

Conversion Kinetics of Oxyfluoride-Derived YBCO Films

by

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Master of Science in
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