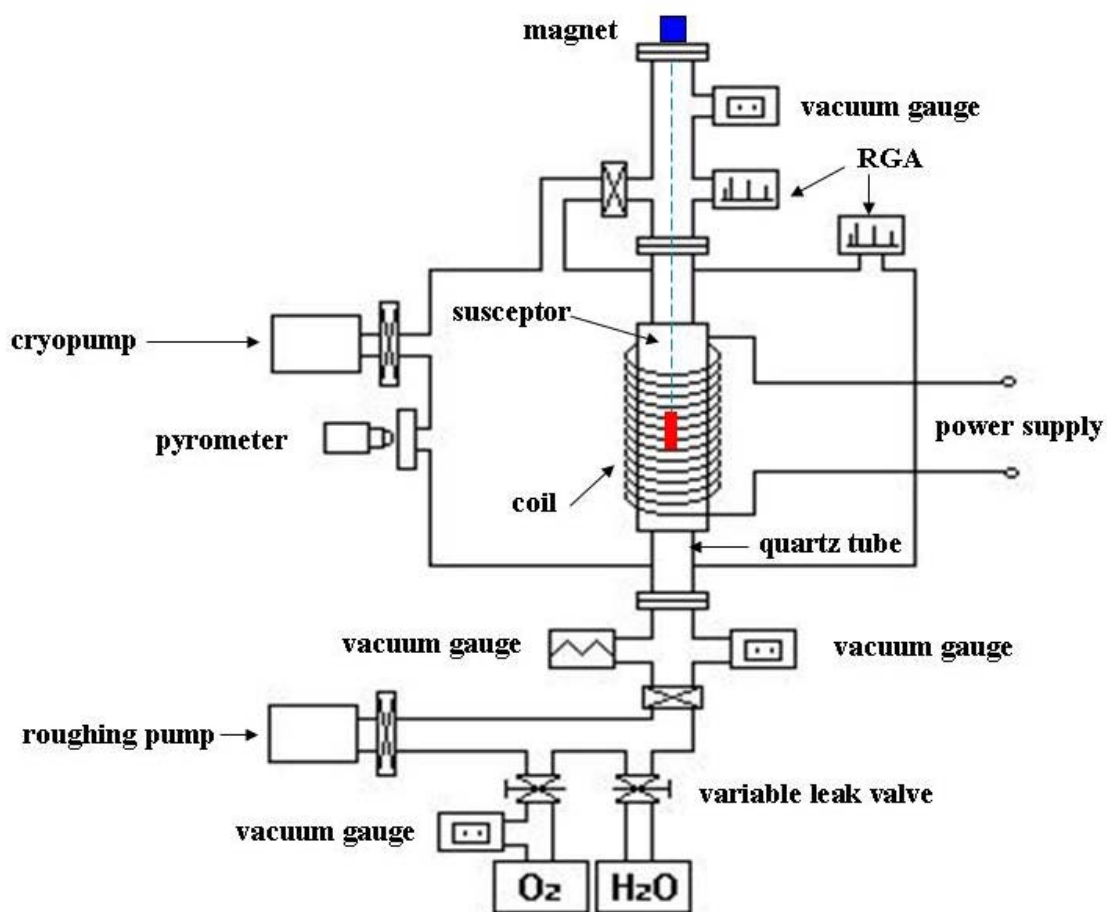


Figure 3.7. Schematic diagram of the low-pressure processing system. The sample is kept in the center of the quartz tube during a conversion.

the cool down, the water vapor supply was shut off. The cooling rate was about 30 °C/min, and upon reaching 500 ~ 450 °C, more oxygen was introduced until P_{O_2} reaches hundreds of Torr in order to oxygenate the YBCO. Normally, additional low-temperature oxygenation is not necessary for a fully converted film.

When necessary, a sample can be quenched anytime during a processing simply by removing the retaining magnet at the top flange, which drops the sample basket into the room temperature region at the bottom. Quenched samples are inspected to analyze the phase development during a conversion processing.

3.3.2 Film Characterization

To analyze the phases developed in the films, a Philips model XRG3100 X-ray diffractometer with the Cu K_α radiation is frequently used to record the θ - 2θ diffraction patterns of the films. The X-ray source operates at 50 KV and 30 mA with a wave length of 1.54 Å. For the θ - 2θ scan, a step size of 0.05 ° and a dwelling of 1.0 second are normally used. MDI (Materials Data Inc.) Jade 6.0 is the software for XRD data processing and phase analysis.

A four-circle Picker model 3488M-401 diffractometer is used to characterize the texture of films. The out-of-plane alignment of the YBCO films is usually represented by the full width at half maximum (FWHM) ($\Delta\omega$) of the YBCO (005) reflection peak obtained from a ω -scan pattern (rocking curve). The in-plane of the YBCO films is measured by the FWHM ($\Delta\Phi$) of the YBCO (113) reflection peaks obtained from a Φ -scan pattern. For a detailed survey of the texture, the YBCO (113) pole figure is recorded and analyzed using the software Surfer 6. The background noise is removed by subtracting a 1° offset pole figure signal from the (113) pole figure signal. The overall texture can be approximately represented by the volume fraction of cubic phase (VF_{CP}), which is defined as of the ratio of the integral cube peak intensity to the total intensity. The configuration of the four-circle diffractometer goniometer is schematically shown in figure 3.8.

A JEOL JSM-840 scanning electron microscope is used to observe the film surface morphology, with an electron beam voltage of either 7 or 10 KV. The attached X-

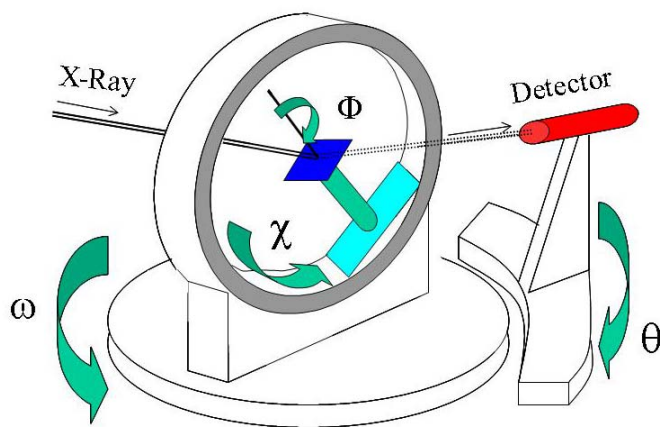


Figure 3.8. Schematic goniometer configuration of the four-circle X-ray diffractometer for inspecting film texture.

ray energy dispersive spectroscopy (EDS) provides qualitative information on the film composition. For a fully converted film, the surface morphology is a good indicator of the YBCO orientation. So, an optical microscope is also used for a quick inspection of film surface morphology, with further detail obtained using the atomic force microscopy, a Nanoscope III Multimode AFM system, normally in the contact mode.

Film composition is occasionally measured using inductively coupled plasma optical emission spectroscopy (ICP-OES) to confirm the stoichiometry. The system is a model IRIS Intrepid II XSP manufactured by Thermo Electron Corporation. A Dektak IIA stylus profilometer is used for the film thickness measurement. Cross-sectional structure of selected samples is inspected by transmission electron microscopy (TEM) for detailed phase and microstructural information. The phase and structural information revealed by the TEM inspection is helpful in understanding the conversion and epitaxy mechanism.

During the process of precursor conversion and YBCO phase formation, the valence of the cations and the chemical bonds between the cations and the anions, namely F^- and O^{2-} undergo constant changes. There is interest in exploring these changes so the conversion mechanism can be better understood. The *ex-situ* YBCO precursor conversion behavior is strongly correlated with the precursor chemistry. In order to study this

correlation, the precursors, YBCO films and the partially converted quenched films are inspected using the X-ray photoelectron spectroscopy (XPS).

In an XPS experiment, a sample surface is irradiated by X-ray, and the core-level electrons are emitted as the result of the photoelectron effect. An electron spectrometer or a detector is used to measure the energy distribution of the photoelectrons as well as the Auger electrons emitted from the sample near-surface. Peaks in this distribution correspond to photoelectrons that emerge without inelastic scattering in the sample. These emitted electrons have the kinetic energies given by:

$$KE = h\nu - BE - \Phi \quad (3.8)$$

where KE and BE are the kinetic energy and binding energy of the emitted electron, respectively, $h\nu$ is the X-ray photon energy. Φ is the spectrometer work function. The kinetic energies of the photoelectrons contributing to these peaks are thus related to the core-level binding energies which are characteristic of the element, and therefore can be used for elemental identification. Moreover, the sensitivity of the photoelectron energy to the atom's valence state makes XPS an efficient tool to study the element chemical state changes in a material. The photoelectron emission process is shown schematically in figure 3.9.

X-ray photoelectron spectroscopy (XPS) inspections were carried out using a PHI 5600 system with a non-monochromatic Al K_α source. The configuration of the XPS system is shown in figure 3.10. The energy of the X-ray photons is 1486.6 eV. The x-ray beam spot size was about 0.8 mm in diameter. The electron binding energy scale was calibrated using the Au 4f7/2 and Cu 2p3/2 lines from pure Au and Cu. Depth profiling involves iterative etching using a 3 keV Ar⁺ ion beam, with XPS data collection after each etching. The sputtering rate was calibrated as about 0.5 nm/min. The software used for the XPS spectrum analysis is Compro7.

One example of using XPS in this study is the inspection of the CeO₂-buffered YSZ. Cerium has two different major oxides, namely CeO₂ and Ce₂O₃. While CeO₂ has a cubic structure having a good lattice match with YBCO, Ce₂O₃ is hexagonal. The valence of cerium is Ce⁴⁺ in CeO₂, but Ce³⁺ in Ce₂O₃. With the change of the oxygen concentration, the valence of cerium may vary. An oxygen deficient ceria is believed to

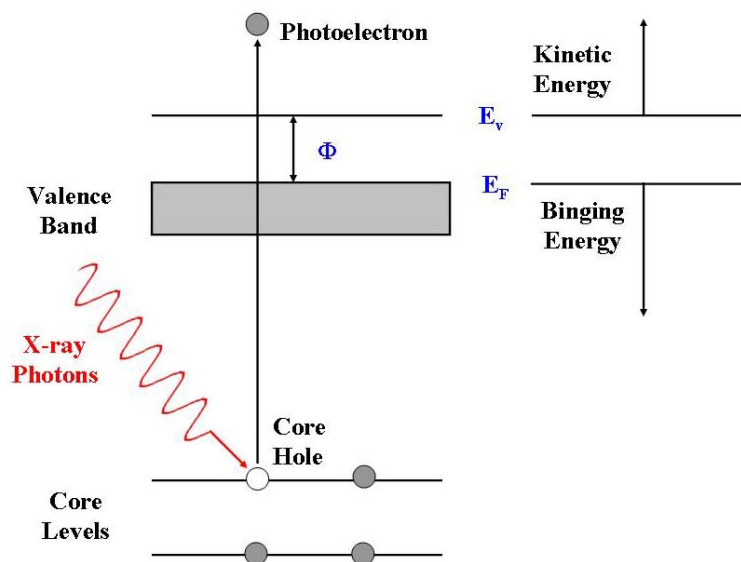


Figure 3.9. The photoelectron emission process.

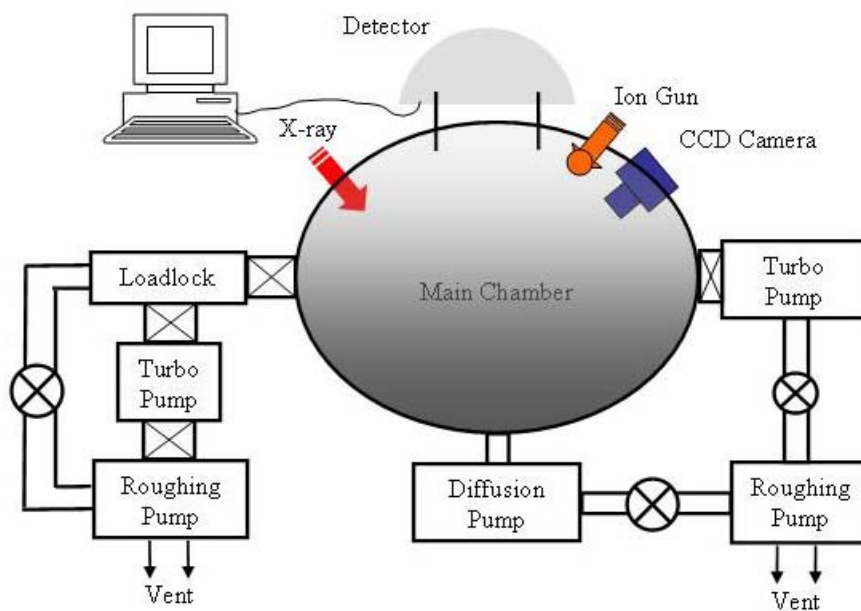


Figure 3.10. Schematic diagram of the X-ray photoelectron spectroscopy system.

be more reactive to the precursor, which is disadvantageous to the conversion. XPS is sensitive to the valence of cerium, so it can be used to inspect the stoichiometry of the ceria buffer deposited.

The electric transport measurements were done in a cryostat system using the standard four-probe method. The superconducting transition behavior including a resistance versus temperature (RT) curve and the corresponding critical temperature T_c can be obtained. The critical current density J_c values are determined by the 1 $\mu\text{V}/\text{cm}$ criterion. When in-field J_c is measured, the magnetic field is applied in a direction perpendicular to the film surface. The method of the standard four-probe measurement is described in figure 3.11. When the film thickness is t , the sample width is W , and the distance between the voltage leads is L , the resistivity is simply $\rho = RWt/L$. The critical current density is $J_c = I_c/Wt$, where I_c is the critical current. To obtain the good electric contacts needed for current injection, silver is deposited by dc magnetron sputtering to form both current and voltage leads using a mask. In order to further enhance the contacts, the deposition of Ag is followed by a 30 minute oxygenation annealing at 500 $^{\circ}\text{C}$ under 1 atmospheric pure oxygen pressure with a slow furnace cooling.

Superconducting properties can also be determined through the magnetization measurement of the film using a SQUID (Superconducting QUantum Interference device)-based magnetometer. The system used is a Quantum Design model MPMS 7 SQUID magnetometer. It's a fully automated magnetometer, capable of measuring magnetic moment ranging from 10^{-7} to 300 emu. Sample temperature ranges from 2 K to 400 K, and the magnetic field can vary from 1 Gauss to 7 Tesla.

The MPMS system comprises two main sections: the dewar, probe and SQUID assembly, and the electronic control cabinet. Liquid helium stored in the dewar is used to cool the sample and the superconductor magnet (made of the LTS NbTi) that generates the applied magnetic field. The probe, which is actually a pick-up coil assembly, and the SQUID are the most important parts in the magnetometer. The configuration of this part is shown in figure 3.12. A SQUID is a device composed of two parallel Josephson Junctions, which is a superconductor/insulator/superconductor (SIS) sandwich. The

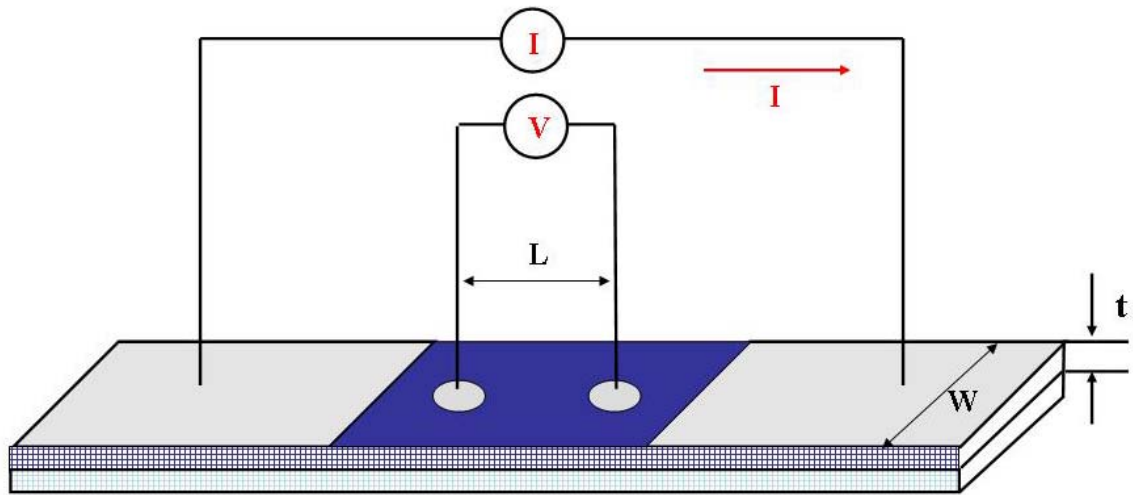


Figure 3.11. Standard four-probe method for the measurement of transport properties of superconducting films.

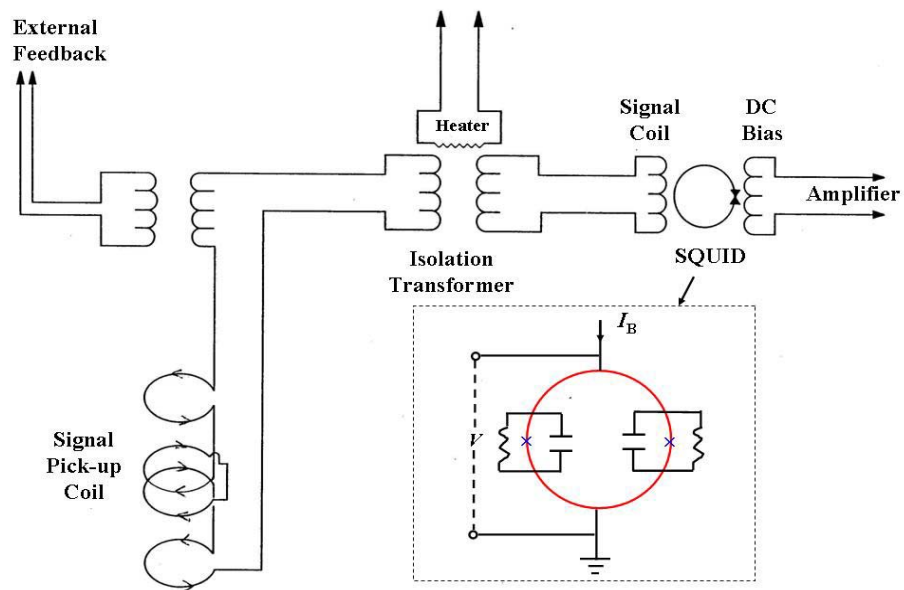


Figure 3.12. The configuration of the signal probe and the SQUID section in the MPMS SQUID magnetometer. The insert is the SQUID ring.

insulating barrier layer between the two superconductors is sufficiently thin that the superconducting current can pass through the barrier without any resistance by virtue of quantum tunneling. This is known as the Josephson Effect [55]. The pick-up coil, which is also made of LTS, senses any changes in the magnetic flux resulting from the longitudinal movement of a sample having certain magnetic moment. The signal input coil transforms the resulting induced current into a magnetic flux in the SQUID sensor. The voltage across the SQUID superconducting loop oscillates with the phase difference between the wave functions in the two junctions, which is affected by the change in the magnetic flux. By proper calibration using a sample of known magnetic moment, the measured voltage is used to determine the magnetic moment in the sample.

In practice, a sample is mounted in a plastic straw tube. Its longitudinal movement is driven by a step motor. When a thin film superconducting sample is measured, the magnetic field is applied in the direction perpendicular to the film surface. For a small applied magnetic field that is below the lower critical field B_{c1} , a bulk sample with no pinning is in the Meissner state. For a thin film sample with significant pinning, geometrical effects concentrate the magnetic field near the edges to levels above B_{c1} ; consequently critical currents are induced near the edge of the film and subcritical currents further from the edge. As the temperature increases, the magnetic moment will decrease, up to the critical temperature, where the magnetic moment becomes zero. In this way, the critical temperature T_c can be easily determined by a low field temperature scan.

The magnetic dipole moment of a superconducting sample is related to the circulating current according to the following equation,

$$m = \frac{1}{2c} \int (r \times J) dV \quad (3.9)$$

where J is the current density at the location r . The Bean critical state model [56, 57] for a bulk sample assumes that whenever a current flow in a superconductor, the current density at the outside of the sample will immediately jump up to the critical current value J_c . To transport more current, the shallow layer thickens, again carrying J_c . In this way, the current is always flowing with the critical current density J_c , but only the outer

portion of the superconductor carries a current other than zero. Correspondingly, the magnetic flux distribution inside the superconductor is in a sand pile mode. That is, the flux gradient is a constant wherever there is current flow. Based on the Bean model, for a rectangular shaped sample with the magnetic field perpendicular to the surface, the critical current J_c is given as,

$$J_c = \frac{20\Delta M}{a(1 - \frac{a}{3b})} \quad (3.10)$$

where $\Delta M = (M^- - M^+)$ is the difference between the decreasing magnetization M^- and the increasing magnetization M^+ . Here, $b > a$ are the lateral dimension of the sample. In practice, ΔM has the unit in emu/cm³, b and a in cm, and J_c is in unit A cm⁻². For thin film geometry, the current distribution is more complex during penetration of the magnetic field [58]. However, when the film is fully penetrated by the field, as done in this work, the simple results given above are valid.

3.4 Results and Discussion

3.4.1 Thin Films on STO

The first investigations of low-pressure conversion were conducted on 0.14 μ m thick precursors deposited by *e*-beam co-evaporation on STO single crystal substrates. The low-pressure conversion was conducted in the system shown in figure 3.7. The typical processing parameters are as follows: ramp rate ~ 70 °C/min; water partial pressure $P_{H_2O} = 0.08$ mTorr; oxygen partial pressure $P_{O_2} = 20$ mTorr; processing temperature $T = 730$ °C; conversion time (the wet dwell time when sample is at the processing temperature) = 60 min; cooling rate ~ 10 °C/min. A 500 °C oxygenation in one atmospheric pressure of pure oxygen was given to the sample after the Ag contact was deposited.

The XRD $\theta \sim 2\theta$ scan pattern and the SEM surface image for the thin film are shown in figure 3.13. It can be seen that pure *c*-axis YBCO film was obtained in this sample, indicated by only (00*l*) reflections in the XRD pattern. The sharp peaks are consistent with the SEM surface image that has typical *c*-axis YBCO feature characterized as the fine equal-axial and uniformly distributed particulates. The film's properties were measured using the standard four-probe transport method. The critical temperature T_c is 90.3 K, the critical current density J_c at self-field, 77 K is 3.2 MA/cm², and the irreversibility field B_{irr} is 7.3 Tesla at 77 K. The resistivity versus temperature curve and the J_c versus magnetic field relationship are shown in figure 3.14.

3.4.2 Thicker Films on STO

Precursors with thickness ranging from 0.32 μm to 1.04 μm were deposited on the STO substrates by the *e*-beam co-evaporation. The conversion conditions were similar to the 0.14 μm thick films except that the processing time was longer for the thicker films in order to fully convert the precursors. The processing time for a 0.34 μm is 90 min, and the P_{O_2} and P_{H_2O} were 40 mTorr and 0.08 mTorr, respectively. Again, the XRD $\theta \sim 2\theta$ scan pattern and SEM surface morphology indicated a phase pure *c*-axis YBCO film. Here, the properties of the film were measured by the SQUID magnetometer. The critical temperature T_c is 90.1 K and the 77 K self-field J_c is 3.1 MA/cm², as shown in figure 3.15.

The 1.04 μm precursors were processed at $\sim 730^\circ\text{C}$ with different water partial pressures and oxygen partial pressures. One of the precursors was first annealed in $P_{H_2O} = 0.08$ mTorr and $P_{O_2} = 20$ mTorr for 180 min. The XRD $\theta \sim 2\theta$ scan result indicated that besides the predominant *c*-axis oriented YBCO phase there remained certain amount of BaF₂ in the precursor, as shown in figure 3.16. This implies that the conversion was not completed. So, an additional 60 min annealing under the same condition was given to the film and that lead to a fully converted film with a T_c of 90.3 K and a 77 K self-field J_c of 1.45 MA/cm².

With about the same oxygen partial pressure of 20 mTorr, different water partial pressures ranging from 0.08 to 2 mTorr were tested. For the *e*-beam co-evaporated precursors deposited on STO, there is a general tendency that lower water partial

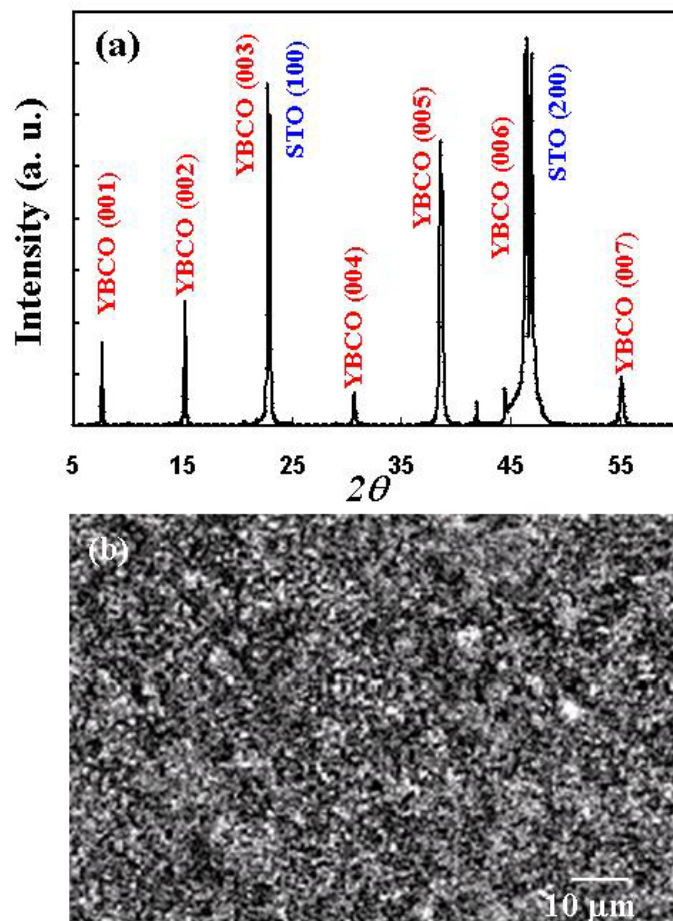


Figure 3.13. (a) XRD $\theta \sim 2\theta$ pattern, and (b) SEM surface image of the 0.14 μm film converted in the low-pressure processing system.

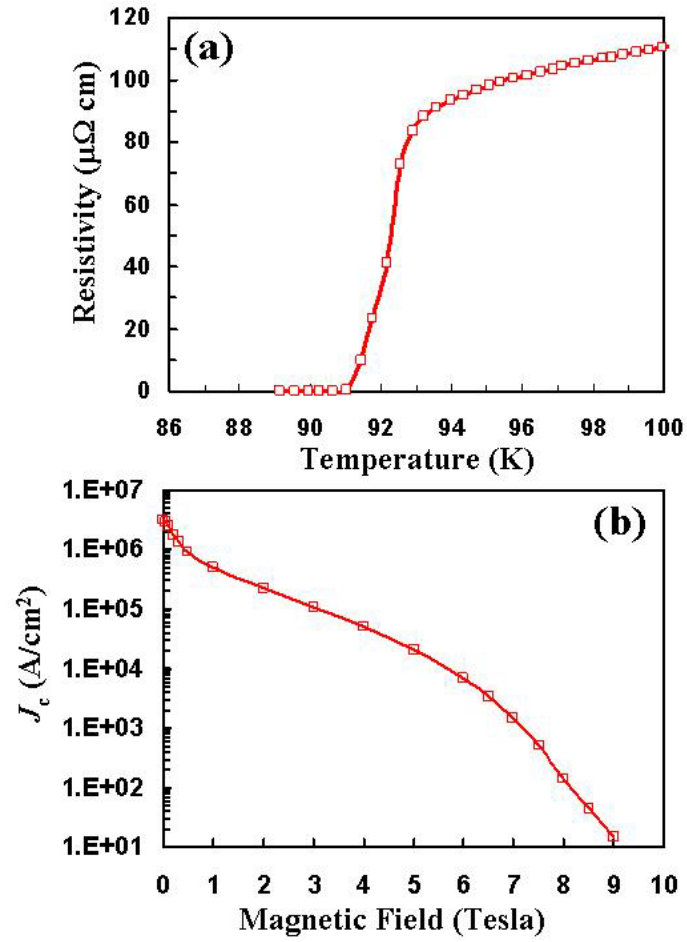


Figure 3.14. (a) Resistivity versus temperature relationship, and (b) Magnetic field dependence of the critical current density J_c at 77 K of the 0.14 μm thick film converted in the low-pressure processing system.

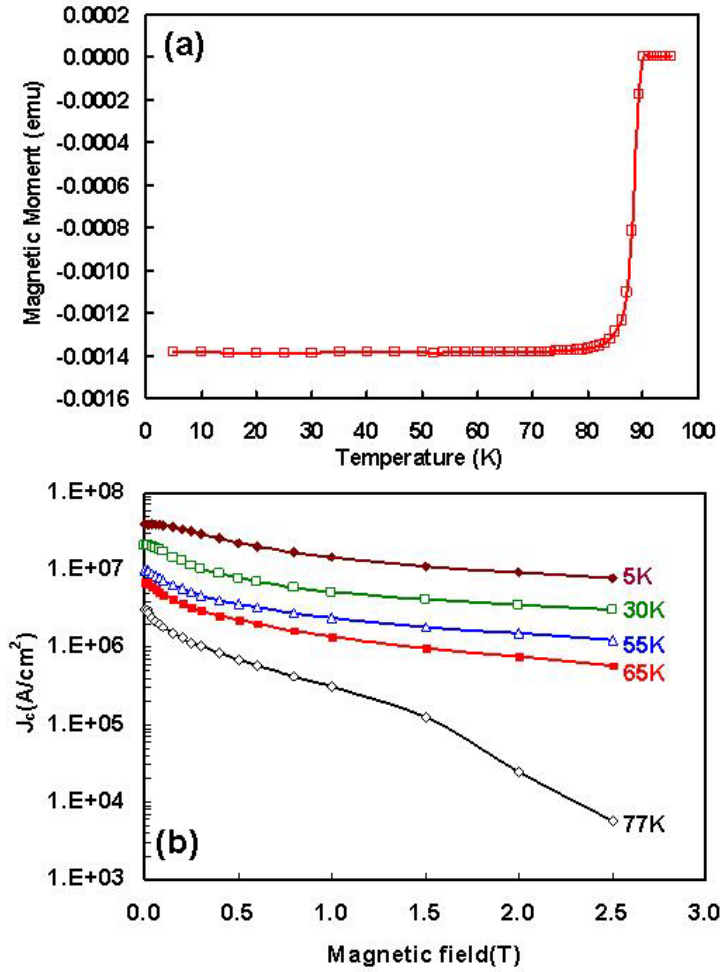


Figure 3.15. (a) The magnetic moment versus temperature relationship, and (b) The magnetic field dependence of J_c at different temperatures of the 0.34 μm thick film converted in the low-pressure processing system.

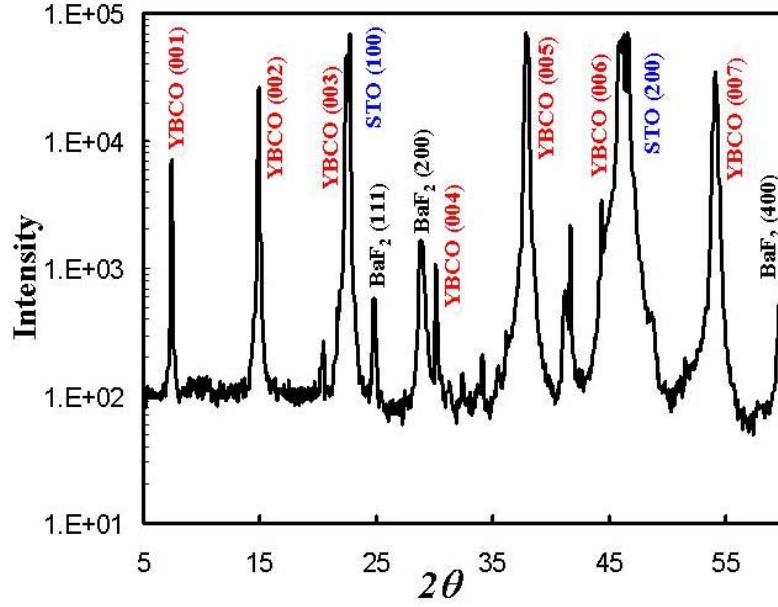


Figure 3.16. XRD $\theta \sim 2\theta$ scan pattern for the 1.04 μm film processed for 180 min. The BaF_2 peaks indicated that the conversion was not completed.

pressure results in better films. When $P_{\text{H}_2\text{O}} = 0.08$ mTorr, the estimated conversion rate is about $0.5 \sim 0.8 \text{ \AA/sec}$, for all the films with various thickness ranging from 0.14 to 1.04 μm . This conversion rate is apparently too low from a practical point of view.

3.4.3 Films on CeO_2/YSZ and RABITS

CeO_2 -buffered YSZ substrates were used in this study to best simulate the standard configuration of the RABiTS template, which has a stacking structure of $\text{CeO}_2/\text{YSZ}/\text{Y}_2\text{O}_3/\text{Ni-alloy}$. E-beam co-evaporated precursors with various thicknesses ranging from 0.3 to 1.04 μm were deposited on CeO_2 -buffered YSZ and processed in the low-pressure system. High J_c films were routinely obtained for films with thickness $< 0.5 \mu\text{m}$. For example, a 0.35 μm precursor was processed at 740 $^\circ\text{C}$ for 90 min with $P_{\text{H}_2\text{O}} = 0.8$ mTorr and $P_{\text{O}_2} = 100$ mTorr. T_c of 93 K was obtained for this film. Its XRD $\theta \sim 2\theta$ scan pattern is shown in figure 3.17. The 77 K magnetic field dependence of J_c (transport data) is shown in figure 3.18, compared with J_c values from an YBCO film made by PLD and another *ex-situ* YBCO film which is also on CeO_2/YSZ but processed under

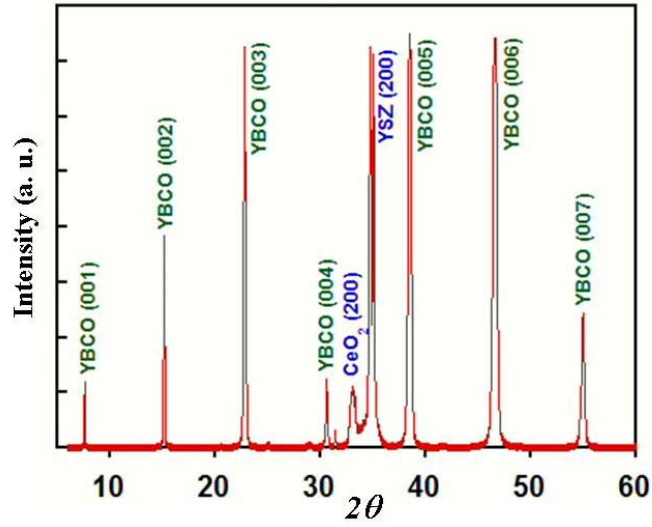


Figure 3.17. XRD $\theta \sim 2\theta$ scan pattern for the 0.35 μm YBCO film on CeO₂-buffered YSZ substrate.

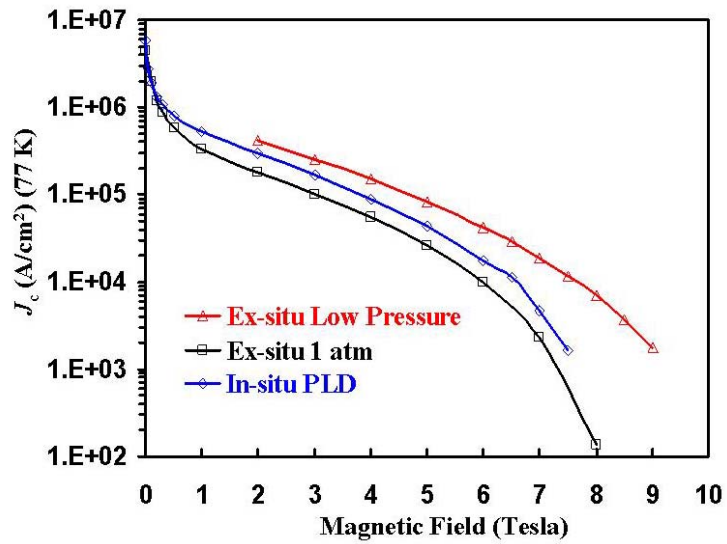


Figure 3.18. Magnetic field dependence of the J_c values for films equivalent in thickness but made by different techniques.

atmospheric pressure. The PLD *in-situ* film was deposited on a single crystal substrate and has a 77 K self-field J_c of 5.8 MA/cm². The *ex-situ* film processed at atmospheric pressure has a 77 K self-field J_c of 4.4 MA/cm². These values are among the best that can be obtained. The low-pressure processed film shows somewhat better in-field behavior and has an irreversibility field B_{irr} as high as 8.9 Tesla. Its 77 K self-field J_c is 4.7 MA/cm² measured by SQUID magnetometer.

E-beam co-evaporated precursors were also deposited on standard RABiTS templates provided by AMSC and processed in the low-pressure system. T_c of 91 K and 77 K self-field J_c of 2.3 MA/cm² were obtained on a film which is 1.3 μ m thick.

In conclusion, biaxially-textured YBCO films with high J_c can be fabricated by converting the *e*-beam co-evaporated precursors deposited on single crystal substrates, ceria buffered YSZ and RABiTS templates at low pressures. During the low-pressure conversion, there is no carrier gas present in the atmosphere. Compared with the routinely used one atmosphere pressure post-deposition processing, the oxygen partial pressures are relatively lower. Being consistent with the low oxygen partial pressures, the processing temperatures are also correspondingly low, determined by the YBCO phase diagram. It can be deduced that this combination of lower temperature and lower oxygen partial pressure would minimize the oxidation of the substrates when RABiTS templates are used. It would also reduce the interaction between the buffer layer and the precursor.

As the water partial pressures used for one atmospheric pressure processing are normally at the level of tens of Torr, it is obvious that the water partial pressure for low-pressure annealing is much lower. However, the precursor conversion rates are equivalent for the two different conditions to make good *c*-axis YBCO films. This result can be attributed to the much lower HF partial pressure at the precursor surface under the low-pressure conditions, so that the ratio of P_{H_2O} to P_{HF} is about the same as that in the atmospheric pressure condition.

3.4.4 Effects of Processing Parameters

The most important processing parameters are the oxygen partial pressure (P_{O_2}), water partial pressure (P_{H_2O}) and the processing temperature (T).

Oxygen is essential in the process of YBCO film formation. One test process was conducted on an *e*-beam co-evaporated precursor with reasonably sufficient water vapor pressure but without any oxygen supply. The resulting film has well crystallized BaF₂ but no YBCO. This is good demonstration that the precursor conversion is not simply a process in which BaF₂ can simply decomposes by reacting with water. In fact, up to a low P_{O_2} of 2 mTorr, little YBCO can form after a 90 min anneal. Only when the P_{O_2} reaches at least 10 mTorr, can good quality YBCO films be obtained at a processing temperature of 720 ~ 730 °C. This result is consistent with extrapolation of the measured thermodynamic stability diagram shown in figure 2.3. It can be seen from the phase diagram that the processing conditions used here are marginally within the YBCO stability region. By extension, we may speculate that *c*-axis YBCO films can be formed at an even lower P_{O_2} provided the annealing temperature is further lowered. The concern with a low processing temperature of 700 °C or lower is that there might not be sufficient cation diffusion for phase formation.

XRD examination of other samples indicated that there is no appreciable difference in the phase composition and YBCO orientation as P_{O_2} varies from 10 mTorr to 100 mTorr, with P_{H_2O} fixed at 0.1 mTorr. However, further increase in P_{O_2} results in the appearance of *a*-axis YBCO in the film, which deteriorates the properties, especially for the precursors on single crystal STO substrates. A typical *a*-axis YBCO film surface micrograph is shown in figure 3.19, which is obtained from a sample processed at $P_{O_2} = 250$ mTorr.

To investigate the effect of P_{H_2O} on YBCO formation, different P_{H_2O} values ranging from 0.02 mTorr to 30 mTorr were used with P_{O_2} fixed at 40 mTorr. When the P_{H_2O} is as low as about 0.02 mTorr appreciable BaF₂ peaks always appeared in the XRD $\theta \sim 2\theta$ pattern even after a long time processing, indicating an incomplete conversion. As stated previously, P_{H_2O} is increased to accelerate the conversion rates. However, the investigation indicated that YBCO films with complete *c*-axis orientation were formed only at P_{H_2O} around 0.1 ~ 0.2 mTorr. For an annealing with $P_{H_2O} > 0.2$ mTorr, some randomly oriented YBCO appeared along with the predominant *c*-axis YBCO. As P_{H_2O}

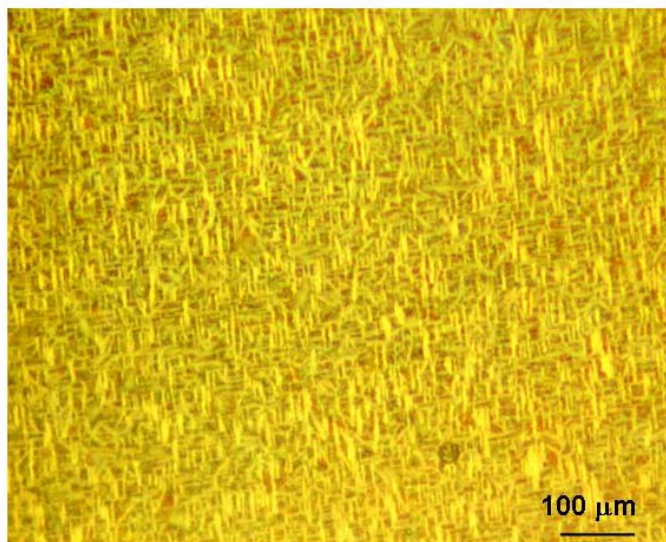


Figure 3.19. Optical microscope surface micrograph of the film processed at higher oxygen partial pressure showing *a*-axis oriented YBCO featuring needles perpendicular to each other.

increases, the intensities of the random crystalline peaks, such as YBCO (103) peak, in the XRD $\theta \sim 2\theta$ scan pattern increased while the intensities of *c*-axis YBCO (00*l*) peaks decreased. The dependence of *c*-axis (005) peak intensity on the water partial pressures is shown in figure 3.20 for $P_{\text{H}_2\text{O}}$ ranging from 0.1 to 8 mTorr. Also shown in the figure is the $P_{\text{H}_2\text{O}}$ dependence of the 77 K self-field J_c values. The influence of water partial pressure on YBCO orientation can also be seen in the SEM surface morphology. Typical *c*-axis YBCO morphology has been shown in figure 3.14(b), where the sample was annealed at $P_{\text{H}_2\text{O}} = 0.08$ mTorr. The randomly oriented YBCO starts to appear when $P_{\text{H}_2\text{O}} > 0.2$ mTorr. With a $P_{\text{H}_2\text{O}}$ within the range between 0.2 mTorr and a couple of mTorr mixed oriented YBCO usually forms and J_c is within a moderate level. When $P_{\text{H}_2\text{O}}$ reaches 10 mTorr or higher YBCO is almost totally randomly-oriented, yielding very low J_c values. Figure 3.21 shows the SEM film surface morphology changes with the $P_{\text{H}_2\text{O}}$ level.

The selection of conversion temperature for the *ex-situ* processing of YBCO film is basically determined by the YBCO phase diagram. For certain oxygen partial pressure,

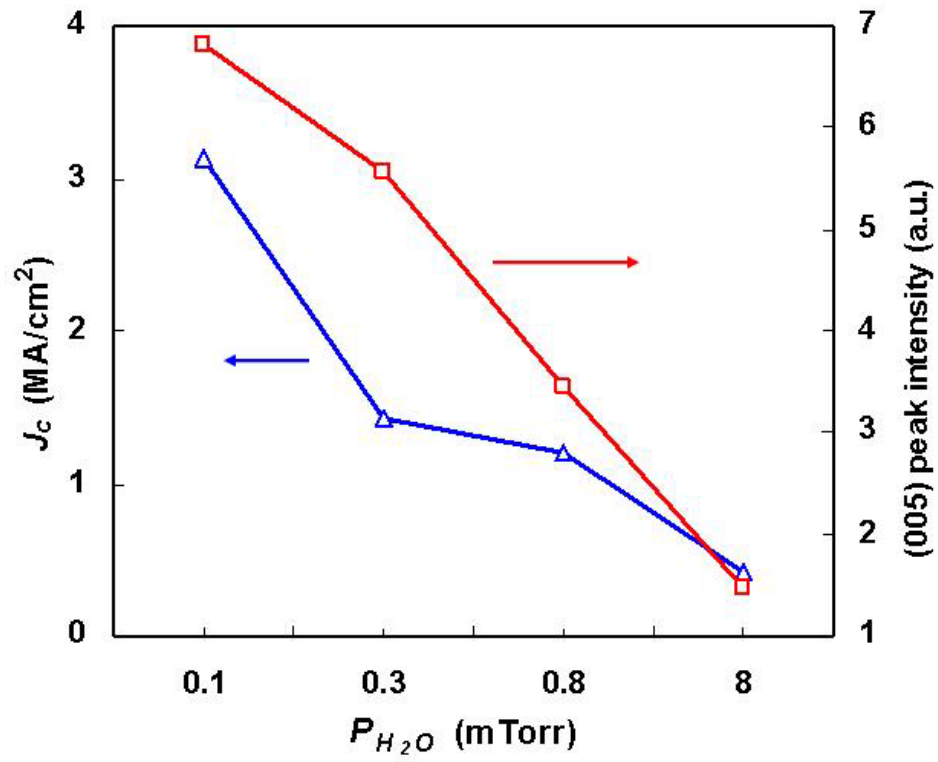


Figure 3.20. The dependence of J_c and the XRD $\theta \sim 2\theta$ YBCO (005) peak intensities on the water vapor partial pressure, for the 0.34 μm thick films processed at $P_{O_2} = 40$ mTorr.

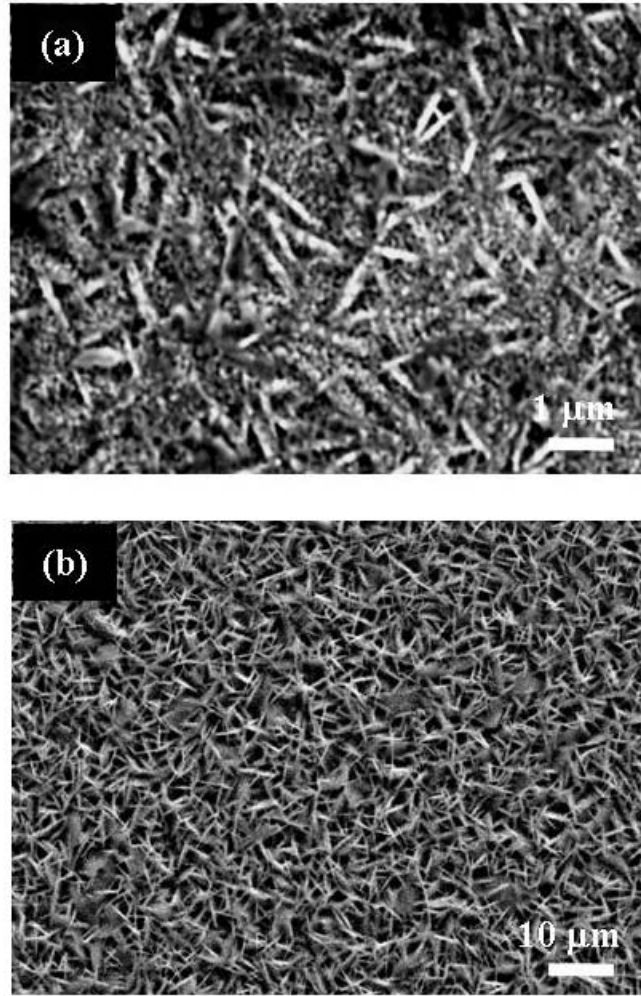


Figure 3.21. SEM surface images showing the YBCO orientation is affected by the water partial pressure. (a) $P_{\text{H}_2\text{O}} = 8$ mTorr, mixed c -axis and randomly oriented film, and (b) $P_{\text{H}_2\text{O}} = 20$ mTorr, predominantly randomly oriented film.

a properly matched temperature range is important to obtain the *c*-axis oriented films. YBCO film cannot form if the temperature is too high such that the condition is out of the YBCO stability region. On the other hand, if the temperature is not high enough, it will either result in the *a*-axis oriented YBCO component or the formation of secondary phases. If the temperature is too low, there is not enough cation diffusion required for the YBCO film nucleation and growth at all.

Most the low-pressure conversions were conducted at the temperatures between 720 and 750 °C, corresponding to the low oxygen partial pressure $P_{O_2} < 100$ mTorr. 720 °C is about the lowest temperature that can still provide enough driving force for the reaction and phase transformation to achieve reasonable conversion rates. It was found that higher temperature does require higher oxygen partial pressure. Moreover, as has been calculated that, for the low total pressure used here, the gas flow mode actually is within an intermediate regime, rather than pure molecular flow. The removal of HF is more or less still influenced by the boundary layer effect. Therefore, to achieve an equivalent conversion rate, the water partial pressure has to be correspondingly higher to compensate the increase in the total pressure. An example of a good *c*-axis oriented YBCO was obtained by converting an *e*-beam evaporated precursor at 800 °C at an oxygen partial pressure $P_{O_2} = 250$ mTorr and a water partial pressure $P_{H_2O} = 6.4$ mTorr. The film was on a CeO₂-buffered YSZ. A side effect of the higher temperature and higher P_{O_2} processing is that it exacerbates the interaction between the buffer and the precursor, resulting a substantial formation of BaCeO₃, as shown in the XRD $\theta \sim 2\theta$ pattern in figure 3.22.

3.4.5 TFA-MOD Precursor Conversion

TFA-MOD precursors were deposited on single crystal STO and LAO substrates as well as the RABiTS templates. The film thickness is about 0.3 ~ 0.4 μm as measured by the stylus profilometer. The precursors were first processed in the low-pressure system at the conditions similar to those used for the *e*-beam co-evaporated precursors, typically near 730 °C with $P_{O_2} \approx 40$ mTorr and $P_{H_2O} \approx 0.1$ mTorr. Under these conditions, it was found by XRD inspection that no YBCO films formed through the conversion. By

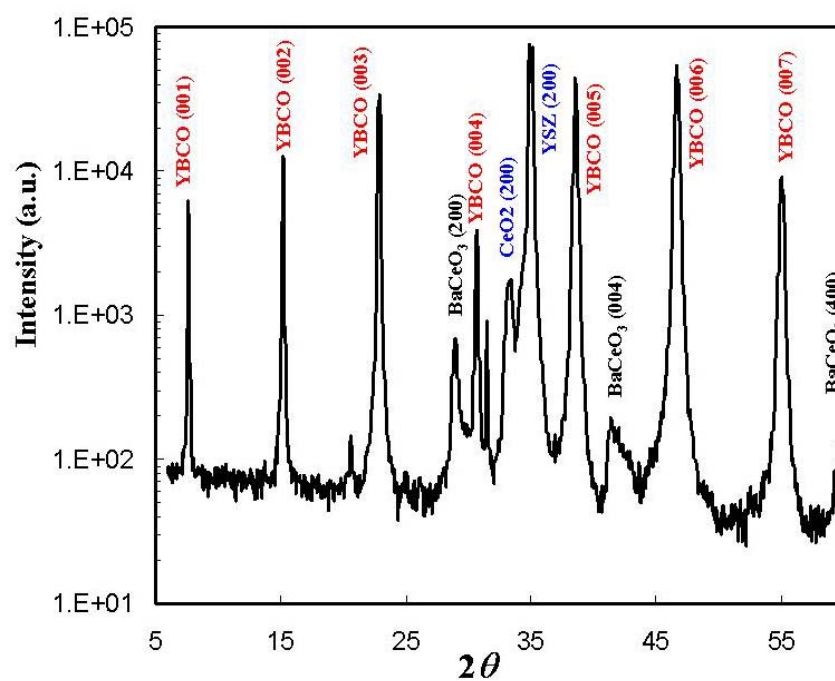


Figure 3.22. XRD $\theta \sim 2\theta$ scan pattern of an YBCO film obtained through a conversion at higher temperature (800 °C) and higher oxygen partial pressure (250 mTorr) showing the substantial formation of BaCeO₃.

increasing the water partial pressure and/or the processing temperature, more and more YBCO could be obtained. A 77 K self-field J_c of 2.2 MA/cm² was obtained for a 0.3 μ m film by a 100 min conversion at 780 °C with $P_{H_2O} = 10$ mTorr and $P_{O_2} = 100$ mTorr.

Given in table 3.2 are the conversion conditions and the properties of several TFA-MOD films. It can be seen that for the conversion of TFA-MOD precursors both higher processing temperature and higher water partial pressures are needed, compared to that for the conversion of the *e*-beam co-evaporated precursors. For example, the P_{H_2O} is 100 times of that used for the *e*-beam co-evaporated precursors.

In conclusion, the structure and properties of the YBCO films fabricated by the low-pressure conversion are sensitive to the processing parameters, including the oxygen partial pressure, the water partial pressure and the temperature. These three major parameters and other parameters, such as time, ramp rate, cooling rate and ramp path (meaning the atmosphere during the heating, especially the oxygen partial pressure), are entangled inseparably, making the conversion a very complex process. High quality films can be made but only within a small processing window. Moreover, the conversion rates are limited to less than 1 Å/sec due to the deviation of the film orientation resulting from the higher water partial pressure.

The observed different conversion behaviors of the *e*-beam co-evaporated precursors and the TFA-MOD precursors imply that there are differences in the chemistry and/or structure between the two types of precursors. Then the questions are: what are the

Table 3.2: Processing conditions and film properties for the TFA-MOD precursors.

Sample ID	Substrate	P_{H_2O} (mTorr)	P_{O_2} (mTorr)	T (°C)	Time (min)	T_c (K)	J_c (77K, 0T) (MA/cm ²)
Y0416*	LAO	0.3	40	730	90	—	—
Y1222	RABiTS	5	100	750	90	89.7	0.5
Y1219	LAO	5	100	760	100	92.1	1.05
Y0116	STO	10	100	780	100	90.3	2.15

* T_c and J_c not applicable.

differences? How do the precursor chemistry and/or structure affect the conversion? What are the characteristics that qualify a precursor as ideal for a conversion to make high performance YBCO film? How can a precursor be modified so that an efficient and robust conversion can be made? These questions will be addressed in the next chapter.

Chapter 4

MODIFICATION OF E-BEAM CO-EVAPORATED PRECURSOR

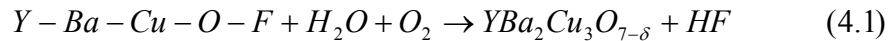
4.1 Motivation

The motivation of the precursor modification is to change the precursor chemistry and structure by implementing a post-deposition intermediate treatment, so that the precursor can be converted more efficiently and robustly.

4.1.1 Challenges in *Ex-situ* Process

Although both *e*-beam co-evaporation and TFA-MOD have been developed for more than ten years, there are still many technical challenges in the practical application of these two approaches for fabricating biaxially-textured YBCO films. The main difficulty since the very beginning has been in the precursor conversion.

There are several reasons behind the difficulty. First, there is very limited understanding or knowledge about the as-deposited precursors. That is why there are so many different versions of the conversion reaction equations presented in the literature describing the conversion process. The fact is there is no common agreement on the detailed characteristics of the precursors. A widely used general expression for the reaction equation is



which is true in principle, but not very informative. There might be certain variations for precursors made from different systems or procedures, but generally the BaF₂-based precursors, either of *e*-beam co-evaporated or TFA-MOD, are basically in an amorphous or pseudo-amorphous state. By pseudo-amorphous state, it is meant that although there is no long range ordered structure, there might be many short range ordered clusters or nano-crystallites where a cation has a specific chemical environment. The difficulty is that many widely used materials characterization techniques may not be very effective for inspecting this type of structure.

Secondly, the YBCO formation during the *ex-situ* conversion is a solid state epitaxy process. The nucleation begins at the substrate/precursor interface, which can be best revealed through a cross-sectional inspection. This is much more difficult than, for example, a typical PVD epitaxy where a careful surface inspection (e.g., RHEED or LEED) can be very helpful. Presently, the mechanism of the conversion reaction and the YBCO film formation is still far from fully understood.

Thirdly, there are so many processing parameters that are effectively involved in the precursor conversion, regardless of whether it is an atmospheric pressure processing or a low-pressure processing, so that the control of the conversion process is very complex. The way the processing parameters affect the conversion reaction and film crystallographic orientation are not clear, and may actually “crosstalk” with each other. The would-be optimized processing window is so small that the film quality strongly depends on the processing condition.

Processing conditions represent the external factor that would change the quality of the converted film. The conversion behavior is intrinsically determined by the precursor itself, its chemistry and structure, and the nature of the substrate/precursor interface. As discussed in the previous chapter, this difference has been observed in comparing the *e*-beam co-evaporated precursors and the TFA-MOD precursors, as processed under low-pressure conditions. It is the structural and chemical states of the precursors that define the thermodynamics and kinetics of the conversion reaction and film formation. In other words, for a given processing condition the precursor conversion behavior differs when the precursor state is changed. Therefore, it is possible to make the precursor more “conversion-friendly” by changing the precursor characteristics, or by a modification of the precursor. In principle, precursor modification can be implemented not only through the deposition, but also by a post-deposition treatment.

While great efforts have been made to study the conversion annealing and to optimize the processing parameters, there is little investigation on the modification of the *e*-beam evaporated precursors. It was once reported that a thin layer of Ag coating on the precursor surface prior to the conversion could help enhance the YBCO orientation [59]. On the other hand, for the solution technique, precursor modification has been pursued

extensively. From the baseline TFA method, modified precursors such as fluorine-free and fluorine-less precursors have emerged, offering more options and potential [60 - 62].

It has been demonstrated that high quality YBCO films can be made through low-pressure processing, but the limitation is in the conversion rate. A slow conversion rate would especially trouble the long-length, thick-film processing. E-beam co-evaporation has the advantage over the TFA-MOD approach in making thicker precursors, so it would be valuable if the *e*-beam co-evaporated precursors could be modified to accommodate a fast conversion.

4.1.2 Conversion Reaction Thermodynamics

According to thermodynamics, the Gibbs free energy of a chemical reaction is given by

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (4.2)$$

where ΔG° is the Gibbs free energy change of the reaction when all the chemicals are in their standard states. Q is the reaction's quotient, which is determined by the fugacities of the substances involved in the reaction. $R = 8.3145 \text{ J/mol K}$ is the gas constant and T is temperature in Kelvin. When the reaction is at equilibrium,

$$\Delta G = 0 \quad (4.3)$$

and Q takes the equilibrium value designated by K :

$$Q_{eq} = K \quad (4.4)$$

Equation (4.2) then yields

$$\Delta G^\circ = -RT \ln K \quad (4.5)$$

K is called the equilibrium constant of the reaction and is dependent on temperature, but independent of the actual composition of the system (i.e., the individual concentrations of the species) [63].

Rewriting equation (4.2) as

$$\Delta G = RT \ln \frac{Q}{K} \quad (4.6)$$

it is seen that if $Q < K$ the reaction proceeds, and if $Q > K$ the reaction proceeds backward.

On the other hand, at a certain temperature T ,

$$\Delta G = \Delta H - T\Delta S \quad (4.7)$$

where ΔH and ΔS are the enthalpy (heat) and entropy of the reaction, respectively. At equilibrium, $\Delta G = 0$ and $\Delta H = T\Delta S$. When all the substances are in their standard states

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4.8)$$

Combining equations (4.5) and (4.8) yields

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (4.9)$$

Since

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P = H \quad (4.10)$$

thus

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S, \quad \frac{d\Delta G^\circ}{dT} = -\Delta S^\circ \quad (4.11)$$

and

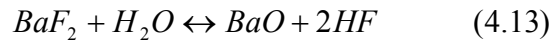
$$\frac{d(\Delta G^\circ / T)}{d(1/T)} = -\frac{d(R \ln K)}{d(1/T)} = \Delta H^\circ \quad (4.12a)$$

or

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^\circ}{R} \quad (4.12b)$$

This equation is referred to as the Van't Hoff equation, which is the basis for the YBCO phase diagram.

The first chemical reaction relevant to the precursor conversion that needs to be considered is the decomposition of BaF_2 under the reaction with water.



The Gibbs free energy change for this reaction can be written as

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{P_{\text{HF}}^2}{P_{\text{H}_2\text{O}}}\right) \quad (4.14)$$

where P_{HF} and $P_{\text{H}_2\text{O}}$ are the HF and water partial pressures, respectively. By assuming a value of

$$Q = \frac{P_{HF}^2}{P_{H_2O}} \quad (4.15)$$

we can calculate the temperature dependence of ΔG . The result is shown in figure 4.1 with three different Q values.

It can be seen that at a temperature between 700 and 800 °C, $\Delta G < 0$ only when the Q value is as low as 10^{-13} . That means for an atmospheric pressure processing when a typical P_{H_2O} is 20 Torr, P_{HF} has to be less than 3.8×10^{-5} Torr. For low-pressure processing when P_{H_2O} is 1 mTorr, P_{HF} has to be less than 2.7×10^{-7} Torr. With these low-pressures of HF, it is not easy to decompose BaF_2 solely by reaction (4.13).

Chemical reaction thermodynamics can change when the reactants are different, although the products may be the same. This is the reason why the precursor chemistry has strong effect on the conversion behavior. The chemistry of a BaF_2 -based precursor

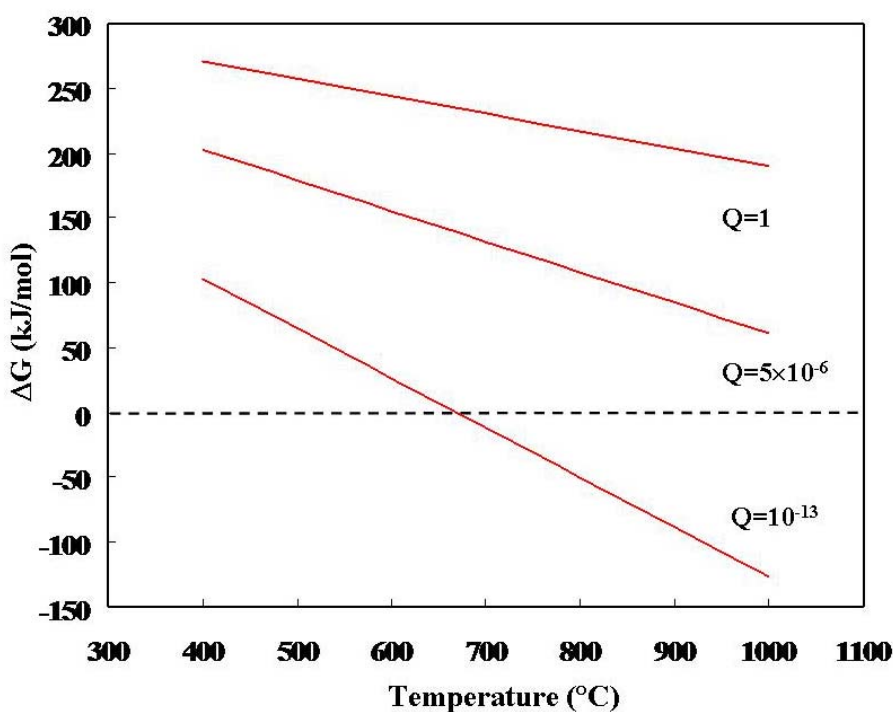
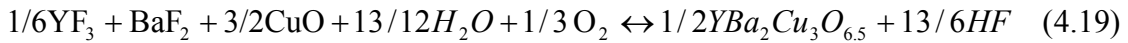
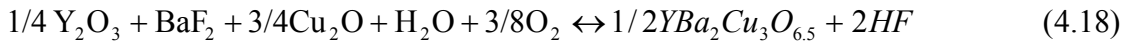
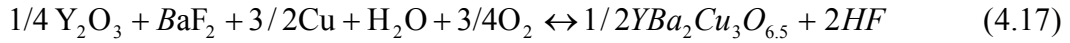
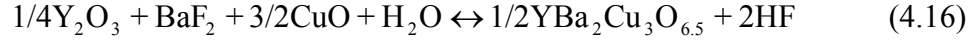


Figure 4.1. Temperature dependence of the Gibbs free energy change ΔG for the decomposition of BaF_2 via reaction (4.13).

depends on the approach making the precursors. Chemical substances that may possibly be involved in a BaF₂-based precursor are listed in table 4.1 with their thermodynamics properties [51]. Note that for barium we assume that it is always in BaF₂. The decomposition of BaF₂ present in a precursor is different when the reaction product is YBCO. Yttrium and copper may be in different states in the precursor. Possible chemical reactions that can lead to the formation of YBCO include:



Similarly, the ΔG for the reactions (4.16) through (4.19) can be expressed as

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{P_{HF}^2}{P_{H_2O}}\right) \quad (4.14)$$

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{P_{HF}^2}{P_{H_2O}}\right) + RT \ln\left(\frac{1}{P_{O_2}^{3/4}}\right) \quad (4.20)$$

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{P_{HF}^2}{P_{H_2O}}\right) + RT \ln\left(\frac{1}{P_{O_2}^{3/8}}\right) \quad (4.21)$$

$$\Delta G = \Delta G^\circ + 13/12RT \ln\left(\frac{P_{HF}^2}{P_{H_2O}}\right) + RT \ln\left(\frac{1}{P_{O_2}^{1/3}}\right) \quad (4.22)$$

respectively. Again, we can calculate the temperature dependence of ΔG for these reactions. The results are shown in figure 4.2 for an assumed $Q = 1 \times 10^{-13}$ and a typical oxygen partial pressure $P_{O_2} = 100$ mTorr.

4.2 Comparison of EBE and TFA-MOD Precursors

Although no systematic comparison study has been reported, and most previous investigations were conducted on either *e*-beam co-evaporated precursor or TFA-MOD precursor, it was generally accepted that the conversion of the two types of precursors are basically the same. As we have pointed out, in fact there are certain differences in their conversion behaviors. Clearly, TFA-MOD precursor requires higher water partial pressure and higher temperature for the conversion and YBCO film formation. In other

Table 4.1: Selected thermodynamics properties of the chemical substances relevant to the BaF₂-based precursor conversion.

Chemical Substance	m.p./b.p. (°C)	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/mol K)	C_p (J/mol K)
Y	1522/3345	-	-	44.4	26.5
Y ₂ O ₃	2410/	-1905.3	-1816.6	99.1	102.5
YF ₃	1387/	-1718.8	-1644.7	100.0	
Ba	727/1897	-	-	62.5	28.1
BaO	1382/	-548.0	-520.3	72.1	47.3
BaF ₂	1353/2260	-1207.1	-1156.8	96.36	71.21
Cu	1085/2562	-	-	33.2	24.4
Cu ₂ O	1235/1800	-168.6	-146.0	93.14	63.64
CuO	1326/	-157.3	-129.7	42.63	42.3
H ₂ O	0/100	-241.818	-228.572	188.825	33.577
HF	-	-271.1	-273.2	173.779	29.133
O ₂	-	-	-	205.138	29.355
YBa ₂ Cu ₃ O _{6.5}	-	-2521.9	-	350.54	-

m.p. is melting point.

b.p. is boiling point.

ΔH°_f is the standard molar enthalpy (heat) of formation at 298.15 K.

ΔG°_f is the standard molar Gibbs energy of formation at 298.15 K.

S° is the standard molar entropy at 298.15 K.

C_p is the molar heat capacity at constant pressure at 298.15 K.

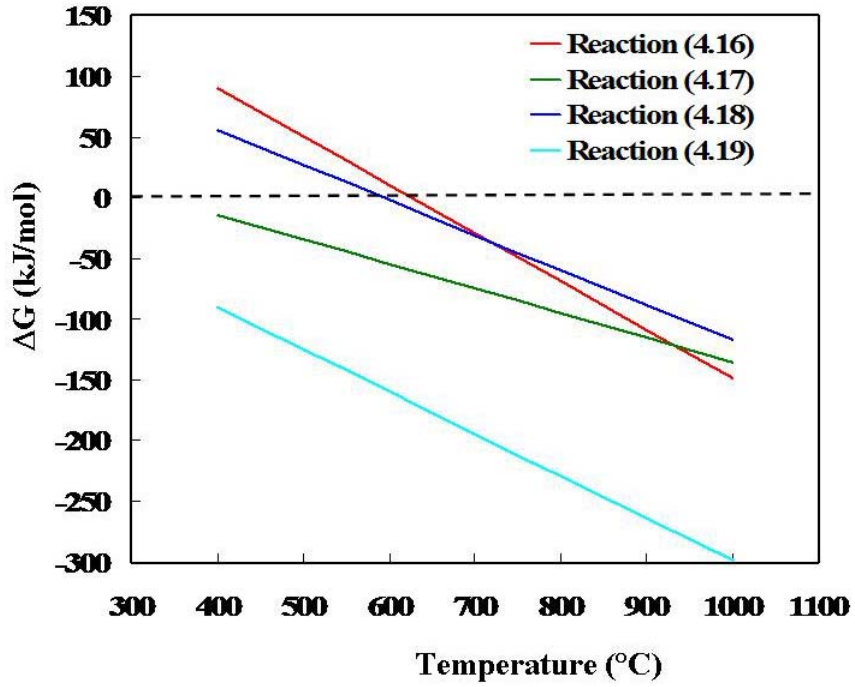


Figure 4.2. Temperature dependence of the Gibbs free energy change ΔG for the chemical reactions (4.16) through (4.19) assuming $P_{HF}^2 / P_{H_2O} = 1 \times 10^{-13}$ and $P_{O_2} = 100$ mTorr.

words, the TFA-MOD precursor is less reactive to the processing ambient, which should be attributed to the precursor's chemistry and structure when same substrates are used. A comparison study on the *e*-beam co-evaporated precursor and TFA-MOD precursor in terms of their composition, crystallinity, surface morphology, structure, elemental chemical state would help understand which characteristics of a precursor are important in determining its conversion behavior [64]. The following questions regarding the conversion mechanism need to be answered. What are the physical and chemical states of all the elements in the precursors? What kinds of changes occur in the precursors upon the heating ramp before YBCO nucleates, and at the elevated processing temperature when YBCO film is growing?

To address these questions, typical *e*-beam co-evaporated and TFA-MOD precursors of about 0.3 μm thick were deposited on single crystal (100) SrTiO_3 (STO)

substrates. STO was used in order to minimize extraneous factors that could affect the quality of the precursors and films.

The as-deposited precursor surfaces were inspected by AFM and the surface micrographs are shown in figure 4.3. It can be seen that the surface of the *e*-beam precursor is much smoother than that of MOD-TAF precursor. The average roughness R_a of the EBE precursor surface is only 0.6 nm, while the average roughness R_a of the TFA-MOD precursor surface is about 3 nm. The difference in the surface roughness implies that there might also be a difference in the precursor density, which is one of the factors affecting the conversion reaction. It was found that the as-coated TFA-MOD gel film experiences significant thickness shrinkage during the calcinations [65]. Further shrinkage was also observed due to the conversion processing. A fully converted TFA-MOD film is more porous than the *e*-beam film. The porosity may be helpful for the in-and-out diffusion of the gases. On the other hand, poorer integrity of the film may result in relatively lower J_c .

As previously stated, identifying the phases and chemicals that exist in the precursors prior to their conversion is important, since it represent the starting point of the conversion reaction. The initial state, that is, the as-deposited state for *e*-beam

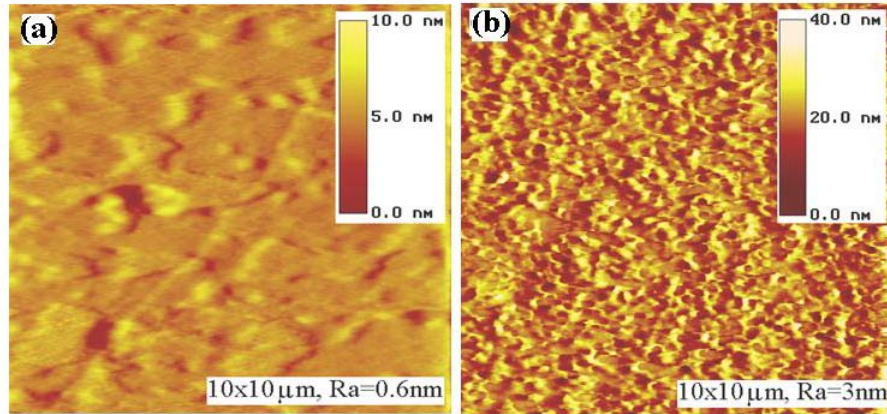


Figure 4.3. AFM surface images of (a) the as-deposited *e*-beam co-evaporated precursor, and (b) the TFA-MOD precursor, showing the differences in surface morphology and smoothness.

precursor and the as-calcinated state for TFA-MOD precursor, is directly related to all the latter changes during processing.

Since the pseudo-amorphous precursors are in principle unstable at elevated temperatures, a continual change in the precursor will be triggered once the heating is initiated. Another essential question is at what critical point in the process the presently existing phases and chemicals are determinative to the reaction that forms epitaxial YBCO films. Therefore, the phases and elemental chemical states at elevated annealing temperature when YBCO film is growing are also important. Accordingly, the analysis needs to focus on both the as-deposited precursors and quenched samples.

Figure 4.4 shows the XRD $\theta \sim 2\theta$ scan patterns of the as-deposited *e*-beam and MOD-TFA precursors as well as the quenched samples. It can be seen from figure 4.4 (a) that in the as-deposited state the *e*-beam precursor is basically amorphous, while TFA-MOD precursor has developed some nano-crystalline fluorides and copper oxides after the calcination. Based on the XRD diffraction data, the size of the fluorides and the copper oxides crystallites, calculated using the Scherrer equation, is about 10 nm. These crystallized clusters of fluorides and copper oxides may play a role in the stabilization of the TFA-MOD precursor; in contrast, the EBE precursor appears to be amorphous according to the XRD inspection.

Figure 4.4 (b) shows the XRD $\theta \sim 2\theta$ scan patterns of the partially converted quenched samples. The EBE precursor was quenched 20 min after reaching the processing temperature of 740 °C with $P_{O_2} = 100$ mTorr and $P_{H_2O} = 1$ mTorr. The TFA-MOD precursor was quenched 20 min after reaching the processing temperature of 780 °C with $P_{O_2} = 100$ mTorr and $P_{H_2O} = 10$ mTorr. It can be seen that YBCO as well as BaF₂ are present in both the quenched samples. For the TFA-MOD precursor, the BaF₂ peak position is coincident with that for the EBE precursor, and the peak positions match that given by standard BaF₂ data (PDF file #04-0452). Apparently, the fluoride peak positions in the as-deposited TFA-MOD precursor have shifted to higher angles with respect to the standard BaF₂ peak positions. This shift indicates that in the as-deposited TFA-MOD precursor the fluoride is not the pure BaF₂ but a multi-component fluoride, or the compound Y-Ba-O-F as we have mentioned earlier in Chapter 2. This compound

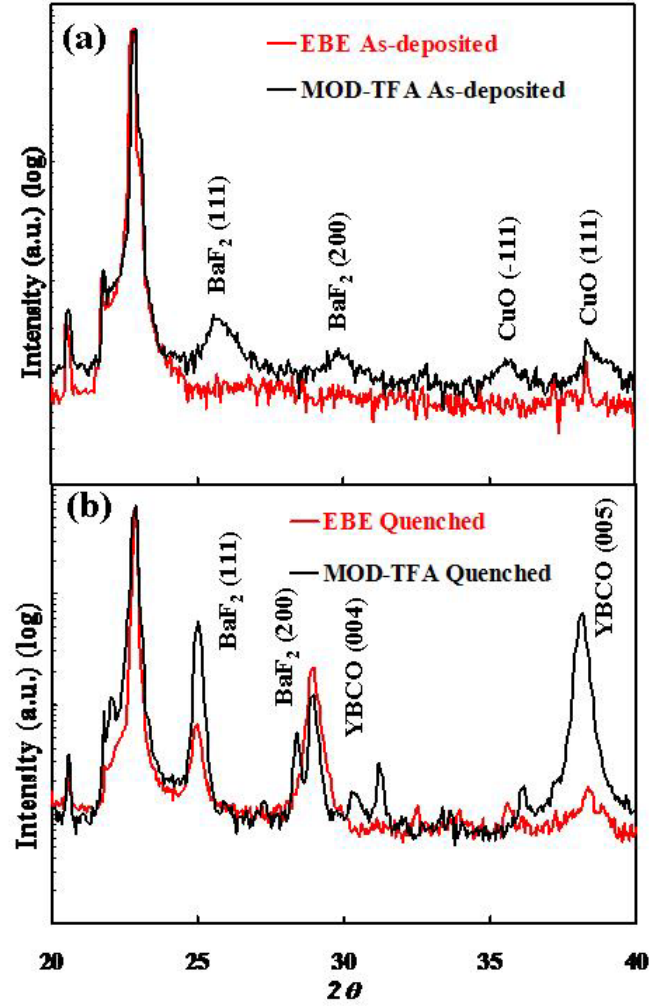


Figure 4.4. XRD $\theta \sim 2\theta$ scan patterns of the EBE and TFA-MOD precursors at (a) the as-deposited states, and (b) the partially converted quenched states.

decomposes first during the ramp and at the processing temperature, releasing yttrium and the extra fluorine with the nearly stoichiometric BaF₂ left in the unconverted precursor.

Since precursors of both the *ex-situ* methods are fluoride-based, the fluorine content and the chemical bonding states of the cations should have significant influences on the later conversion reaction.

X-ray photoelectron spectroscopy (XPS) is used to study the fluorine composition and especially the chemical states of the cations in the precursors. Quantitative composition calculation using XPS measurement data is based on the equation [66]

$$C_x = \frac{\frac{I_x}{S_x}}{\sum_i \frac{I_i}{S_i}} \quad (4.23)$$

where C_x is the atomic concentration of the element of interest, I_i is the integral intensity of the spectral peak of the i^{th} element, and S_i is the atomic sensitivity factor (ASF) of the i^{th} element which is determined by the photoelectric cross-section for the electron orbital and other factors.

The measured surface fluorine atomic composition is 20.4% and 7.5% for the as-deposited and the quenched TFA-MOD precursors, respectively. The fluorine atomic composition is 16.2% and 2.2% for the as-deposited and the quenched EBE precursors, respectively. As XPS is a surface sensitive technique, the results indicates that for both precursors, once heated, the fluorides at the surface start to decompose, which results in the release of HF. Higher fluorine concentration in TFA-MOD precursor is one of the reasons why it is more difficult to convert than the EBE precursor.

The core level electron binding energy (BE) of an atom changes when the atom bonds with different neighbors, i.e., when the chemical environment of the atom changes. The binding energy change basically depends on the electronegativities of the neighboring atoms. In general, a decrease of the electron density in the valence region around an atom produces an increase in the binding energy of core level electrons. The electronegativities of the atoms that are relevant to the BaF₂-based precursor conversion

are listed in table 4.2. The variation of the electron's binding energy is reflected by the peak position shift in a XPS spectrum, which is usually plotted as the electron flux intensity versus either the binding energies or the kinetic energies of the emitted electrons. This is the basis for the elemental chemical state analysis using XPS. Some of the standard core level electron binding energies of the atoms that are relevant to the BaF₂-based precursor conversion for making YBCO films are listed in table 4.3. These standard data are taken mostly from the NIST XPS data base if no other source is given. The listed are the typical values among the data given. For a surface inspection, the binding energy is calibrated against the 1s electron binding energy of the adventitious carbon atoms, that is BE(C1s) = 284.6 eV, for the specific XPS system used.

For more specific analysis, pure BaF₂ and pure Cu films were also deposited using *e*-beam evaporation in the same system used for depositing the EBE YBCO precursors. These films as well as the as-deposited and quenched EBE and TFA-MOD precursors were all studied using XPS for understanding the chemistry of the precursors and their conversion.

Shown in figure 4.5 (a) through (d) are the F1s, Ba3d, Y3d and Cu2p XPS spectra for the surfaces of the as-deposited EBE and TFA-MOD precursors. It can be seen from figure 4.5(a) that the F1s peak position for EBE precursor basically matches that of the standard BaF₂. That means fluorine solely bonds with barium in the EBE precursor. The higher binding energy of F1s for the TFA precursor indicates a certain amount of fluorine is with yttrium, or fluorine is in the fluoride with not only barium but also yttrium, noticing that BE for fluorine in YF₃ is higher than BE for fluorine in BaF₂.

Figure 4.5(b) shows that the Ba3d peak position in the TFA-MOD precursor also shifts to a higher energy with respect to that in the EBE precursor. The binding energy of Ba3d electrons is higher for barium in BaF₂ than for barium in BaO and metallic barium; so that the higher binding energy here means that the barium cation is more positively charged, or it is more tightly bound with the anion F⁻. In contrast, barium in the EBE precursor may not be fully fluorinated.

Table 4.2: Electronegativities of the elements which are relevant to the BaF₂-based precursor conversion.

Element	Y	Ba	Cu	F	O
Electronegativity	1.22	0.89	2.00	3.98	3.44

Table 4.3: Standard core level electron binding energies of the atoms that are relevant to the BaF₂-based precursor conversion.

Core Level Electron	Y3d5/2	Ba3d5/2	Cu2p3/2	F1s	O1s
BE (eV) / Chemical	155.8/YBCO 155.8/Y 159.0/YF ₃ 156.8/Y ₂ O ₃	778.6/YBCO 780.6/Ba 781.7/BaF ₂ 779.4/BaO	934.6/YBCO 932.5/Cu 936.5/CuF ₂ 933.6/CuO 932.3/Cu ₂ O	685.3/YF ₃ 684.2/BaF ₂ 684.7/CuF ₂	-/YBCO 531.2/Y ₂ O ₃ 528.3/BaO 529.6/CuO 530.2/Cu ₂ O

Note: binding energy data for YBCO are from reference [67] and for the orthorhombic structure.

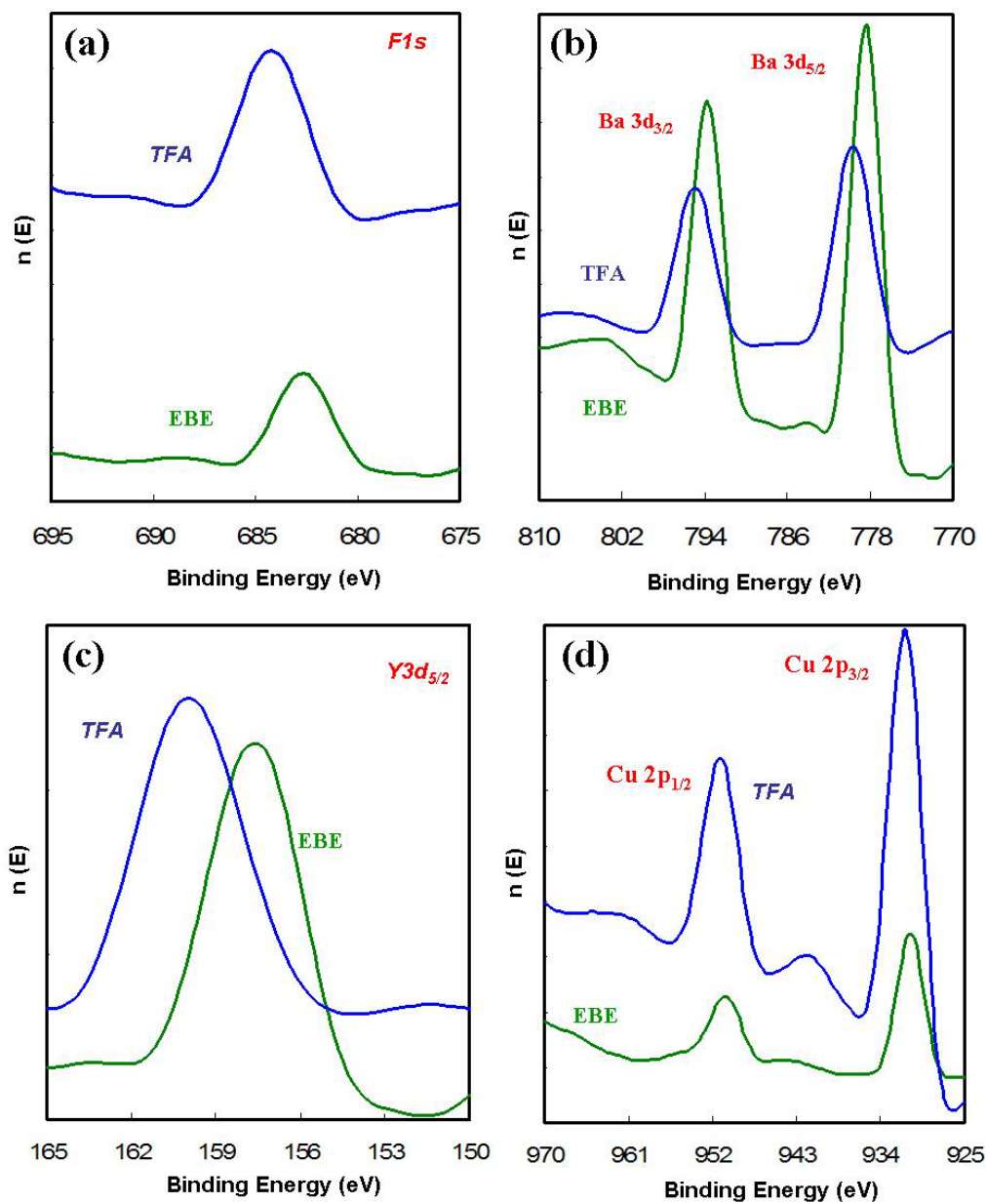


Figure 4.5. XPS spectra of (a) F1s, (b) Ba3d, (c) Y3d_{5/2} and (d) Cu2p for the surfaces of the as-deposited EBE and TFA-MOD precursors.

The higher binding energy of Y3d electrons for the TFA-MOD precursor, shown in figure 4.5(c), confirms the existence of YF₃ in the precursor, while the lower binding energy of Y3d electrons for the EBE precursor indicates that Y in the EBE precursor is basically in Y₂O₃ or even as metallic Y.

A binding energy difference of Cu2p electrons is also observed for the as-deposited EBE and TFA-MOD precursors, as shown in figure 4.5(d). Although the shake-up peak of Cu2p in the spectrum for the TFA-MOD precursor is not significantly obvious, it is evident that copper is more oxidized in the TFA-MOD precursor than that in the EBE precursor. The shake-up satellite peaks associated with the Cu2p peaks are the signature of the existence of Cu²⁺. More detailed analysis of Cu chemical state in the as-deposited EBE precursor will be given later.

Changes in the elemental chemical states were observed after the precursors were quenched from their processing conditions. First, the F1s peak position for the quenched TFA-MOD sample is coincident with that for the quenched EBE sample, and they are all nearly the same as that for the standard BaF₂. This implies that the YF₃ in the TFA-MOD precursor has already completely decomposed prior to the moment of quenching. Notice that although the TFA-MOD precursor was quenched at higher temperature and higher water partial pressure, it still has much higher fluorine concentration than that of the quenched EBE precursor. Interestingly, the Ba3d and Cu2p peak position are also coincident for the quenched TFA-MOD and the EBE samples, as shown in figure 4.6. This means that at least at this point of quenching (after 20 min duration at the processing condition) while YBCO is growing at the lower part of the precursor, the cation chemical states in the unconverted upper part of the precursor are very similar in the two types of precursors. Further study is needed to explain why Cu gets a little more oxidized in the quenched EBE precursor, indicated by the more obvious shake-up satellite.

According to the above observation and analysis, there are two main reasons why the TFA-MOD precursor is more difficult to convert than the EBE precursor. First, the TFA-MOD precursor has higher fluorine concentration, with extra fluorine combined with yttrium. Although YF₃ starts to decompose at the early stage of heating and processing, the released fluorine, which should be in the form of HF, may have an effect

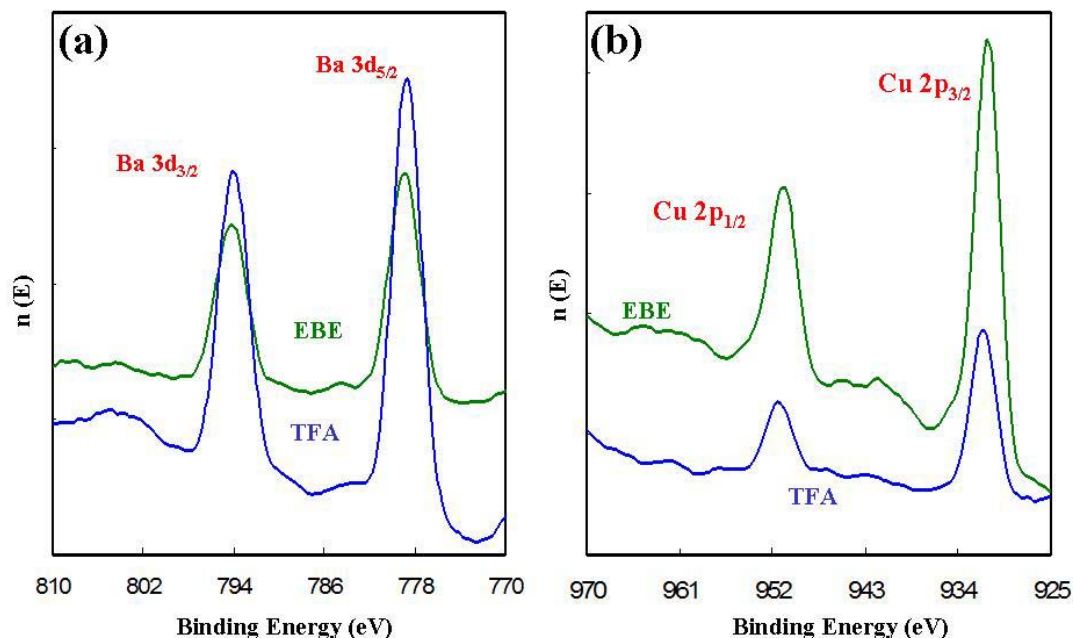


Figure 4.6. XPS spectra of (a) Ba3d, and (b) Cu2p for the surfaces of the quenched EBE and TFA-MOD precursors.

in postponing the decomposition of BaF_2 , which is the prerequisite for the YBCO formation. Secondly, the TFA-MOD precursor has certain amount of nano-crystallites of copper oxide and BaF_2 that formed during the calcinations. These nano-crystallites need to decompose and reorder for the formation of YBCO, which may explain why the conversion of the TFA-MOD precursor requires not only higher water partial pressure but also higher temperature. What we don't know is how the precursor chemistry will affect the precursor/substrate interface, which also plays an important role in the YBCO nucleation and formation.

4.3 Pre-annealing Effects on Precursor Conversion

In the process of epitaxial YBCO film growth during the precursor conversion, the heterogeneous epitaxial nucleation at the substrate/precursor interface and the later homogeneous epitaxial growth at the YBCO/precursor interface has the priority over the homogeneous nucleation and growth inside the precursor (other than the interfaces). This priority results from the interfacial energy, which is mainly determined by the interfacial

chemical bonding energy and strain energy. The priority needs to be maintained throughout the conversion to prevent the homogeneous nucleation and growth that produce randomly-oriented YBCO. The precursor chemistry and structure can be used as the leverage for promoting the heterogeneous epitaxial process while suppressing the homogeneous process. In other words, it is possible to modify the precursor characteristics so that it becomes more “friendly” to the epitaxial conversion.

In principle, the precursor modification can be implemented not only through the deposition, but also after the deposition. Recall that the TFA-MOD precursor is more difficult to convert than the EBE precursor. The reason is believed to be the formation of the nano-crystalline BaF_2 and copper oxide as well as the higher fluorine concentration. The nano-crystalline BaF_2 and copper oxide were formed during the slow calcination process which is conducted in the wet oxygen atmosphere up to 400 °C. As for the EBE precursor, it has been demonstrated that high quality epitaxial YBCO films can be fabricated through the low-pressure processing which could facilitate faster conversion. However, the conversion rate is limited by the formation of randomly-oriented YBCO, produced inevitably through the homogeneous process under more aggressive conditions (i.e., at higher water partial pressure and higher temperature). Presumably, a more stabilized EBE precursor can be achieved by an intermediate treatment similar to the calcination for the TFA-MOD precursor. Then, the idea is to attain an overwhelming priority of the heterogeneous process over the homogeneous process, so that the randomly-oriented YBCO nucleation and growth can be suppressed.

4.3.1 Pre-annealing Effects on EBE Precursor Conversion

In order to evaluate the pre-annealing effects on the precursor conversion behavior, intermediate treatments under different conditions were given to the *e*-beam co-evaporated precursors prior to their high temperature conversion. The substrates include single crystal STO, CeO_2 -buffered single crystal YSZ and standard RABiTS templates. The pre-annealing was conducted in a tube furnace at 1 atmospheric pressure in 100% oxygen or in a mixture of Ar and O_2 with various oxygen partial pressures (P_{O_2}). The temperature is between 400 ~ 500 °C and the time is between 30 ~ 60 min. The pre-

annealed precursors and the as-deposited precursors were processed in the low-pressure system as well as in an atmospheric pressure system under different conditions, with emphasis on higher water partial pressures and higher temperatures. For understanding the effects of the pre-annealing, the film structures were characterized and the properties were measured.

Shown in figure 4.7 is the magnetic field dependence of the critical current density J_c (measured by the SQUID magnetometer) of two YBCO films. One was converted from an as-deposited EBE precursor and the other was from a pre-annealed EBE precursor. For both, the substrates were CeO₂-buffered YSZ. The pre-annealing was conducted in atmospheric pressure 100% oxygen at 500 °C for 30 min. The conversion processing conditions for the two precursors were identical: $P_{O_2} = 40$ mTorr, $P_{H_2O} = 10$ mTorr, $T = 760$ °C and $t = 30$ min. The film from the pre-annealed precursor has a high J_c (77 K self-field) of 3.2 MA/cm², while the film from the as-deposited precursor has a low J_c (77 K, self-field) of only 0.6 MA/cm². Even higher water partial pressure for the conversion further enlarged the difference. Figure 4.8 shows the YBCO (113) pole figures of two films converted with $P_{H_2O} = 30$ mTorr. The high water partial pressure

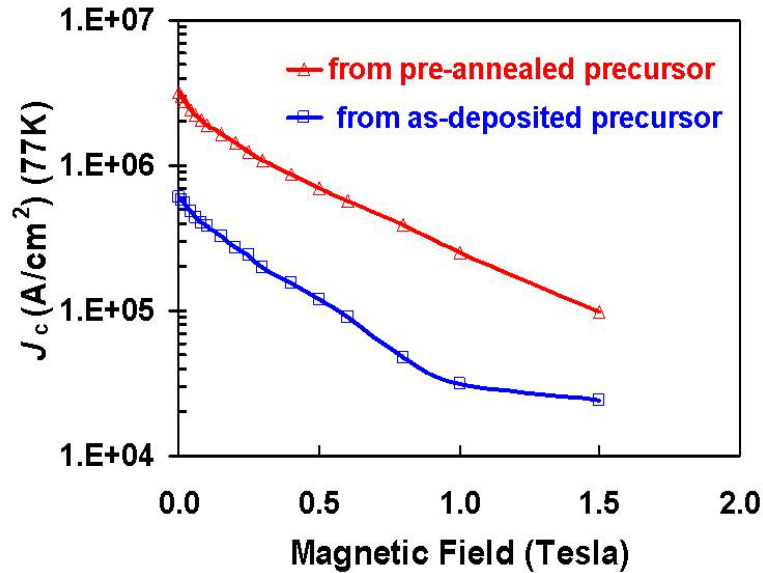


Figure 4.7. Magnetic field dependence of the critical current density J_c at 77 K for YBCO films converted from the pre-annealed and as-deposited precursors.

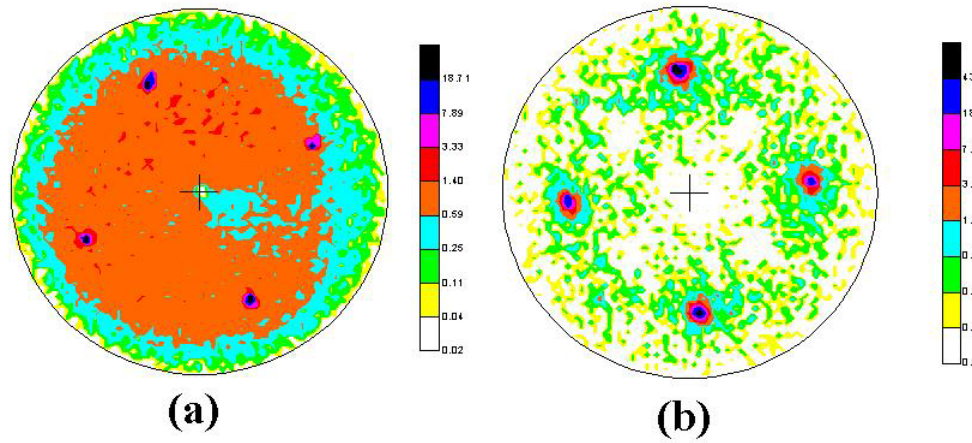


Figure 4.8. YBCO (113) pole figures for the YBCO films converted at $P_{\text{H}_2\text{O}} = 30$ mTorr from (a) the as-deposited precursor, and (b) the pre-annealed precursor.

resulted in the poor texture with a volume fraction of cube texture (VFCT) only about 50% in the film from the as-deposited precursor. Consequently, its J_c is extremely low. In contrast, the J_c value for the film converted from the pre-annealed precursor is much higher. The texture analysis also shows the VFCT is much higher, nearly 90%. This effect was observed on many samples. In fact, the pre-annealed precursor not only tolerates higher water partial pressure but also higher processing temperature. The processing window for making high J_c YBCO films is greatly expended compared with that for the as-deposited precursors. Shown in figure 4.9 is the 77 K self-field J_c values of the YBCO films converted from the pre-annealed precursors. The J_c values (all measured by the SQUID magnetometer) were plotted on the YBCO phase diagram with the processing condition for each film denoted. The precursors were all pre-annealed in atmospheric pressure of 100% oxygen at 500 °C for 30 min. The water partial pressure for all the conversions was 10 mTorr. Under a processing condition of $P_{\text{H}_2\text{O}} = 10$ mTorr, $P_{\text{O}_2} = 100$ mTorr and $T = 800$ °C, the effective conversion rate can be as high as 12 Å/sec.

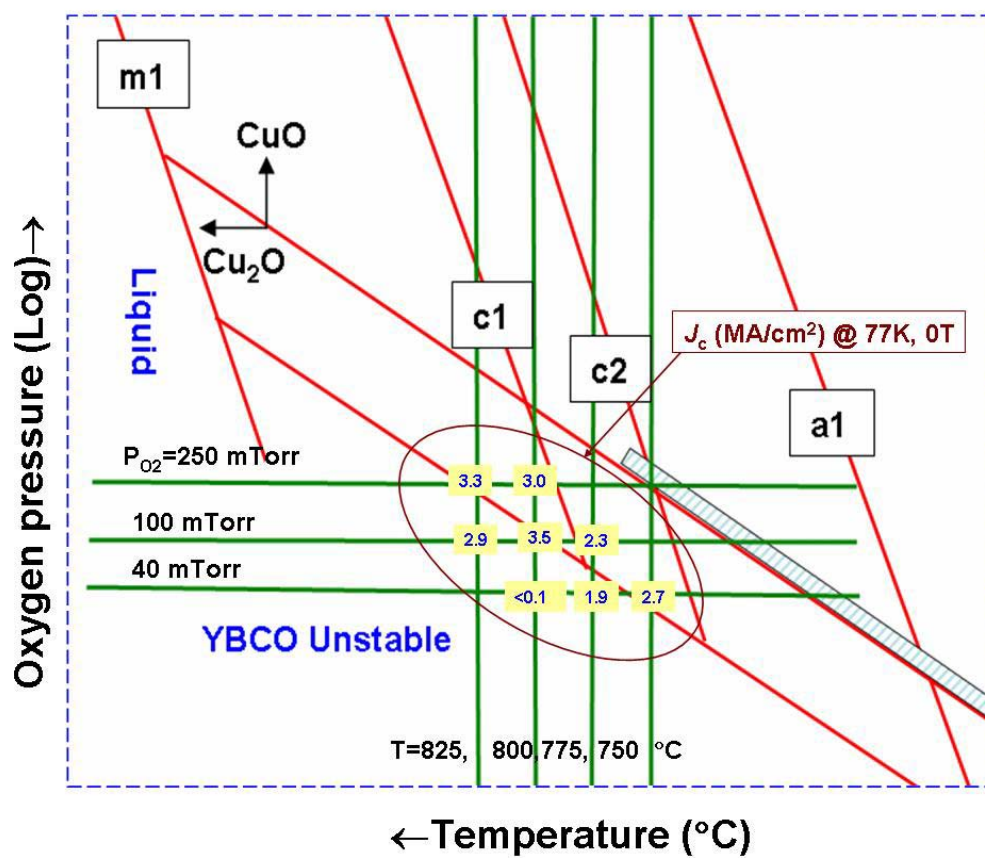


Figure 4.9. The 77 K self-field J_c values of the YBCO films converted from the pre-annealed precursors plotted in the YBCO phase diagram (partially shown) with the conversion condition for each film denoted respectively.

Preliminary experimental results have also shown that the pre-annealing effect is not sensitive to the pre-annealing condition. After the treatment at a temperature between 400 ~ 500 °C and in an atmosphere with oxygen content varying from 0.1 ~100 %, a pre-annealed precursor, in contrast to an as-deposited precursor, can be converted at a faster rate under more aggressive conditions. Shown in figure 4.10 are the J_c versus magnetic field relationships for three YBCO films. The films were about 0.42 μm thick and the substrates were CeO_2 -buffered YSZ. While the pre-annealing atmosphere is different in oxygen content, the three precursors were all processed under the same faster conversion condition with $P_{\text{H}_2\text{O}} = 10$ mTorr. There is certain variation in the J_c value, but overall the critical current density is high.

The pre-annealing effect was studied in a processing system equipped with an *in-situ* energy dispersive X-ray (EDX) diffraction system [68]. The system uses the Bragg-Brentano para-focusing geometry with a tungsten “white” ($\lambda > 0.2479$ Å) X-ray source and a liquid nitrogen cooled Ge detector. Both the incident and diffracted X-rays are at a fixed glancing angle of 5° with respect to sample surface. The development of crystalline phases during a precursor conversion can be continuously monitored using the EDX

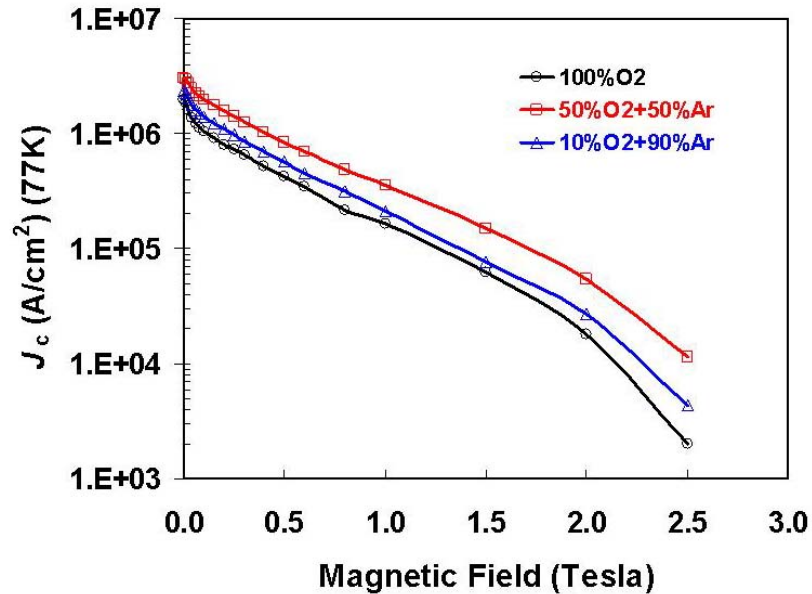


Figure 4.10. Critical current density J_c versus magnetic field relationships for YBCO films converted from three EBE precursors undergone different pre-annealing.

system. Here, 1 μm thick precursors were deposited on RABiTS templates. The as-deposited precursors were processed under both slow (or baseline) and fast conversion conditions in a reduced total pressure of about 2.5 Torr. A pre-annealed precursor was processed under the fast conversion condition. The pre-annealing was conducted in 0.1% atmospheric pressure oxygen at 400 °C for 30 min. The time-dependent normalized BaF_2 (111) and YBCO (002) reflection peak intensities are shown in figure 4.11 [69]. The disappearance of the BaF_2 signal and the saturation of the YBCO intensity occur simultaneously, marking the moment at which conversion is complete. The baseline slow processing resulted in reasonably high J_c for the as-deposited precursor. However, the as-deposited precursor processed under the fast conversion condition has a very low J_c or I_c . In contrast, high critical current I_c of 189 A/cm-width (77 K, self-field) was obtained for the pre-annealed precursor under the fast conversion condition, corresponding to a conversion rate of about 9 $\text{\AA}/\text{sec}$.

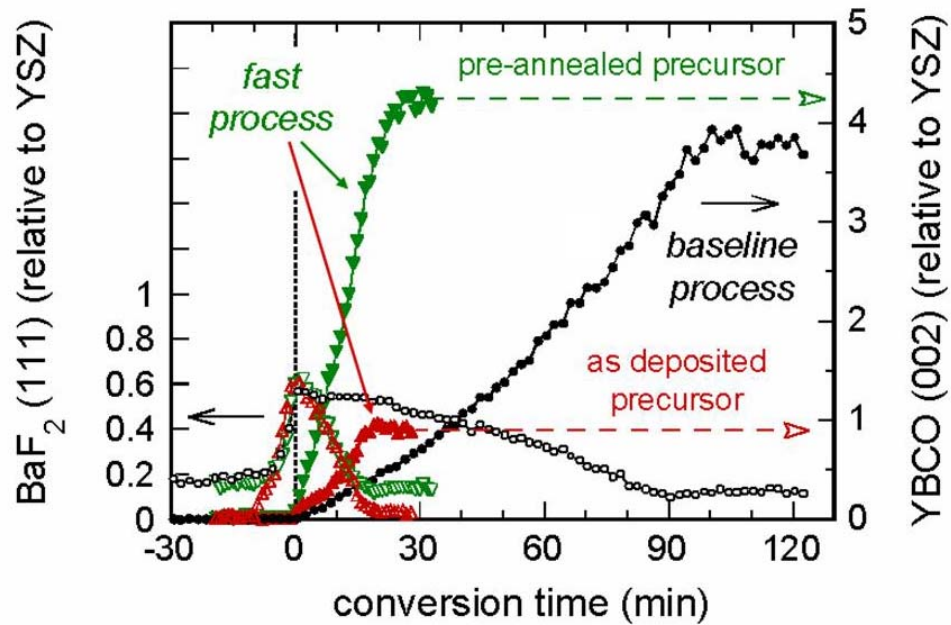


Figure 4.11. Time dependent variations of the peak intensities of BaF_2 (111) (open symbols, left axis) and YBCO (002) (closed symbols, right axis) reflections during the conversion processes.

4.3.2 Comparison of Pre-annealed and As-deposited Precursors

To understand the pre-annealing effect on the *e*-beam co-evaporated precursor conversion, the pre-annealed and as-deposited EBE precursors were studied using XRD, TEM and XPS. The inspections focused on the differences in the precursor structure and chemistry, which could account for the different conversion behavior [70].

The XRD $\theta \sim 2\theta$ scan patterns of a pre-annealed precursor and an as-deposited precursor are shown in figure 4.12. The precursors were deposited on CeO₂-buffered YSZ substrates. Apparently, the as-deposited precursor is basically amorphous, with no peaks shown in the diffraction pattern except that from the substrate. For the pre-annealed precursor, which was annealed in pure oxygen of atmospheric pressure at 500 °C for 60 min, has crystallized BaF₂ and copper oxide CuO. From the Sherrer equation, the size of the nano-crystallites of BaF₂ and CuO can be calculated to be about 15 nm. This size is close to that of BaF₂ and CuO in the as-calcinated TFA-MOD precursors. The formation of the nano-crystallites due to the pre-annealing was further confirmed by transmission electron microscopy (TEM). A cross-sectional dark field TEM image of the pre-annealed precursor is shown in figure 4.13(a), together with the selected area diffraction (SAD) pattern, figure 4.13(b). The image shows that there are two types of nano-crystallites in the precursor (dark and bright precipitates in the image). The indexing of the SAD pattern indicated that these are BaF₂ (dark) and CuO (bright). In contrast to the pre-annealed precursor, the TEM investigation does not reveal any crystallization in the as-deposited precursor, which is consistent with the XRD observation. The essentially amorphous structure of the as-deposited precursor is the basic reason that it is more reactive or less stable under the processing condition.

XPS was also used to study the chemical states of the cations in the pre-annealed and as-deposited precursors. For comparison, pure BaF₂ films deposited in the same *e*-beam evaporated system were also inspected. It was found that the chemical states of barium in the pre-annealed and the as-deposited precursors are the same, and identical to that in the pure BaF₂ film. It implies that under the pre-annealing condition, BaF₂ does not decompose during the crystallization process that forms the BaF₂ nano-crystallites.

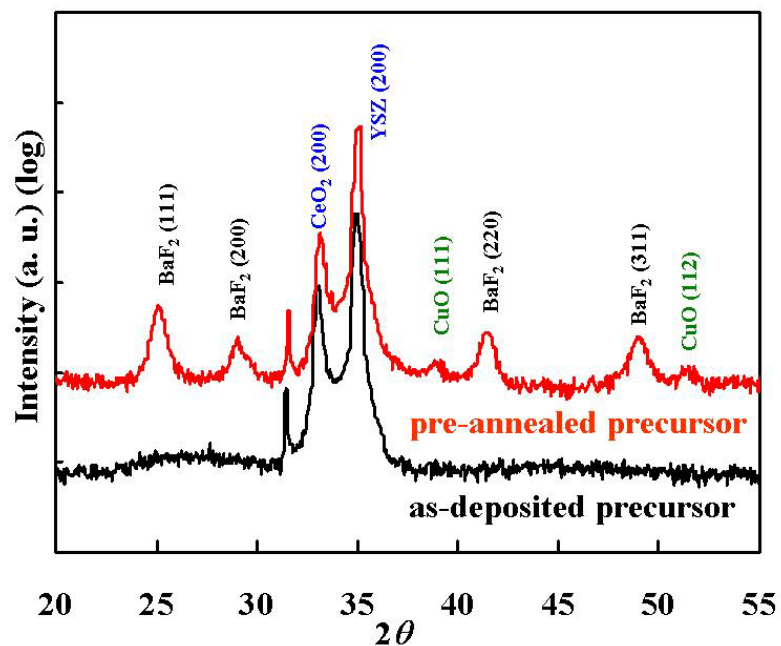


Figure 4.12. XRD $\theta \sim 2\theta$ scan patterns for the as-deposited and pre-annealed EBE precursors on CeO_2 -buffered YSZ substrates.

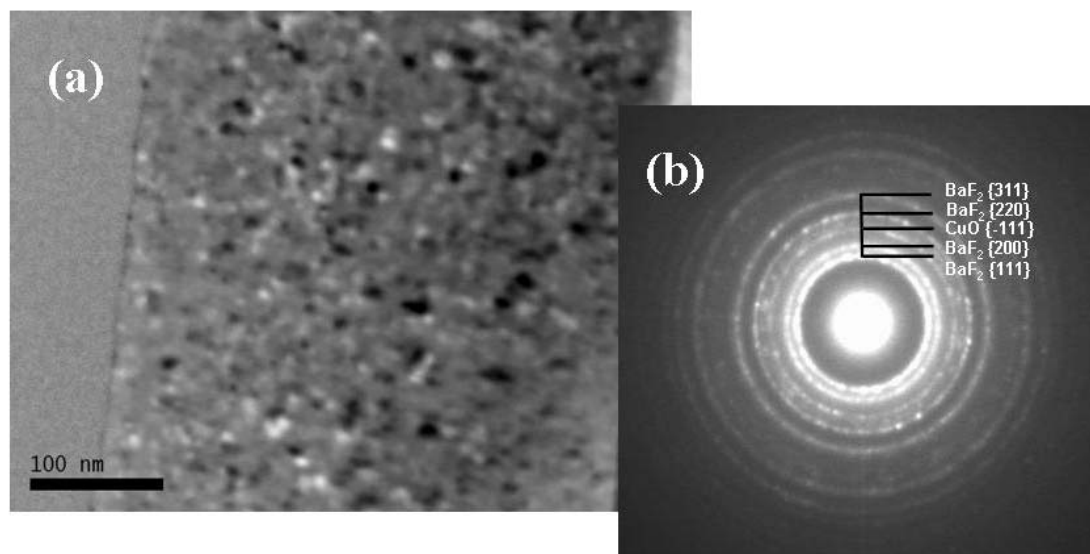


Figure 4.13. (a) Cross-sectional TEM image, and (b) Selected area diffraction pattern of a pre-annealed precursor.

Also, for both the pre-annealed and as-deposited precursors, yttrium exists in the same chemical state as in Y_2O_3 .

In figure 4.14, (a) and (c) are the Cu2p XPS spectra for the surfaces of the pre-annealed and as-deposited precursors respectively, and (b) and (d) are the Cu2p XPS spectra of two copper films, one in the as-deposited state and the other was annealed under the same condition for the pre-annealing of the precursors. The Cu films were deposited in the same system and under the same condition for depositing the precursors. It can be seen that the chemical states of copper are similar for the precursors and the copper films, when they are either at the annealed state or at the as-deposited state. Based on whether the spectrum contains the so-called “shake-up satellites,” which are the signature of Cu^{2+} , it is seen that Cu at the surface of the pre-annealed precursor and the annealed Cu film are in the state of Cu^{2+} as in CuO, while no CuO exists at the surface of the as-deposited precursor and the as-deposited Cu film.

The Auger parameter (AP) is used to further identify the Cu chemical states in the films. The Auger parameter is defined by the summation of the photoelectron binding energy and the Auger electron kinetic energy for an element obtained from an XPS scan. That is

$$AP = BE_p + KE_A \quad (4.23)$$

Auger parameter is used for chemical state analysis since it is independent of the charging effect [71]. The charging effect could affect the measurement of the exact binding energy values in an XPS experiment. This is a concern, especially when the sample surface is etched inside the XPS system as in a depth profiling, so that there is no external reference (e.g., the adventitious carbon) that can be used for the calibration of the binding energy. The Cu Auger parameters, $AP(Cu) = BE(Cu2p_{3/2}) + KE(CuLMM)$ were 1851.4 and 1848.6 eV for the pre-annealed and as-deposited precursors, respectively. By comparing the above $AP(Cu)$ values with the standard reference data given in the form of the Wagner Plot [72], the existence of CuO at the surface of the pre-annealed precursor is confirmed. Moreover, it can be determined that Cu at the surface of the as-deposited precursor is in the state of Cu^{1+} as in Cu_2O , similar to that in the as-

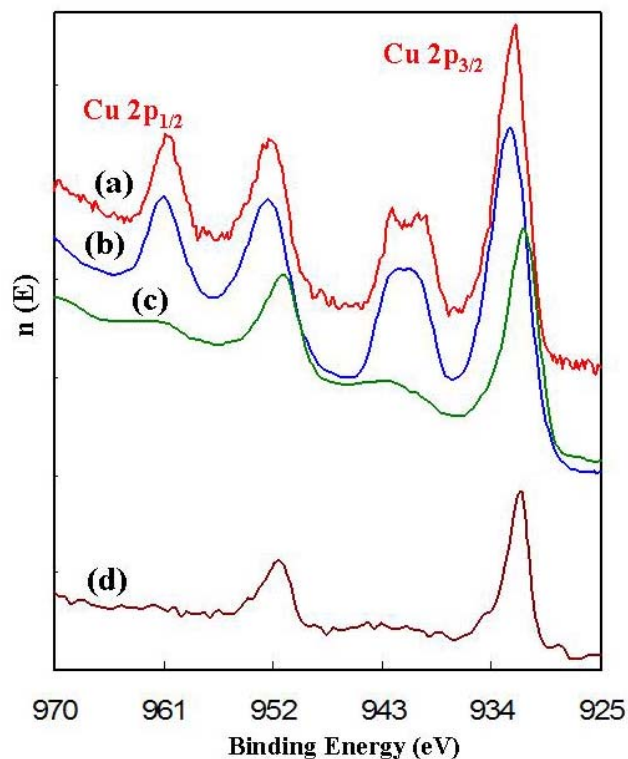


Figure 4.14. Cu2p XPS spectra of (a) the pre-annealed precursor, (b) the annealed Cu film, (c) the as-deposited Cu film, and (d) the as-deposited precursor.

deposited Cu film. In fact, by carefully comparing the spectra (c) and (d) in figure 4.14 it can be seen that the Cu in the as-deposited Cu film is more oxidized than the Cu in the as-deposited precursor.

4.4 XPS Study of Precursor Conversion

There are mainly two aspects of issues when the *ex-situ* BaF₂-based precursor conversion mechanism is considered: (1) phase development; (2) YBCO film nucleation and growth, during the conversion process.

The phase development, or the chemistry and structure evolution, in the precursor before YBCO nucleation and during YBCO growth is relevant because it is these phases that determine how YBCO will nucleate and grow. XRD and TEM are powerful tools in phase analysis, but they are basically more effective for crystallized materials. For chemistry and phase analysis, on the other hand, XPS is not only applicable to crystals

but also suitable to amorphous materials such as in the case of the precursors. In fluoride-based precursors, the decomposition of BaF_2 is the core step in precursor conversion. So the barium related phase development is the most interesting subject in the phase analysis. Having diverse chemical states, copper also warrants attention.

XPS depth profiling was conducted on both the pre-annealed and as-deposited EBE precursors to further reveal the copper chemical state differences [70]. The data analysis is based on the copper Auger parameter $\text{AP}(\text{Cu})$ comparison. Standard Auger parameters of copper, as it exists in different chemical structures, are shown in the copper Wagner plot, figure 4.15, obtained from the NIST XPS data base. The $\text{AP}(\text{Cu})$ value for orthorhombic YBCO film comes from this study. There are few reports on the $\text{AP}(\text{Cu})$ values for the two phases of YBCO. Our $\text{AP}(\text{Cu})$ for the orthorhombic film is in good agreement with that for the orthorhombic bulk-sintered YBCO given by reference [73].

The $\text{AP}(\text{Cu})$ depth profiles for the pre-annealed and the as-deposited precursors are shown in figure 4.16. The etching of the films was conducted by sputtering the sample surface using an Ar^+ ion gun before each XPS scan. The etching rate was calibrated as about 0.5 nm/min. It can be seen that the copper chemical states are different for the precursor surface and the subsurface, for both the pre-annealed and the as-deposited.

For the pre-annealed precursor, $\text{AP}(\text{Cu})$ decreases from top surface down into the precursor, where the copper chemical state changes from Cu^{2+} to Cu^{1+} . For pure CuO the handbook intensity (height) ratio of $I(\text{Cu}2p_{3/2} \text{ satellite})$ to $I(\text{Cu}2p_{3/2})$ is about 0.45. For the pre-annealed precursor this ratio decreases gradually from surface to subsurface. Cu in subsurface layer has an $\text{AP}(\text{Cu})$ value of 1848.2 eV, which is about the characteristic value of Cu_2O . Further curve fitting (deconvolution) of the subsurface $\text{Cu}2p_{3/2}$ peak shows both $\text{Cu}^{2+}(\text{CuO})$ and $\text{Cu}^{1+}(\text{Cu}_2\text{O})$ components.

For the as-deposited precursor, it was known from the absence of the shake-up satellite peaks that the copper is not in the Cu^{2+} state. Distinguishing between Cu^{1+} and metallic pure Cu relies on the Auger electron kinetic energy or the Auger parameter. It is shown that, down into the subsurface, the $\text{AP}(\text{Cu})$ value increases to around 1850.5 eV, which is an indication of more metallic (pure Cu) feature. Although it is difficult to

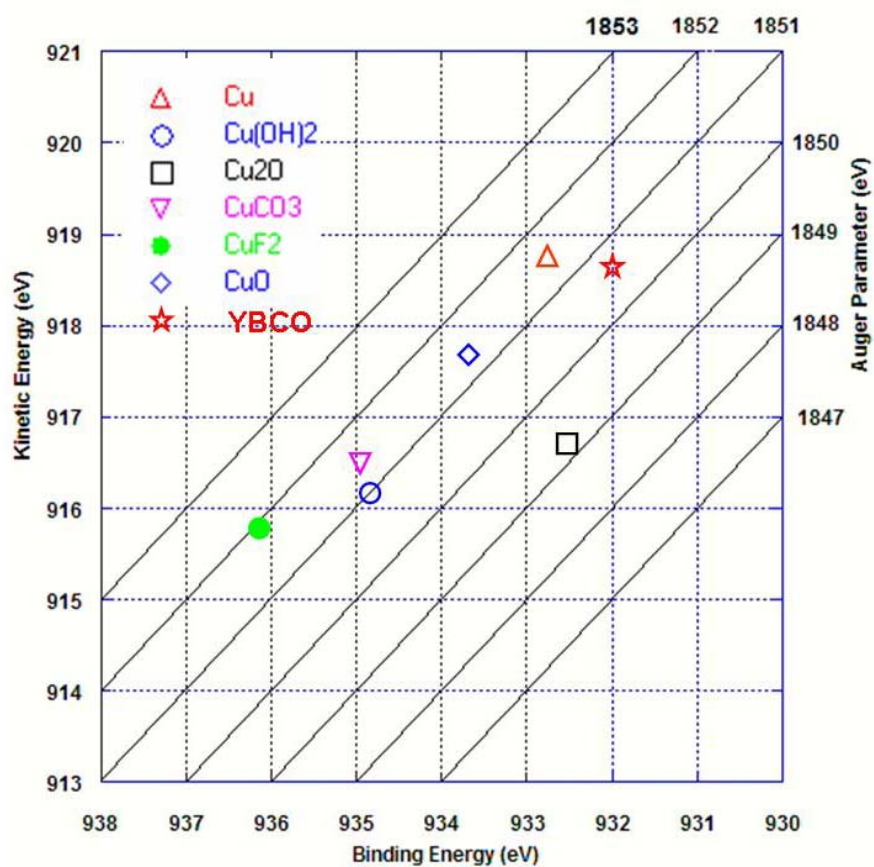


Figure 4.15. Copper Wagner plot showing standard Auger parameters of copper when it is in different chemicals.

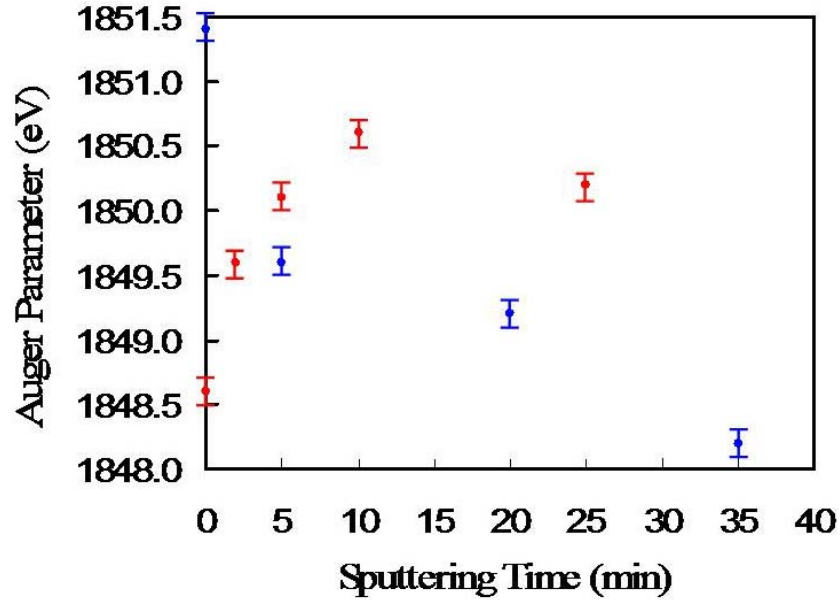


Figure 4.16. XPS copper Auger parameter depth profile showing the variation of copper chemical state through thickness for the as-deposited (red) and pre-annealed (blue) precursors.

estimate the effect of the top layer copper chemical state on the conversion processing, the existence of either Cu_2O or pure Cu inside the precursor greatly influences the conversion thermodynamics, according to our earlier calculation concluded in figure 4.2. Because the reaction (4.17) has lower Gibbs free energy than the reactions (4.16) and (4.18), it is expected that the metallic copper in the precursor would make the precursor less stable.

A pre-annealed precursor was quenched from an intermediate processing condition for inspecting the phase evolution during YBCO film formation. The precursor is about $0.35\ \mu\text{m}$ thick. The pre-annealing was done in atmospheric pressure of pure oxygen at $500\ ^\circ\text{C}$ for 60 min. The processing was at $760\ ^\circ\text{C}$ with $P_{\text{O}_2} = 40\ \text{mTorr}$ and $P_{\text{H}_2\text{O}} = 10\ \text{mTorr}$. The sample was quenched 6 min after reaching the processing temperature. An XPS wide-range survey spectrum of this quenched sample is shown in figure 4.17. The scan was conducted after a total 35 min ion etching.

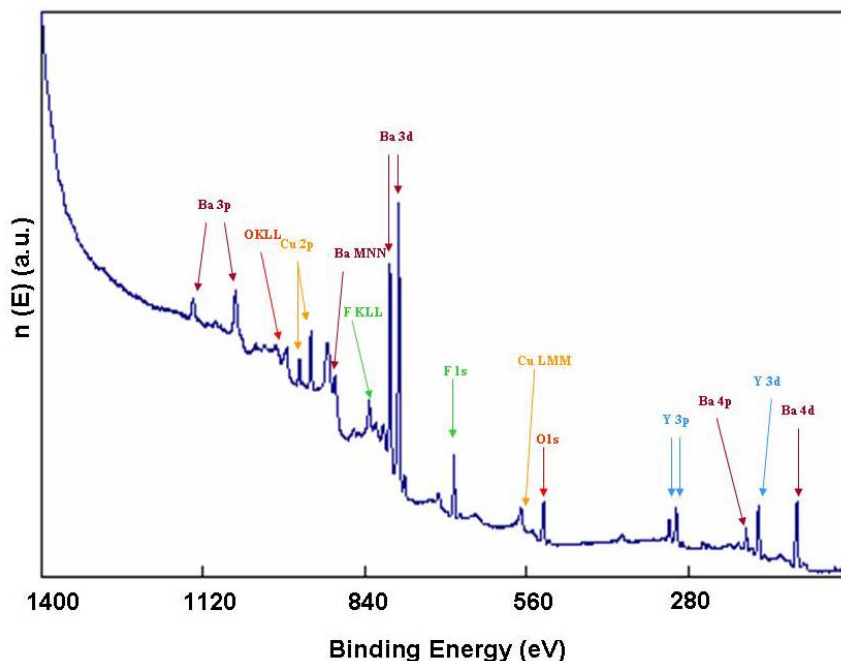


Figure 4.17. XPS survey spectrum of the pre-annealed precursor quenched from its processing condition, giving an overall view on the elemental components in the unconverted precursor.

Through-thickness copper chemical state was inspected on the partially converted quenched sample using XPS depth profiling. The thickness dependence of the AP(Cu) value is shown in figure 4.18. Here, the depth profile starts from the sample surface and runs all the way to the film/substrate interface. Although it was not fully converted, the quenched sample has considerable amount of YBCO film, which was verified by XRD. The AP(Cu) depth profile shows that the copper is basically in two different chemical states. In the lower part of the precursor where YBCO already formed, the AP(Cu) has a value of 1850.2 eV, which is close to the typical AP(Cu) value for the orthorhombic YBCO (1850.6 eV). In the upper part of the film, the AP(Cu) value is around 1849.8 eV, which is close to the standard AP(Cu) value for Cu_2O . There is no evidence for the existence of CuO in the unconverted precursor, which is inconsistent with the XRD and TEM results. A possible explanation is that CuO, if there is any, might be reduced to Cu_2O by the high energy X-ray photons via the photoelectron process during the scan or

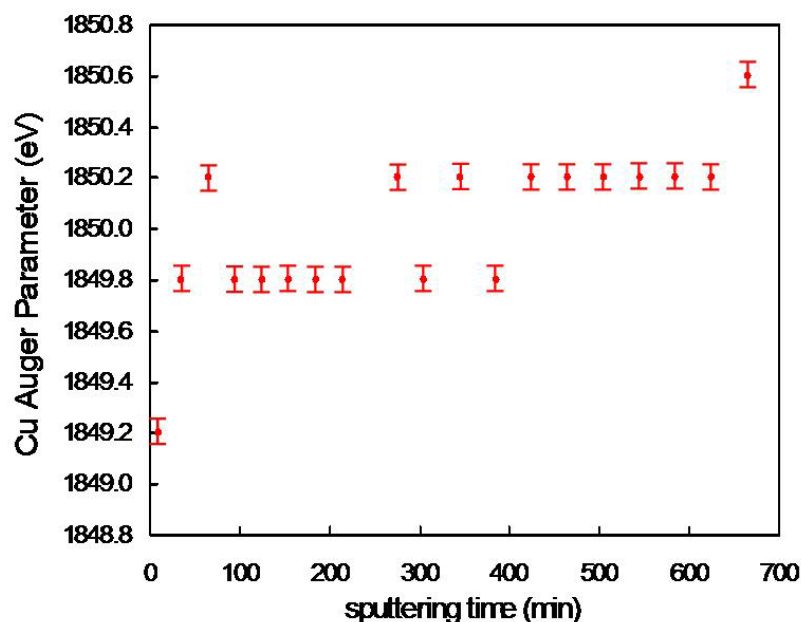


Figure 4.18. AP(Cu) depth profile of the quenched sample showing the thickness dependence of copper chemical state in the film being converted.

by the ion etching [74, 75]. According to the thermodynamics calculation, there should not be much difference whether copper is in CuO or Cu₂O states, in terms of the precursor stability.

The standard barium Auger parameters AP(Ba) for barium in different chemicals are indicated in the barium Wagner plot in figure 4.19, in which only the datum for YBCO is from this study; all others are from the NIST XPS data base. Here, the barium Auger parameter is defined as $AP(Ba) = BE(Ba3d_{5/2}) + KE(BaMNN)$. For a fully converted orthorhombic YBCO film, the measured AP(Ba) is 1377.5 eV, which is the same as that of Ba in BaO according to the standard reference data. This agreement in AP(Ba) values implies that Ba in YBCO should have similar chemical bonding state as that in BaO.

Because their AP(Ba) values are about 5 ~ 6 eV apart, from the Wagner plot it can be seen that it is very easy to distinguish the metallic barium from the barium in BaF₂. A general tendency is that the more positively charged the barium the smaller the AP(Ba)

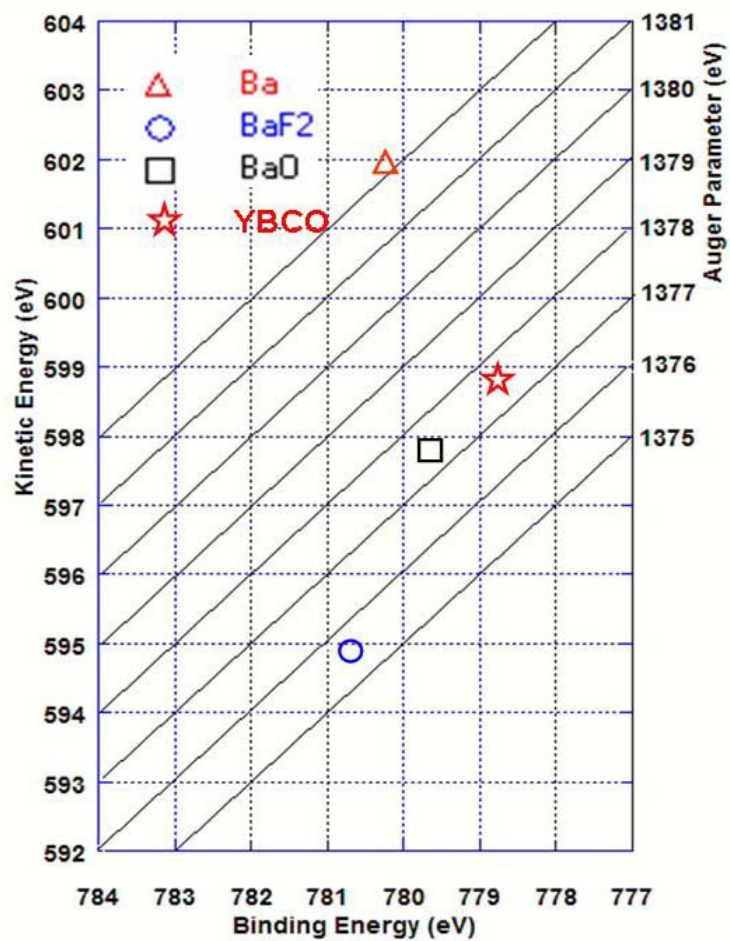


Figure 4.19. Barium Wagner plot showing standard Auger parameters of copper when it is in different chemicals.

value. The Ba Auger parameter depth profile was established for the partially converted precursor with the aim to reveal the Ba chemical bonding state trajectory. From the AP(Ba) depth profile of the quenched sample in figure 4.20, it is clear that there is no metallic Ba in the film. Based on the AP(Ba) values, barium is basically in two different states. In the lower part of the film, where YBCO has presumably formed, the AP(Ba) values are around 1377.6 eV, which is about the same as that in YBCO. There is a transition region in the YBCO film growth front where AP(Ba) has intermediate values.

In the upper part of the film, the AP(Ba) values are 1376.6 eV, which is about 1 eV higher than the standard AP(Ba) value for BaF₂. Further comparison indicated that this AP(Ba) value is almost the same as that in the “pure” BaF₂ film deposited in the same system and under the same deposition condition as the precursor. Two arguments can be made upon this observation: (1) during the YBCO growth, the BaF₂ in the

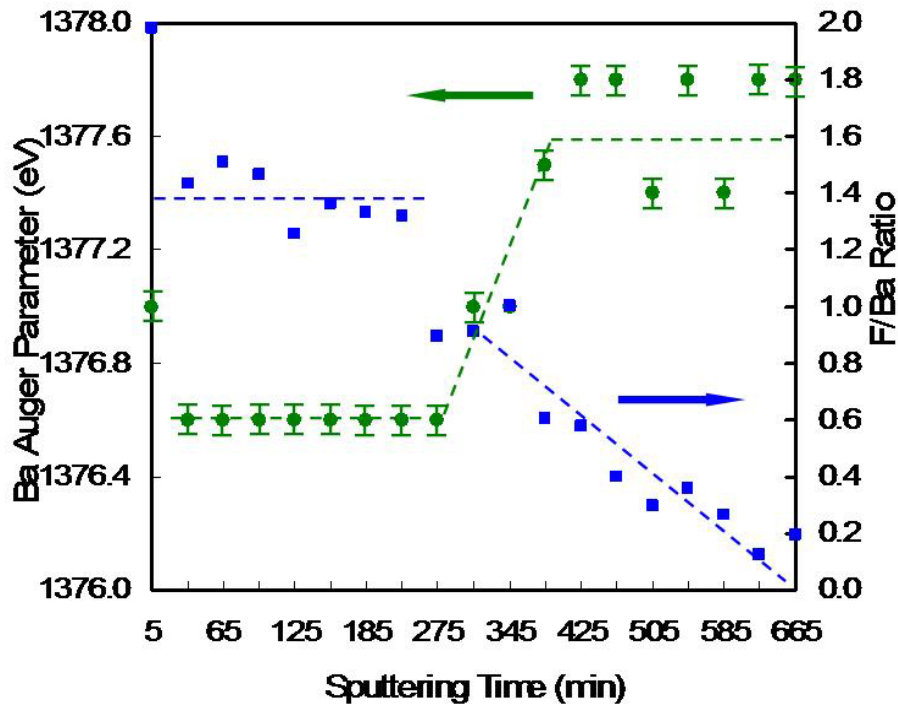


Figure 4.20. Depth profiles of barium Auger parameter and the fluorine-to-barium ratio (F/Ba) of the quenched sample.

precursor does not decompose in the unconverted precursor above the YBCO growth front; (2) the BaF_2 in the precursor and even in the “pure” BaF_2 film are not as pure as the standard BaF_2 . The latter is consistent with the fluorine to barium atomic ratio (F/Ba) depth profile, which is also shown in figure 4.20. The F/Ba ratio was determined according to the composition measurement based on the XPS data. The F/Ba ratio in the unconverted precursor is constant at a value of 1.4, which is about the same as that for the “pure” BaF_2 film, but is lower than that of stoichiometric BaF_2 . Rather than indicating a practical decomposition of BaF_2 prior to the quenching, this result may imply that both the precursor and the “pure” BaF_2 film are somewhat fluorine deficient, due to a small amount of fluorine loss during the *e*-beam evaporation. F/Ba ratio in the precursor is concerned mainly for two reasons. First, fully fluorinated barium or even pre-crystallized BaF_2 is essential and helpful in stabilizing the unconverted precursor while YBCO film is growing. A stabilized precursor in the region above the YBCO film growth front should not decompose so that the premature random nucleation of YBCO away from the growth front can be prevented. Secondly, too much fluorine deficiency may lead to high reactivity so that the precursor becomes unstable, even when exposed to air at room temperature.

The F/Ba ratio in the lower part of the film decreases almost linearly with the depth, but is non-zero. It is possible that a certain amount of fluorine is incorporated in the YBCO film being formed, by the atomic fluorine occupancy of the oxygen-vacancy sites in the YBCO chain layer. An island growth mode of YBCO, rather than an ideal laminar growth may also result in the non-zero F/Ba ratio at a position where YBCO has partly formed.

Chapter 5

FLUORINE-FREE PRECURSOR AND CONVERSION

5.1 Motivation

The motivation to investigate a fluorine-free precursor and its conversion is to probe the feasibility of an alternative *ex-situ* process for fabricating biaxially-textured YBCO films. It is expected that the conversion of a both fluorine-free and carbon-free PVD precursor could be much simpler compared with that for the BaF₂-based precursors made by *e*-beam co-evaporation or TFA-MOD, since no water vapor is necessarily required and no resultant HF is released. Moreover, it is possible that a fluorine-free precursor can accommodate a wide range of buffer materials, while CeO₂ has been the only buffer material so far compatible with the BaF₂-based precursors.

5.1.1 Complexity of BaF₂-based *Ex-situ* Processes

The BaF₂-based *ex-situ* processes are very promising to become practical techniques for fabricating biaxially-textured YBCO films. It has been demonstrated in the last chapter that, by appropriate modification of the *e*-beam co-evaporated precursor, the conversion rate can be raised to about 12 Å/sec while maintaining high J_c . The conversion rate is crucial when the technique is to be used for a practical production. In fact, the inefficient processing rate is one of the reasons why *e*-beam co-evaporation has not been adopted by the coated conductor industry. The TFA-MOD process has been successfully used in a pilot production making a YBCO HTS wire of 94 m long with critical current I_c of about 350 A/cm-width [76]. The low cost of the TFA-MOD method makes it more commercially attractive.

The main advantages of the TFA-MOD process are: (1) the precursor can be made in a non-vacuum condition; (2) it is easier to deposit the precursor on larger area substrates; (3) the overall film stoichiometry can be precisely controlled. However, the complexity of this process is also obvious. To prepare a TFA-MOD precursor, the

calcination step for burning out the organic solvent and extra fluorine normally takes a long time, up to 10 hours or more with a very slow heating rate of about 0.5 °C/min [14]. The tedious calcination greatly compromises the efficacy of the process. Faster heating rate and shorter calcination time tend to result in cracks and pores in the precursor, which inevitably degrade the properties of the ultimate YBCO film [77, 78]. Moreover, faster heating rate was found to cause segregation of copper in the vicinity of the film surface. This copper segregation in the precursor might lead to differences in crystallinity and properties in the final film [79]. In addition to the heating rate, the water partial pressure and the water input temperature were also found to effectively influence the precursor quality. To shorten the time for the calcination, modified TFA-MOD methods with reduced amount of fluorine in the precursor are under investigation. It is expected that by partially replacing trifluoroacetates with fluorine-free salts such as copper naphthenate [80], copper acetate [81], or yttrium and copper trimethylacetates (TMA) [60] would simplify both the calcination and precursor conversion.

A major limitation of the TFA-MOD process is to make crack-free thicker films. One method being tested is using multiple coating, that is, repeated coatings after each burn out. For example, to make a 0.9 μm thick high- J_c film, triple coating was used to obtain the crack-free precursor [82]. To make 1.38 μm thick films, 5 coatings were applied [83, 84]. Apparently, the practical viability of multi-coating needs to be further studied. In fact, compared with the calcinations, the conversion of the TFA-MOD precursor appears to be even more complicated, as has been previously discussed.

Although it is relatively easier to deposit thicker precursors using the *e*-beam co-evaporation approach, the conversion of the PVD precursor is also very complicated and difficult to control. The complexity is again basically due to the fluoride nature of the precursor, which is similar to the TFA-MOD precursor. One problem with BaF_2 -based precursor conversion is that the critical current density J_c of the films is always thickness dependent. For TFA-MOD films, a decrease of J_c with increasing thickness was observed when film thickness is less than 1 μm [36]. Substantial J_c decrease was also observed for the *e*-beam co-evaporated films when the thickness is greater than 1 to 1.5 μm [85, 86]. Although the J_c values of YBCO films made by other techniques, such as *in-situ* PLD,

were also found to be thickness dependent [87 - 89], the degradation of J_c with thickness for the BaF₂-based films is believed to be conversion related. A recent investigation on the conversion of thicker (3 ~ 4 μm) *e*-beam co-evaporated precursors indicated that YBCO orientation is also dependent on oxygen partial pressure [90]. That is, besides the water partial pressure and the total pressure, oxygen partial pressure also strongly affects the YBCO nucleation and growth, and this effect itself is thickness dependent. In other words, the optimal oxygen partial pressure varies with film thickness. It was pointed out that the decrease of J_c in thicker films is mainly due to the randomly-oriented YBCO formation in the near-surface layer of the film [91]. Control of the BaF₂-based precursor conversion is still being intensively investigated.

In addition to the complexity in the precursor conversion, the *e*-beam co-evaporation approach also suffers a number of other potential issues, including [92]: (1) multiple guns to evaporate separate sources, which complicates the process and increases the capital cost; (2) frequent discharges and cross-talk, which critically affect the composition control and therefore long-length uniformity; (3) difficulty to perform rare-earth substitution and doping tasks, which limit the ability to introduce artificial pinning centers and enhance J_c .

5.1.2 Fluorine-free *Ex-situ* Processes

Most of the complexity and efficiency issues about the BaF₂-based processes are related to the fluoride decomposition. Moreover, there are also concerns about the by-product of the decomposition, namely hydrogen fluoride HF. The released HF itself is corrosive and could be environmentally harmful in the case of large scale production. Therefore, there has been a longstanding interest in developing a fluorine-free *ex-situ* process for making YBCO films. A non-fluorine *ex-situ* process produces YBCO films also by converting a pre-deposited precursor, but the precursor film is fluorine-free. In principle, the fluorine-free precursor can be made by chemical solution deposition (CSD), physical vapor deposition (PVD), or other deposition methods.

In fact, many other MOD methods using fluorine-free precursors have been studied and in some cases reasonably high J_c have been achieved. The basic procedure of

making the precursors is similar to that of TFA-MOD, including making solutions, coating and the subsequently calcination. The first difficulty is to make a suitable solution for coating. For a multiple cation system, attaining homogeneity of the constituent metals in a solution is not a trivial process. The constituent metals in YBCO are chemically and physically distinct. Their difference in solubility could significantly affect the solution homogeneity, especially when relatively viscous solution is required for the deposition. The fluorine-free precursors can be made of acetates, citrates, oxalates, neodecanoates, acetylacetonates, trimethylacetates, and naphthenates, *etc* [93 - 97]. Unfortunately, early attempts of using fluorine-free bulk solution were not very successful in fabricating high J_c YBCO films [98]. One problem is that, in the absence of fluorine, the metal organic precursors could have barium carbonate as an intermediate phase. $BaCO_3$ normally forms in the presence of CO_2 , which is the side product of the hydrolysis calcination by which the carbon containing ligands are to be removed. In many cases it was found that the YBCO film orientation is governed by the reactions involving $BaCO_3$ or $Ba(OH)_2$. Since metal organic salts have very limited solubility in most organic solvents, such as methanol, acetone, benzene, and xylene, organic acids are sometimes used in solvent. To achieve appropriate solution concentration and viscosity without precipitation, extra organic additives are also necessary. The usage of organic acids and additives could further complicate the removal of carbon ligands, especially in the case of fatty acid ester ligands. Residuals of carbon, particularly along the grain boundaries, could account for the relatively lower J_c of the fluorine-free solution approach. With the improvement of solution chemistry and optimization of the calcination condition, the carbon effect may be minimized. However, by using a solution method, a long time calcination process is almost always needed. That again is an issue of efficiency. Similar to the TFA-MOD method, the gases generated during the calcination process could lead to the formation of pores in the film, which compromise the properties.

There is a general concern about the presence of fluorine, carbon, or hydrogen in a precursor for an *ex-situ* approach of making YBCO films. These impurities, as they are not necessarily needed in YBCO, may have effects of deteriorating the film structure and properties at any time during a processing. Ideally, a contamination-free precursor that is

composed of only yttrium, barium, copper, and oxygen is expected to result in a better film. Furthermore, an *ex-situ* approach of processing a precursor containing only the constituent metals could be a very simple process, since no water is needed and no resultant gases are released, *etc.* Presumably, this type of precursor can only be made by a PVD technique.

Since the early effort of making *e*-beam co-evaporated precursors from all-metallic sources was troubled by the BaCO₃ problem, there has been very limited development of non-fluorine PVD precursors for *ex-situ* processing of YBCO films. In fact, the BaCO₃ problem may be easily avoided since the as-deposited precursor does not necessarily have to encounter exposure to air before being converted. In other words, the deposition and the conversion can be conducted in a same system in a sequential mode. To further simplify the precursor deposition, a single source is preferred.

5.2 Fluorine-free Precursor Deposition

Using pulsed laser deposition (PLD), fluorine-free precursor films were deposited on single-crystal LaAlO₃ and CeO₂-buffered single-crystal YSZ substrates. A KrF (248nm) excimer laser was used at a fluence of 2 J/cm² and a pulse repetition rate of 10 Hz. The deposition rate was about 5 Å/sec. The ablation source material is a ceramic YBCO target. During the deposition, the substrates were held at room temperature. The PLD system is shown schematically in figure 5.1.

PLD was selected for the deposition process since it is expected that the stoichiometry of a PLD target can be well maintained into the film. The congruent evaporation results from the ablation of an intense energy pulse in a shallow depth of the target material and the consequent explosive evaporation of a thin layer before it has time to disproportionate. Moreover, PLD is a very flexible technique. It is expected that the precursor composition can be easily adjusted by doping the target.

The target was made by solid state reaction from Y₂O₃, BaO and CuO. The Y₂O₃ powder was pre-fired overnight at 1000 °C in air to remove CO₂ and H₂O, and subsequently stored in a dessicator. Pure BaO was prepared by heating BaCO₃ in a high vacuum furnace at 1100 °C for 4 ~ 6 hours, followed by slow cooling and storage in a dry

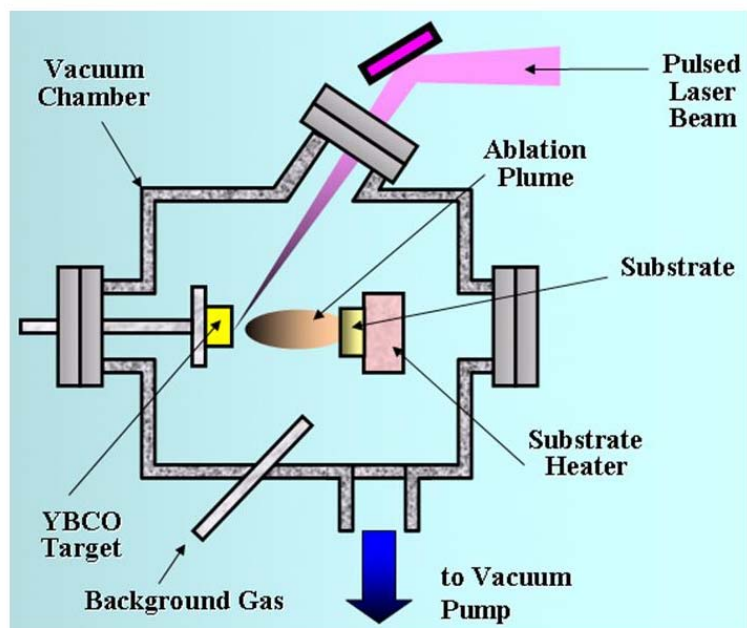


Figure 5.1. Schematic diagram of the PLD system used for the deposition of the fluorine-free precursor.

box. CuO was also stored in a dry box. Starting materials of stoichiometry 1Y:2Ba:3Cu were mixed and ground thoroughly. The mixture was first heat treated in air at 880 °C for 48 hours. After an intermediate grinding, a second heat treatment was given at 900 °C for 12 hours. The mixed powder was then cold-pressed at 8 tons in a mold of 1 inch diameter. The final heat treatment was conducted at 915 °C in pure oxygen for 12 hours and then slowly cooled to room temperature. An XRD inspection confirmed the polycrystalline YBCO 123 phase in the target.

The deposition condition was varied from no oxygen introduction (~ vacuum) to different oxygen pressures. The compositions of the precursor films deposited under different conditions were inspected by inductively coupled plasma optical emission spectroscopy (ICP-OES). The results in table 5.1 suggest that the composition of the precursor does not change much with the deposition condition. With a $P_{O_2} = 100$ mTorr, the composition is closest to the stoichiometric cation ratio of 1:2:3 for yttrium, barium, and copper.

The surface of a precursor deposited on LAO was inspected by SEM. The SEM image in figure 5.2 shows that the precursor surface is uniform and smooth except some circular particulates. Further inspection by EDS indicated that the isolated particulates are compounds consisted of yttrium, barium and copper. As is known, due to the high energy ablation the PLD plume may contain clusters, micro-sized particulates and molten globules in addition to atoms, ions, and molecules. Those particulates on the precursor surface with equiaxed shape may originate from the molten micro globules in the plume.

5.3 Fluorine-free Precursor Conversion and Film Characterization

To form YBCO films, the fluorine-free precursors, typically of 0.1 ~ 0.5 μm thick, were processed either in the PLD system directly following the deposition or in the low-pressure processing system used for the BaF₂-based precursor conversion. The conversion in the PLD system is a quasi *ex-situ* process, as the precursor is never exposed to air prior to conversion. This process completely excludes any possible reaction of the

Table 5.1: Compositions of fluorine-free precursors deposited under different oxygen ambient.

Oxygen Pressure (mTorr)	Y at% (normalized to 3 Cu)	Ba at% (normalized to 3 Cu)	Cu at% (normalized to 3 Cu)
Vacuum	19.1107 (1.080)	31.0782 (1.853)	50.3043 (3.000)
0.2	19.5975 (1.219)	31.4824 (1.958)	48.2457 (3.000)
100	17.6214 (1.074)	32.6575 (1.991)	49.2060 (3.000)

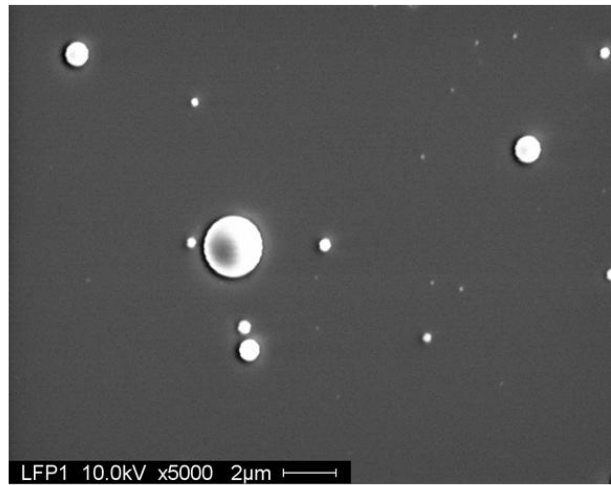


Figure 5.2. SEM surface image of a fluorine-free precursor deposited on LAO substrate under an oxygen pressure of 100 mTorr.

precursor with air that could form certain intermediate phases interfering with YBCO formation. For a precursor to be converted *ex-situ* in the low-pressure system, a thin layer (~100 nm) of silver was deposited on top of the precursor in the same PLD system before the precursor was exposed to air. It is expected that the silver layer can serve as a barrier to prevent the precursor from deteriorating in air. The concern was that the BaO in the precursor may react with CO₂ in air, forming BaCO₃.

According to the YBCO phase diagram in figure 2.3, YBCO has a wide stability region in terms of oxygen partial pressure and temperature. However, the processing window to form YBCO, especially epitaxial YBCO film, is much smaller than the stability region. General *in-situ* YBCO deposition conditions are indicated in the figure. For *in-situ* YBCO formation by PLD, typical conditions are 100 ~ 200 mTorr oxygen pressure, with substrate temperature between 760 ~ 800 °C (laser energy density between 1 ~ 3 J/cm² and pulse duration from 20 to 35 ns). For *ex-situ* precursor conversion, again several factors need to be considered when selecting the processing parameters. First, both lower temperature and lower oxygen pressure are preferred, which are beneficial to the metallic templates and buffers for a coated conductor. Second, the temperature needs to be high enough to provide the driving force needed for the cation diffusion and YBCO phase formation. Third, an appropriate processing parameter combination is required to promote epitaxial nucleation and growth, and to suppress the formation of randomly-oriented polycrystalline YBCO. Finally, in addition to oxygen pressure and temperature, other parameters such as ramp rate and heating path (referred to the atmosphere during the heating) have to be well designed so that secondary phase formation is excluded. This is simply because that in the YBCO stability region, there are other phases which co-exist with YBCO.

A different presentation of the YBCO phase diagram is shown in figure 5.3, indicating, together with YBCO, the stability regions for other phases of Y-Ba-Cu-O system [99]. YBCO is stable in the grey region in the phase diagram based on the results from references [100 - 102]. The upper-right boundary defines the stability limit where YBCO decomposes into Y₂BaCuO₅ (“211”) and Ba₂Cu₃O₅ (“023”) at the condition above the boundary line. The upper-left line is the stability boundary where YBCO

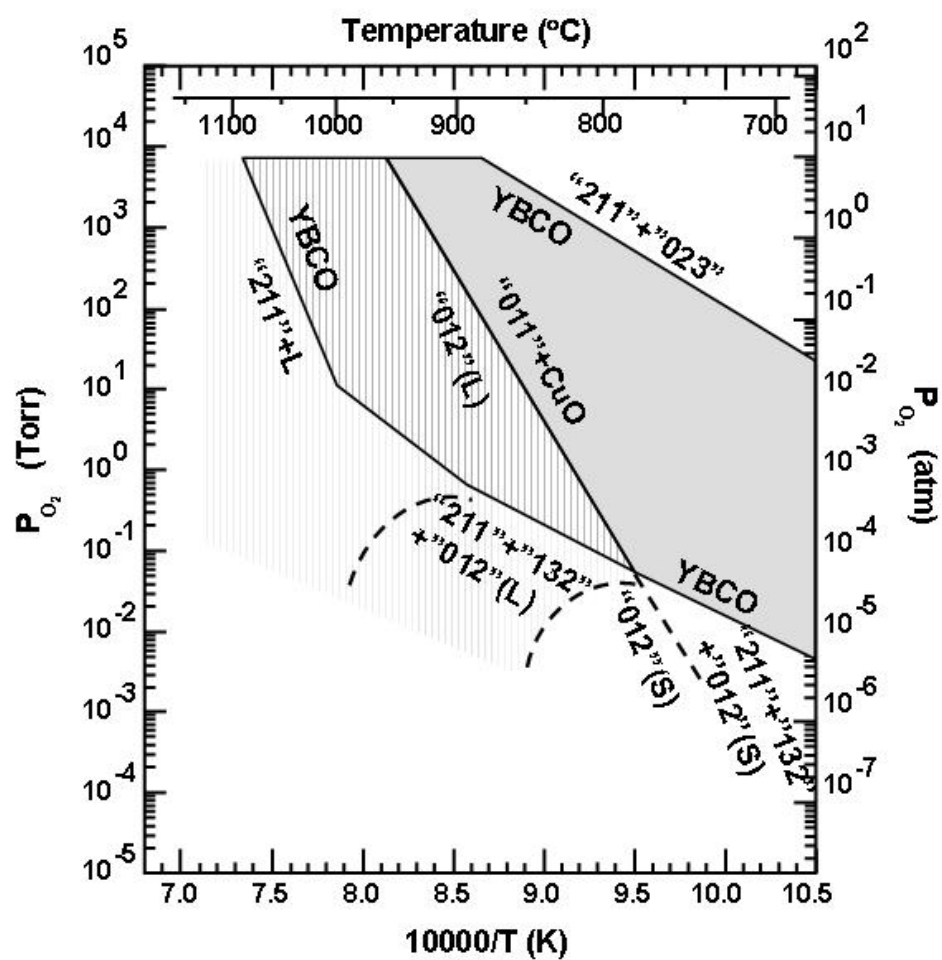


Figure 5.3. Stability phase diagram for YBCO and BaCu₂O₂ or "012" phase.

decomposes into “211” and Ba-Cu-O liquid (L) below the line, i.e. the peritectic melting of YBCO. The middle-left line stands for the boundary where YBCO decomposes into “211”, $\text{YBa}_3\text{Cu}_2\text{O}_6$ (“132”), and liquid BaCu_2O_2 (“012”). The “012” phase is solid if the temperature is lower than $780 \sim 800^\circ\text{C}$ in the region near the bottom boundary line. Superimposed inside the YBCO stability region is the “012” liquid line where the “012” phase becomes unstable and decomposes into solids BaCuO “011” and CuO as the temperature-pressure parameters cross over the line [103]. Apparently, YBCO and “012” phase coexist in an overlapping region as shown in the phase diagram. It has been suggested that the epitaxial YBCO growth could be assisted by the “012” liquid phase. This result was based on an *in-situ* XRD observation on YBCO formation from the *e*-beam co-evaporated films deposited using metallic sources [99]. That is, processing parameters that define a condition just to the left of the “012” liquid line could be beneficial to the epitaxial YBCO formation.

For the quasi *ex-situ* conversion in the PLD chamber, two heating paths were selected to investigate the effect of heating atmosphere on the epitaxial YBCO formation. In one case, the precursor was heated to the processing temperature in a reducing atmosphere of 1 Torr gas mixture of Ar/4%H₂. After reaching the processing temperature, oxygen was introduced rapidly until the desired processing point, in the proximity of the “012” line. Hereafter, this is referred as path “ ΔP ”. In the second case, oxygen was introduced to an appropriate level before starting heating up to the same final processing point. This is referred as path “ ΔT ”. In both cases, after a few minutes of conversion processing the temperature was decreased at fixed oxygen pressure. When the sample had cooled down to 500°C , the oxygen pressure was raised to about 400 Torr. Similar to the typical *in-situ* YBCO film fabrication, the resulting YBCO films were annealed at 450°C in atmospheric pressure oxygen for further oxygenation.

Shown in figure 5.4 are the XRD $\theta \sim 2\theta$ scan patterns of two films, both processed in the PLD chamber at 820°C under a $P_{\text{O}_2} = 1$ Torr. For both precursors, the substrates are LAO. One of the films was processed using path ΔP , while path ΔT was used for the other. For the path ΔT , the oxygen pressure during the heating was about 300

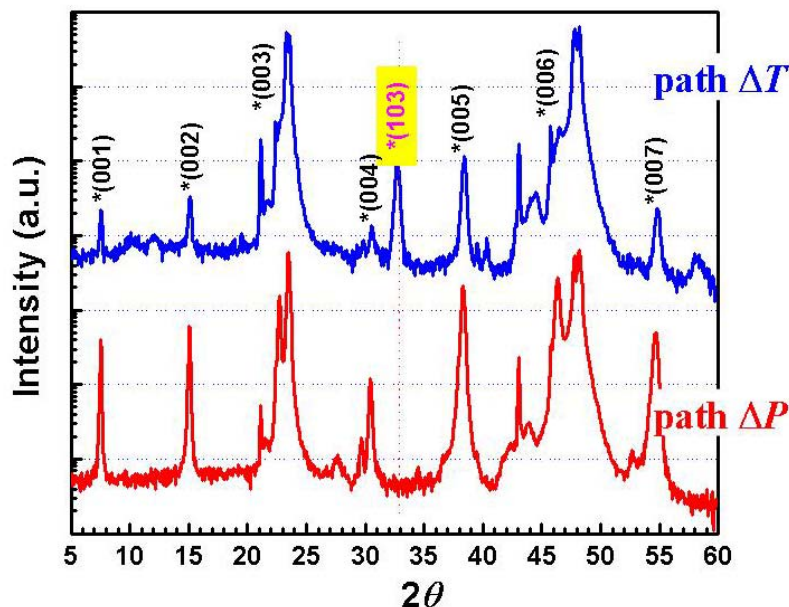


Figure 5.4. XRD $\theta \sim 2\theta$ scan patterns of YBCO films converted at the same conversion point, but heated up through different paths.

mTorr. It can be seen that the film processed using the path ΔP has predominately c -axis oriented YBCO, while obvious randomly-oriented YBCO component shows in the film through path ΔT . The formation of the randomly-oriented YBCO suggests that the precursor is highly supersaturated. That is, the homogeneous nucleation and growth of YBCO could not be suppressed as the path ΔT traverses the low temperature YBCO stability region. On the other hand, with no oxygen present during the heating ramp of the ΔP path, YBCO could not form. The subsequent sudden introduction of oxygen into the reaction region apparently enables the overwhelming nucleation and growth of the c -axis YBCO.

For the ΔP path, different processing temperatures were tested to investigate its effect on epitaxial YBCO formation. Three precursors were heated up in the reducing atmosphere to temperatures, 780, 820, and 850 °C. The oxygen pressure for each was 880 mTorr. The XRD $\theta \sim 2\theta$ scan patterns shown in figure 5.5 indicate that predominately c -axis oriented YBCO formed in all the three films, although the one processed at 780 °C shows a little randomly-oriented component. There are small amounts of unidentified

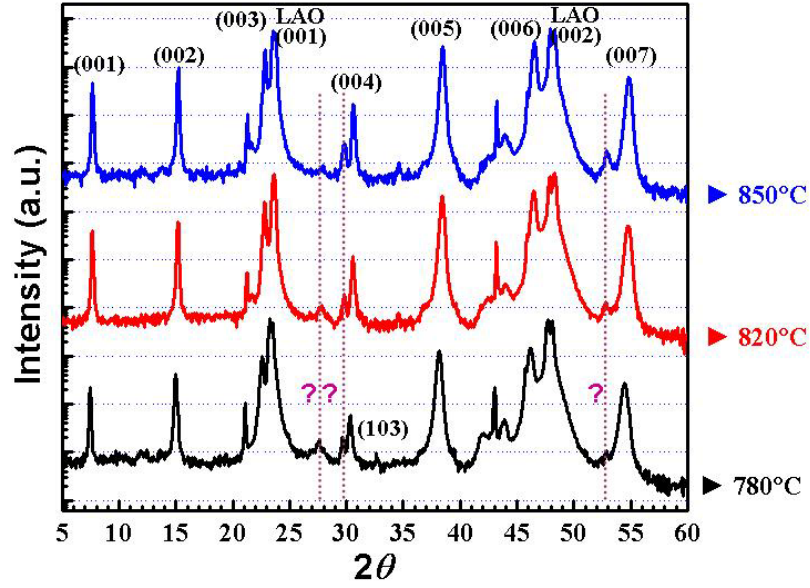


Figure 5.5. XRD $\theta \sim 2\theta$ scan patterns for three films converted at different temperature near the “012” liquid line.

secondary phases in the films indicated by the reflection peaks with question marks. The peak near 28° in the XRD pattern for the 780°C processed film could be the (102) reflection contributed by the randomly-oriented YBCO. This peak was nearly absent when the processing temperature was raised to 850°C . The peaks near 30° and 53° may be attributed to a same phase, as they become stronger at higher processing temperatures. For all the films, RHEED inspections on the film surfaces, which were conducted after the conversion was finished, did not show a good surface crystalline pattern. SEM surface inspections were consistent with the RHEED result, and failed to show the typical YBCO morphology observed on film surfaces. This implies that secondary phases might be rejected to the surface during the YBCO crystallization process.

The superconducting critical temperature T_c 's of the three films were measured by the SQUID magnetometer. The films were zero-field cooled to 5 K. The ramp-up temperature scans were conducted under a magnetic field of 4 Oe. Shown in figure 5.6 is the temperature dependence of the magnetic moments of the previously discussed three films labeled “before.” The magnetic moments were normalized to their 5 K values, respectively. It is obvious that the T_c values were very low for the as-grown films and the

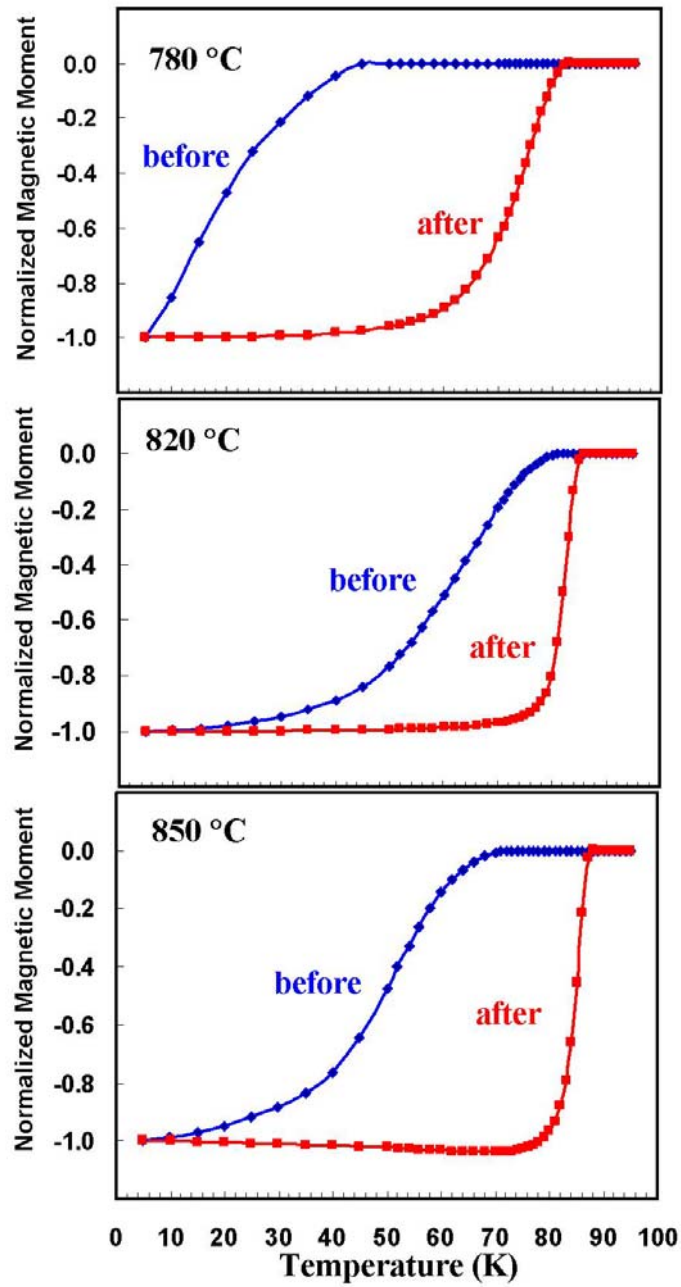


Figure 5.6. Temperature dependence of the normalized magnetic moments of the YBCO films processed at three different temperatures, before and after an 18 hour 450 °C oxygenation in pure flowing oxygen.

superconducting transitions were broad. After an 18 hour oxygenation annealing in pure flowing oxygen at 450 °C, significant increases in T_c were observed, labeled “after.” The onset T_c ’s for the three films processed at 780, 820, and 850 °C are 82, 86, and 88 K, respectively. The annealing effect on T_c implies that the main reason for the low T_c values is the oxygen deficiency, as T_c decreases with the decreasing oxygen content in YBCO (see figure 1.5). Typical *in-situ* PLD YBCO films normally can be fully oxygenated through a 30 min annealing in oxygen at 450 °C. The T_c values of the quasi *ex-situ* converted films are still relatively low even after the long time annealing, indicating that it is difficult to oxygenate these films.

Silver-passivated fluorine-free precursors were processed in the low-pressure system under different conditions to explore the feasibility of a real *ex-situ* conversion. The oxygen pressure used was similar to that for the conversion of the BaF₂-based precursors, typically 100 mTorr. The processing temperature was varied within the vicinity of the “012” liquid line, i.e., from 750 °C up to 840 °C. The temperatures used for the BaF₂-based precursor conversion were actually also within this range. High temperature duration was between 15 min to 60 min, depending on the precursor thickness. When finishing the conversion, oxygen pressure was raised to 1 atmosphere as sample was cooled down to a temperature between 450 ~ 500 °C. The films were oxygenated at this temperature for about 60 min before being cooled to room temperature. EDS inspection of the converted precursor did not show any silver residual on the surface, indicating that the protecting silver layer may have evaporated during the conversion.

The critical temperatures T_c of a series of films deposited on the CeO₂-buffered YSZ substrates are shown in figure 5.7(a). The films were about 0.2 μm thick and processed at different temperatures. It can be seen that the T_c values of the *ex-situ* processed films are also quite low, similar to the films processed in the precursor deposition chamber. A longer time post-conversion oxygenation annealing raises the critical temperature a few degrees, but not significantly. Secondary phases that were detected by XRD and oxygen deficiency are possibly the main reasons for the low T_c ’s as well as the broad transitions. The dependence of the lattice parameter c on processing

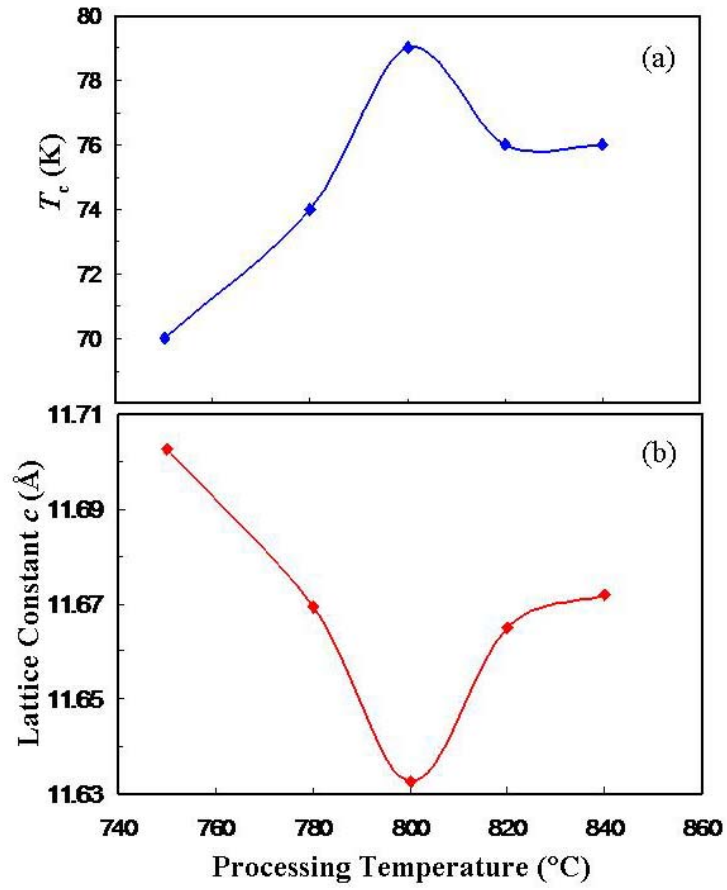


Figure 5.7. Processing temperature dependence of (a) the critical temperature T_c , and (b) the lattice constant c of the YBCO films converted in the low-pressure system.

temperature is shown in figure 5.7(b). The relationship between the critical temperature and the lattice parameter c is consistent with the typical data shown in figure 1.4. The reason for the correlation between the processing temperature and the critical temperature T_c needs to be further investigated.

Oxygen plays an important role in determining YBCO film properties. Oxygen deficiency suppresses the critical temperature T_c , which consequently suppresses the critical current density J_c . The difficulty in oxygenating the fluorine-free YBCO films, converted either quasi *ex-situ* in the deposition chamber or *ex-situ* in the low-pressure system, may result from the low diffusivity of oxygen in the films.

For example, consider one of the quasi *ex-situ* processed films where the as-grown film processed at 850 °C had a T_c just above 60 K, which corresponds to a δ -value of about 0.4 in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ according to figure 1.5. Thus the oxygen content can be calculated as

$$C_0 = \frac{6.6}{V_{\text{cell}}} = \frac{6.6}{1.74 \times 10^{-22}} = 3.79 \times 10^{22} \text{ cm}^{-3} \quad (5.1)$$

where $V_{\text{cell}} = 1.74 \times 10^{-22} \text{ cm}^3$ is the volume of YBCO unit cell. After an 18-hour oxygenation at 450 °C in pure oxygen, T_c was raised to 88 K, which corresponds to a δ -value of about 0.15. That is, after the oxygenation the oxygen concentration is

$$C_1 = \frac{6.85}{V_{\text{cell}}} = \frac{6.85}{1.74 \times 10^{-22}} = 3.93 \times 10^{22} \text{ cm}^{-3} \quad (5.2)$$

The film oxygenation is a doping process similar to a typical “pre-deposition” for semiconductors. In this situation, the solution for the Fick’s law of diffusion

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (5.3)$$

is [104]

$$C(x, t) - C_0 = \frac{C^* - C_0}{2} \left[1 - \text{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad (5.4)$$

where C^* is the oxygen concentration at the surface, which can be approximated to the value when $\delta = 0$; t is the time, which is 18 hours in this case; x is the distance, which can be taken as the film thickness 0.2 μm ; and the error function erf defined is as

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2) dy \quad (5.5)$$

After the oxygenation when $C(x, t) = C_1$ for $x = 2 \times 10^{-5}$ cm and $t = 64800$ seconds, substituting all the numbers into equation (5.4) yields the oxygen diffusivity $D = 1.3 \times 10^{-14}$ cm²/sec. This oxygen diffusivity is close to the value along the c -axis direction determined for a single crystal YBCO [105]. In fact, without other defects serving as the diffusion path, the interstitial oxygen diffusion along the c -axis direction is much more difficult than along the a - b plane. Typical oxygen diffusivity along the a - b plane for a single crystal YBCO is on the order of 10^{-9} cm²/sec [106].

To reveal its microstructural characteristic, the quasi *ex-situ* processed YBCO film was further inspected using both regular TEM and Z-contrast scanning transmission electron microscopy (STEM). To prepare the cross-sectional TEM specimen, the sample was first cut, then ground with diamond papers to a thickness about 20 μm . Further thinning was conducted using an ion miller with the ion energy of 3.5 keV at a glancing angle of 5°. Shown in figure 5.8 is the cross-sectional bright field image and the SAD pattern of a 0.1 μm thick film deposited on LAO substrate. The film was processed in the PLD chamber and had a T_c of 87 K after a long-time oxygenation. It can be seen that the c -axis oriented YBCO film is epitaxially grown on the LAO substrate with the orientation relationship YBCO[001]//LAO[001] and YBCO[010]//LAO[010]. A STEM image of the cross section at higher magnification is shown in figure 5.9. It is apparent that the film is very uniform and homogeneous. Further observation at higher magnification indicates that the YBCO film has near-perfect structure with almost no defects except some stacking faults in the vicinity to the film/substrate interface, as shown in figure 5.10.

The formation of such highly crystalline YBCO film is possibly related to the film growth assisted by a liquid phase formed at the growth front, which is similar to the tri-phase PLD *in-situ* epitaxy of single crystal ReBCO films reported in [107]. A YBCO film growing from the liquid phase is assumed to be in a near-perfect two-dimensional mode. The YBCO film precipitates from a thin layer of liquid phase and Y, Ba, Cu atomic mixture continually dissolved into that liquid phase. This type of growth mode was

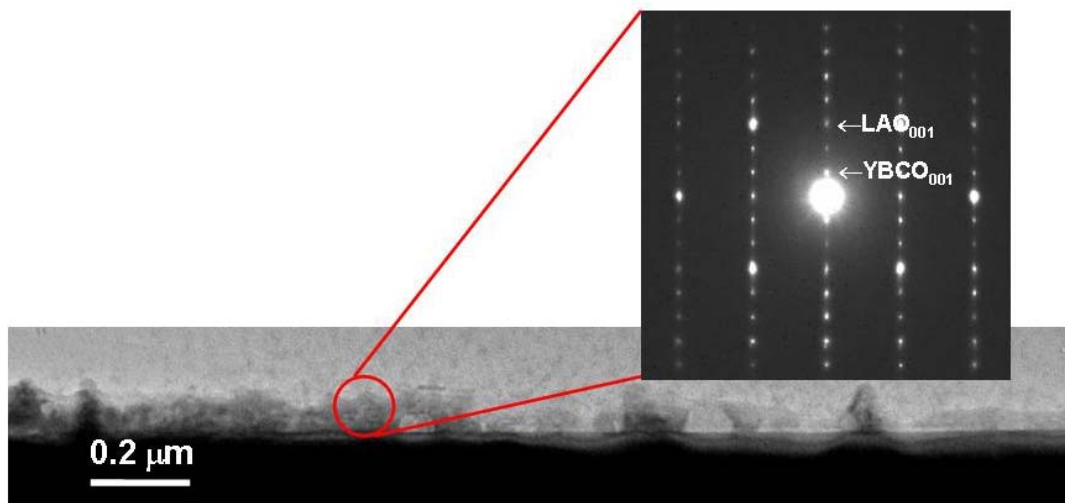


Figure 5.8. Cross-sectional TEM bright field image and selected area diffraction (SAD) pattern of the YBCO film ($\sim 0.1 \mu\text{m}$ thick) processed in the PLD chamber.

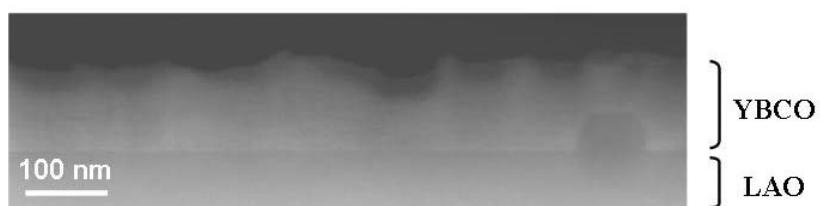


Figure 5.9. Cross-sectional STEM image of the YBCO film ($\sim 0.1 \mu\text{m}$ thick) processed in the PLD chamber.

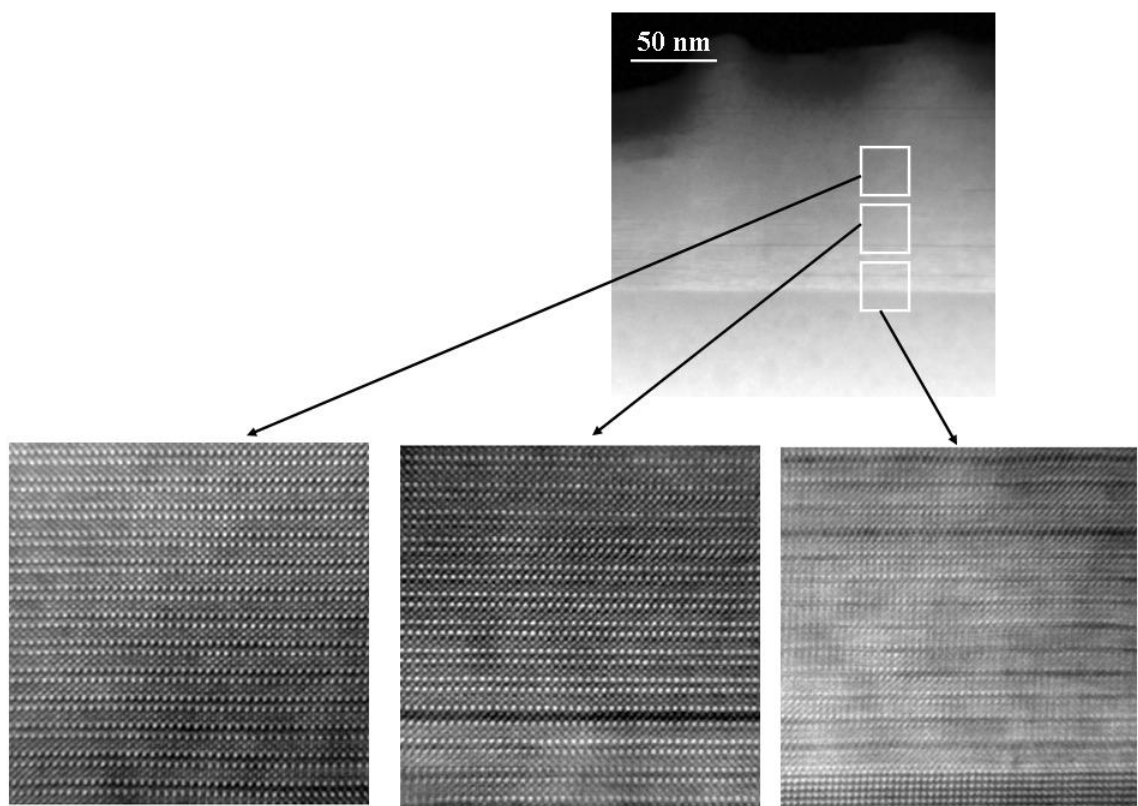


Figure 5.10. High resolution cross-sectional STEM images of the YBCO film ($\sim 0.1 \mu\text{m}$ thick) processed in the PLD chamber.

previously reported for an *in-situ* deposition of YBCO films from *e*-beam co-evaporation of separate metallic sources. In that case, defect-free YBCO was observed in the bottom part of the film, which was related to the layer-by-layer growth mode. In the upper part of the film, island-type faulted layers were grown, and there was an amorphous layer on top of the film. The film with this structure has a unique thickness dependence of J_c , with lower J_c at the lower part and higher J_c at the upper part [108]. For the film processed in the PLD chamber, there are some stack faults of extra Cu layer in the lower part near the substrate. This is possibly due to the small amount of Ba deficiency of the precursor. The upper part of the film is more perfect. As calculated above, the oxygen diffusivity for the films is very low. That is because the oxygen diffusion is in the *c*-direction. Without any threading defects in this direction, it is very difficult to oxygenate the films.

High resolution XRD was used to precisely determine the lattice constant of the YBCO films before and after the oxygenation annealing. Usually, the largest source of error in measuring crystal *d* spacing using XRD is the displacement of the sample from the diffractometer axis. This error is of the form [109]:

$$\frac{\Delta d}{d} = -\frac{D \cos^2 \theta}{R \sin \theta} \quad (5.6)$$

where *D* is the displacement of the sample surface from the center of the diffractometer circle and *R* is the radius of the diffractometer circle. The error approaches zero as $\cos^2 \theta / \sin \theta$ approaches zero or as θ approaches 90°. The precise YBCO film lattice parameter *c* was determined by plotting the *c* values calculated from all the (00*l*) reflections as a function of $\cos^2 \theta / \sin \theta$ and extrapolating to $\cos^2 \theta / \sin \theta = 0$. The values of the lattice constant *c*, before and after the oxygenation, for the films processed at the three different temperatures are shown in figure 5.11. After the long-time oxygenation, lattice parameter *c* values decreased for all the three films, indicating additional oxygen uptake, which results in the T_c improvement.

As previously discussed, both quasi *ex-situ* and *ex-situ* processed films did not show any typical YBCO surface features under SEM and RHEED, which implies that the “impurity” components may be rejected to the film surface. An SEM surface image of a YBCO film converted in the low-pressure system is shown in figure 5.12. The film was

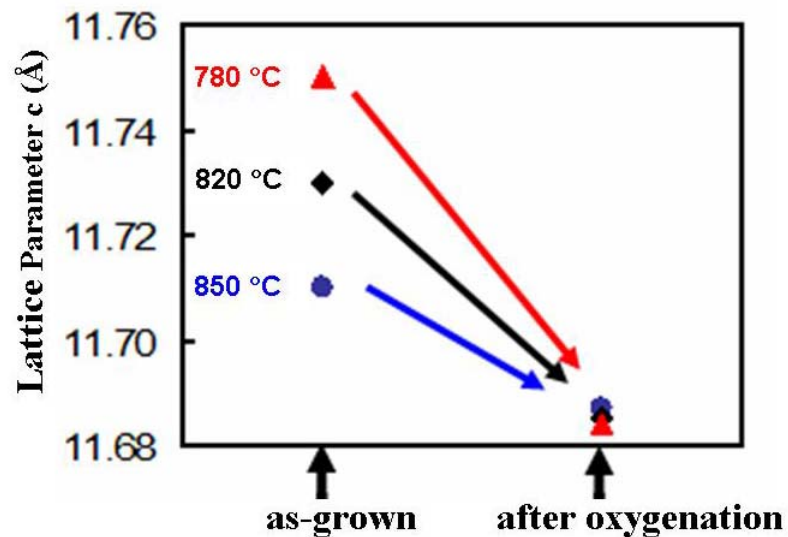


Figure 5.11. Lattice parameter c of the YBCO films processed at three different temperatures, before and after an 18 hour 450 °C oxygenation annealing in pure flowing oxygen.

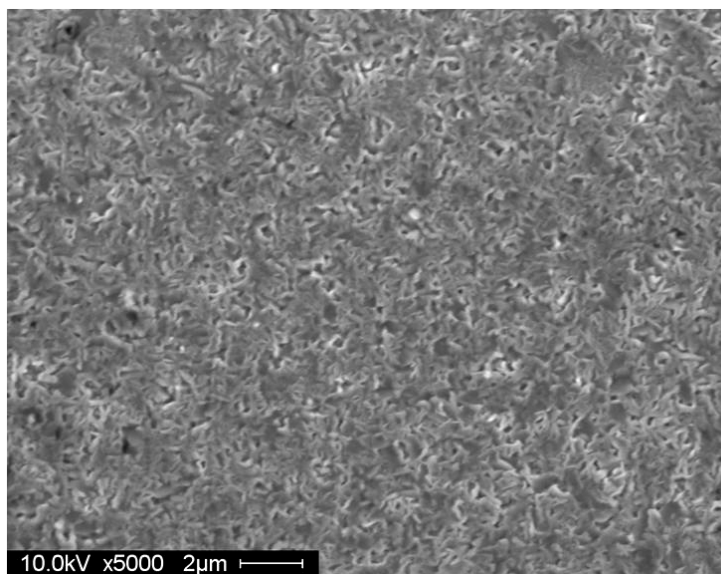


Figure 5.12. SEM surface image of a YBCO film processed in the low-pressure system showing atypical YBCO features.

processed at 800 °C for 20 min. XRD shows that good *c*-oriented YBCO formed in the film and a T_c of 79 K was obtained. However, the surface does not exhibit typical YBCO morphology.

Critical current densities of the YBCO films converted from fluorine-free precursors were measured using the SQUID magnetometer. The results are shown in figure 5.13. With suppressed critical temperatures, the J_c 's of both the quasi *ex-situ* and *ex-situ* processed films are inevitably low. The highest J_c (77 K, zero field) obtained is at a magnitude of 1 MA/cm², which is only one third or one fourth of the typical best J_c values obtained from the BaF₂-based *ex-situ* films or the PLD *in-situ* films. The low critical temperature due to the oxygen deficiency is only one reason that accounts for the low J_c values. The nearly perfect film structure is another important cause, as there are few defects serving as the pinning centers for magnetic flux. Similar to single crystal bulk YBCO, the YBCO film made from the fluorine-free precursor is too perfect to carry any significant electrical current. This is confirmed by the correspondingly lower J_c values of about 10 MA/cm² at zero field, measured at a low temperature such as 5 K. Typical 5 K zero field J_c values for good YBCO films converted from the BaF₂-based precursors are nearly 40 MA/cm².

The liquid-phase assisted film growth is a possible reason the nearly defect-free YBCO formed during the high temperature processing of the fluorine-free precursors. Liquid involved film growth is now recognized to be involved in many processes for fabricating YBCO films, including *in-situ* *e*-beam co-evaporation [99], as well as the BaF₂-based *ex-situ* processes [32, 110 - 112]. However, the microstructure of the BaF₂-based *ex-situ* films, either from *e*-beam co-evaporation or TFA-MOD, is different from the films obtained here from the PLD F-free precursors. Generally, the BaF₂-based *ex-situ* films contain many different types of defects, including pores, twin boundaries, point defects, stacking faults, Y₂O₃ particles, Y₂Cu₂O₅ precipitates as well as atomic-scale disorder [113, 114]. The high J_c values for the BaF₂-based *ex-situ* films are closely related to the multiple defect structures that may originate from the inhomogeneity or non-stoichiometry of the precursors, the conversion reaction involving reacting and resulting gas in/out diffusion, and the different liquid mediated film growth mode.

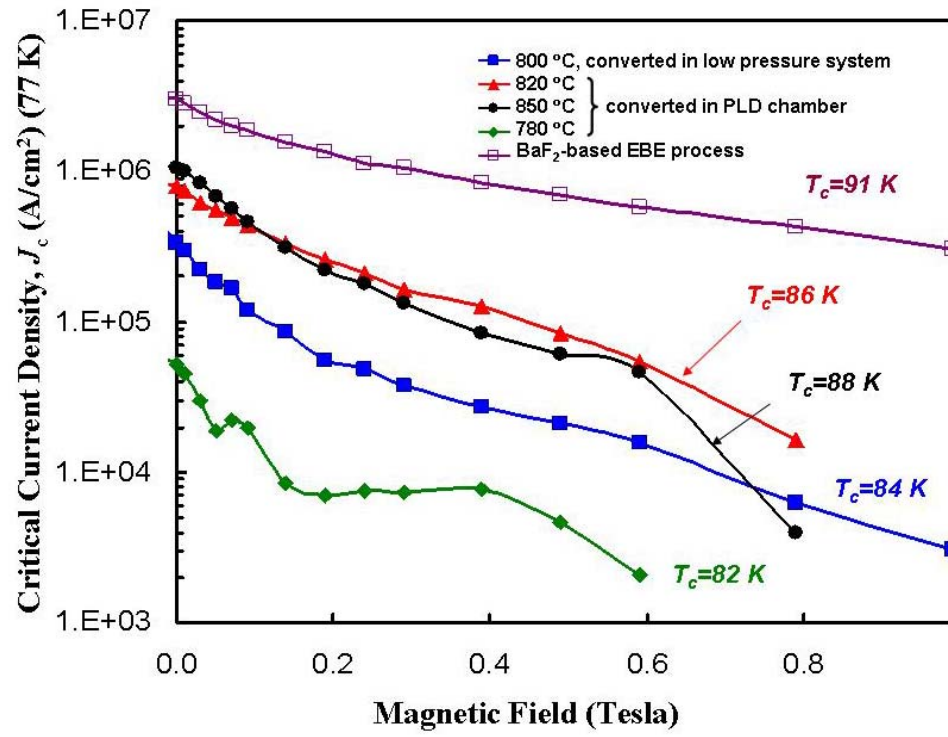


Figure 5.13. Critical current density versus magnetic field relationships for YBCO films quasi *ex-situ* and *ex-situ* converted from the fluorine-free precursors at different temperatures.

The mechanism of the YBCO film formation from the fluorine-free precursors needs to be further studied. It is obvious that in order to raise the critical temperature and increase the critical current density, appropriate defects need to be introduced into the film, in order to enhance the oxygen diffusion and flux pinning. In principle, the defects can be introduced by many different methods, including (1) doping the PLD target with “impurities,” which is similar to what has been exercised in the *in-situ* PLD process [115 - 117], so that nano-size secondary phases such as BaZrO₃ could form in the film; (2) using non-stoichiometric targets to create secondary precipitates such as Y₂O₃; and/or (3) decorating the substrate surface with proper nano-particles to generate structural defects in the film [118, 119].

Chapter 6

CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Conclusions

In this research, BaF₂-based precursors made by electron beam co-evaporation and the trifluoroacetates-involved metal organic deposition were processed using low-pressure conversion for fabricating biaxially textured superconducting YBCO films. The motivation for this research is to enhance the film uniformity and increase the conversion rate. The effects of the processing conditions on YBCO film structure and properties were studied. The conversions of the two types of BaF₂-based precursors were compared in terms of the precursor characteristics and conversion behaviors. Modification of the *e*-beam co-evaporated precursors was made to achieve more efficient conversion. As-deposited and pre-annealed precursors were compared and the YBCO films were studied using various characterization techniques. The conversion of the fluorine-free precursors, made by pulsed laser deposition from a YBCO target, was studied as an alternative fabrication route, which could be much simpler than the BaF₂-based precursor conversion methods. From the research, the main conclusions are as follows:

1. A low-pressure processing system was established and high J_c epitaxial YBCO films were successfully fabricated by the low-pressure conversion of BaF₂-based *e*-beam co-evaporated and TFA-MOD precursors. The total pressure of the gas mixture of oxygen and water vapor during the processing falls within an intermediate gas flow regime. The lowest oxygen pressure that yields high J_c films was about 10 mTorr. Very limited gas consumption and potentially better film uniformity make the low-pressure conversion a promising candidate for large scale, cost-effective batch production of YBCO-based second generation high temperature superconducting wires.

2. E-beam co-evaporated and TFA-MOD precursors with thickness ranging from 0.3 ~ 1.3 μm were processed in the low-pressure system. The substrates included single crystal SrTiO₃ (STO) and LaAlO₃ (LAO), CeO₂-buffered single crystal YSZ, and standard rolling assisted biaxially textured substrate (RABiTS) templates. At a film

thickness of 0.3 ~ 0.5 μm , the highest J_c of over 4 MA/cm^2 was obtained from the conversion of the *e*-beam co-evaporated precursors on both STO and CeO_2 -buffered YSZ substrates. J_c values of over 2 MA/cm^2 were obtained from the conversion of 0.3 μm TFA-MOD precursors on STO.

3. The structure and properties of the YBCO films made by the low-pressure conversion is very sensitive to the processing parameters, including processing temperature, oxygen partial pressure, and water vapor partial pressure, *etc.* The optimal processing window for making high J_c films was small, which complicated the control of the low-pressure conversion. More importantly, due to the formation of the randomly-oriented YBCO under the more aggressive processing condition implemented by higher temperature and higher water partial, the conversion rate for the as-deposited *e*-beam co-evaporated precursors was limited to less than 1 $\text{\AA}/\text{sec}$.

4. A comparison study on the conversion of the *e*-beam co-evaporated and TFA-MOD precursors indicated that the latter requires higher temperature and higher water partial pressure for the conversion. The different conversion behavior results from the distinct precursor characteristics, such as crystallinity, fluorine content and cation chemical states. The TFA-MOD precursor contains more fluorine with the existence of YF_3 in addition to BaF_2 . The extra fluorine plays a role in stabilizing the unreacted part of the precursor during the epitaxial YBCO film formation, and suppressing the formation of randomly-oriented YBCO. Moreover, the nano-crystallites of both BaF_2 and copper oxides formed during the calcination step make the TFA-MOD precursor relatively more difficult to decompose. Conversely, the lower fluorine content and basically amorphous structure of the *e*-beam co-evaporated precursor make it less stable, which is disadvantageous to the suppression of randomly-oriented YBCO formation.

5. Thermodynamics calculations suggest that the copper state in the precursor strongly affects the precursor stability. The existence of metallic pure copper results in a relatively less stable precursor, which is more easily decomposed compared with the precursor containing copper oxides CuO and/or Cu_2O .

6. To achieve more efficient conversion with a faster conversion rate, the *e*-beam co-evaporated precursor was modified by a post-deposition anneal prior to the

conversion reaction. The pre-annealing was conducted for a short time in an ambient with different oxygen content at a temperature between 400 °C and 500 °C. Compared with the as-deposited precursor, the pre-annealed precursor can tolerate much more aggressive processing conditions implemented with higher temperature and higher water partial pressure, yielding a conversion rate as high as 12 Å/sec, with a maintained high critical current density.

7. A comparison study indicated that the as-deposited precursor and the pre-annealed precursor are distinct in terms of their structure and chemistry. The pre-annealed precursor contains nano-crystallites of BaF₂ and copper oxides, while the as-deposited precursor is basically amorphous, and Cu is much less oxidized or close to its metallic state. The conversion behavior difference is partially attributed to the variation in the copper oxidation state.

8. X-ray photoelectron spectroscopy (XPS) is an effective tool for investigating the precursors and their conversion. Careful XPS data analysis using electron binding energy, Auger parameter and Wagner plots can provide important information about the chemical states of the precursor, the partially converted precursor and of the fully converted YBCO film. Characteristics such as fluorine or oxygen concentration, and cation chemical state can be revealed by XPS inspection, regardless of whether and how much the precursor and/or the film are crystallized. XPS depth profiling can help understand the conversion reaction mechanism and the process of YBCO formation.

9. The XPS depth profiling study on a partially converted, pre-annealed and subsequently quenched precursor revealed that copper is in the chemical state of Cu¹⁺ as in Cu₂O, in the unreacted upper part of the precursor. In this region, BaF₂ was not decomposed, indicated by the constant barium Auger parameter, AP(Ba), and the constant F/Ba ratio. The delayed decomposition of BaF₂, which is important to the suppression of the randomly-oriented YBCO, may be attributed to crystallization of BaF₂ during the pre-annealing, and to the released HF from the reacted lower part of the precursor. This observation suggests that it could be advantageous for a precursor,

especially a thick precursor, to have a through-thickness gradient in fluorine concentration, or even a gradient in crystallinity.

10. Epitaxial YBCO films can be made through the conversion of the fluorine-free precursors deposited by pulsed laser deposition from a ceramic YBCO target. The conversion can be either quasi *ex-situ* conducted in the deposition chamber directly following the deposition or *ex-situ* in the low-pressure system after the precursor surface is appropriately passivated. A YBCO film with T_c of 88 K and J_c at the magnitude of 1 MA/cm² has been obtained from the conversion of the F-free precursor followed by a long-time, lower-temperature oxygenation.

11. The relatively lower T_c and J_c are attributed to the nearly perfect *c*-axis oriented YBCO film structure, which lacks effective oxygen diffusion path and magnetic flux pinning centers. To improve the T_c and J_c of the YBCO films, appropriate defects need to be introduced into the films, which can be conducted through various techniques. The F-free precursor conversion has the potential to become a much simpler alternative *ex-situ* approach for the fabrication of biaxially textured YBCO films. The conversion mechanism and formation of epitaxial YBCO film in the fluorine-free precursor need to be further investigated.

6.2 Future Directions

1. For precursors with thickness around 1 μm , it has been demonstrated that high J_c YBCO films can be fabricated under the low-pressure conditions. A subsequent investigation on the conversion of thicker precursors ($> 2 \mu\text{m}$) is the first priority for follow-on research. While the preparation of thicker TFA-MOD precursors is a complicated project, thicker *e*-beam co-evaporated precursors may be more readily achievable. However, it can be expected that the deposition as well as the conversion of thicker *e*-beam co-evaporated precursors will be a challenge.

2. The mechanism of YBCO nucleation and growth needs to be further studied to pinpoint the determining precursor characteristics that control YBCO film orientation. Detailed microscopy inspection complemented with XPS, Raman spectroscopy and other characterization techniques on samples at different stages of the

processing would be helpful in the campaign to suppress randomly-oriented YBCO and promote epitaxy.

3. As has been discussed, modification of *e*-beam co-evaporated precursors can be implemented either during or after deposition. The precursor needs to be modified in order to: (a) facilitate fast conversion without disturbing the epitaxial film growth mode; and (b) facilitate thick precursor conversion without changing the epitaxial film growth mode throughout the entire conversion. Therefore, the modification should focus on how to enhance the epitaxial heterogeneous nucleation at the precursor/substrate interface and how to stabilize the upper layer and suppress the homogeneous randomly-oriented nucleation. The cation oxidation state can be changed by controlling oxygen impingement on the substrate during precursor deposition. Different types of source materials, such as YF_3 instead of Y, can be tested. More importantly, for processing thicker precursors ($2 \sim 4 \mu\text{m}$), it may require through-thickness gradients in precursor structure and/or chemistry to assure the epitaxial conversion. A post deposition fluorination treatment on thicker precursor may be worthwhile.

4. The precursor/substrate interface needs further investigation to understand the effects of buffer layer surface on epitaxy. So far, CeO_2 has been the only buffer material shown to be widely compatible with the BaF_2 -based *ex-situ* processes. However, it is still not clear what characteristics are most important to qualify a CeO_2 surface as the optimal for promoting the epitaxial YBCO film growth.

5. For fluorine-free precursor conversion, further understanding of the YBCO film nucleation and growth mechanism would be helpful in optimizing the process and improving the film properties. Since the lower T_c and J_c are apparently due to a nearly perfect crystalline structure, and the consequent low oxygen content and low defect density, different techniques can be tried to introduce appropriate defects into the YBCO film.

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APPENDIX

LIST OF PUBLICATIONS AND PRESENTATIONS

Publications

1. **Y. Zhang**, R. Feenstra, J. R. Thompson, A. A. Gapud, T. Aytug, and D. K. Christen, "High Critical Current Density $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Thin Film Growth by Post-Deposition Processing at Low Pressures." Mater. Res. Soc. Symp. Proc. MRS. **EXS-3**, EE5.11.1 (2004).
2. **Y. Zhang**, R. Feenstra, J. R. Thompson, A. A. Gapud, T. Aytug, P. M. Martin, and D. K. Christen, "High Critical Current Density $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Thin Films Fabricated by *Ex-situ* Processing at Low Pressures." Supercon. Sci. Tech. **17**, 1154 (2004).
3. **Y. Zhang**, M. P. Paranthaman, R. Feenstra, T. Aytug, and D. K. Christen, "Comparison of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Precursors made Using TFA-MOD and BaF_2 *Ex-situ* Processed and their Post-deposition Processing Under Low-Pressure Conditions." IEEE. Trans. Appl. Supercon. **15**, 2659 (2005).
4. **Y. Zhang**, R. Feenstra, and D. K. Christen, "X-ray Photoelectron Spectroscopy Study on E-beam Co-evaporated YBCO precursors and their Post-deposition Conversion." Mater. Res. Soc. Symp. Proc. MRS. **858E**, C7.9.1 (2005).
5. K. Kim, **Y. Zhang**, R. Feenstra, D. K. Christen, H. M. Christen, S. Cook, F. A. List, J. Tao, S. J. Pennycook, and Y. Zuev, " $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Formation by Processing of Laser-Ablated, Fluorine-Free Precursor Films." IEEE. Trans. Appl. Supercon. Submitted.
6. R. Feenstra, F. A. List, **Y. Zhang**, D. K. Christen, V. A. Maroni, D. J. Miller, and D. M. Feldmann, "Characterization of Phase Evolution in YBCO Coated Conductors Produced by the *Ex-situ* BaF_2 Process." IEEE. Trans. Appl. Supercon. Submitted.
7. **Y. Zhang**, R. Feenstra, and D. K. Christen, "Effects of Pre-annealing on the Conversion of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Precursor Films Made by E-beam Co-evaporation." in preparation.

8. M. V. Rane, H. Bakhru, R. Moore, E. Stinzianni, K. Dunn, P. Haldar, R. Feenstra, **Y. Zhang**, and D. K. Christen, "Investigation of the Role of Intermediate Heat Treatment in Obtaining High J_c Films in BaF_2 *Ex-situ* Films." in preparation.

Presentations

1. **Y. Zhang**, R. Feenstra, J. R. Thompson, A. A. Gapud, T. Aytug, and D. K. Christen, "High Critical Current Density $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Thin Film Growth by Post-Deposition Processing at Low Pressures." Poster, MRS Fall Meeting 2003, Boston, MA.
2. **Y. Zhang**, M. P. Paranthaman, R. Feenstra, T. Aytug, and D. K. Christen, "Comparison of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Precursors made Using TFA-MOD and BaF_2 *Ex-situ* Processed and their Post-deposition Processing Under Low-Pressure Conditions." Poster, ASC 2004 Meeting, Jacksonville, FL.
3. **Y. Zhang**, R. Feenstra, and D. K. Christen, "X-ray Photoelectron Spectroscopy Study on E-beam Co-evaporated YBCO precursors and their Post-deposition Conversion." Talk, MRS Spring Meeting 2005, San Francisco, CA.
4. **Y. Zhang**, R. Feenstra, and D. K. Christen, "Effects of Pre-annealing on the Conversion of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Precursor Films Made by E-beam Co-evaporation." Poster, MRS Spring Meeting 2006, San Francisco, CA.
5. K. Kim, **Y. Zhang**, R. Feenstra, C. Cantoni, D. K. Christen, and H. Christen, " $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Formation by In Situ Processing of Laser-Ablated, Fluorine-Free Precursor Films." Poster, MRS Spring Meeting 2006, San Francisco, CA.
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7. K. Kim, **Y. Zhang**, R. Feenstra, D. K. Christen, H. M. Christen, S. Cook, F. A. List, J. Tao, S. J. Pennycook, and Y. Zuev, " $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Formation by *In-Situ* Processing of Laser-Ablated, Fluorine-Free Precursor Films." Poster, ASC Meeting 2006, Seattle, WA.

8. R. Feenstra, F. A. List, **Y. Zhang**, D. K. Christen, V. A. Maroni, D. J. Miller, and D. M. Feldmann, "Characterization of Phase Evolution in YBCO Coated Conductors Produced by the *Ex-situ* BaF₂ Process." Poster, ASC Meeting 2006, Seattle, WA.
9. R. Feenstra, A. A. Gapud, E. D. Specht , **Y. Zhang**, D. K. Christen, T. G. Holesinger, D. M. Feldmann, X. Song, D. C. Larbalestier, A. Palau, T. Puig, X. Obradors, " Improving the Thickness Dependence of J_c in BaF₂ *ex-situ* YBCO Coated Conductors." Talk, CCA Meeting 2005, Santa Fe, TX.
10. R. Feenstra, A. A. Gapud, E. D. Specht , **Y. Zhang**, D. K. Christen, T. G. Holesinger, D. M. Feldmann, X. Song, D. C. Larbalestier, A. Palau, T. Puig, X. Obradors, " Growth and Structure Effects in *ex-situ* YBCO Films." Talk, the 12th US-Japan Workshop on Coated Conductors 2005, Delavan, WI.
11. R. Feenstra, **Y. Zhang**, D. K. Christen, V. A. Maroni, D. J. Miller, D. M. Feldmann, and T. G. Holesinger, " Study of Phase Evolution in Thick YBCO Coated Conductors by the BaF₂ *ex-situ* Process." Talk, MS&T Meeting 2006, Cincinnati, OH.

VITA

Yifei Zhang was born in Hefei, China. He graduated from the First High School of Hefei at Hefei and entered Zhejiang University at Hangzhou, China in 1980. In 1984 he graduated with a B. En. Degree in the major of Metal Materials Science & Engineering. The thesis work was on the hydrogen storage alloys. Later that same year, he enrolled into the graduate program at Huazhong University of Science and Technology at Wuhan, China, under Professor Cui Kun. Three years later, he graduated with a M. En. Degree in Metal Materials & Heat Treatment. The thesis was titled “Strengthening Mechanism of Hot Die Steels.”

After the graduation in 1987, Yifei Zhang joined the Mechanical Engineering Department in Nanjing University of Science and Technology at Nanjing, China. The course he taught to the undergraduate students was “Mechanical Properties of Metal Materials.” The research he participated in included “Surface Hardening of Railway Steels” and “Refinement and Strengthening of Aluminum Alloys.” During the time in Nanjing, he also worked in a consultant committee conducting planning investigation on advanced materials R & D for the local government of Jiangsu Province.

In 1991, Yifei Zhang joined the Mechanical and Electrical Engineering Department in Hefei College of Economics and Technology at Hefei, China. The courses he taught to the undergraduate students included “Mechanics of Materials”, “Engineering Materials”, and “Classical Mechanics.” The research was mainly on tobacco processing and cigarette manufacturing system. In 1998, he was awarded as the “National Advanced Teacher” for his accomplishment in teaching and research. In 1999, he went to Tsinghua University, Beijing for further training in the field of electronic engineering. Late in 1999, he joined the University of Science and Technology of China at Hefei, China.

In July 2000, Yifei Zhang started working as a visiting scholar in the Physics Department of Boston College, Boston, MA. His research focused on the synthesis and characterization of high temperature superconducting films that is closely relevant to the development of YBCO-based coated conductors. The work was actually conducted at Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee, in Dr. David K. Christen’s research group. In May 2002, he transferred to Oak Ridge Associated

University, again as a guest researcher. He continued his research in the Superconductivity Program at ORNL.

In January 2003, Yifei Zhang enrolled into the graduate program in the Department of Materials Science and Engineering of the University of Tennessee at Knoxville, Tennessee, under Professor Philip D. Rack. He is basically continuing his research on YBCO films at ORNL and in pursuit of a PhD in Materials Science and Engineering.

Yifei Zhang is a member of the Chinese Society for Metals (CSM), the Materials Research Society (MRS), the Minerals, Metals & Materials Society (TMS), the American Ceramic Society (ACerS), the American Society for Materials (ASM), and the Association for Iron & Steel Technology (AIST).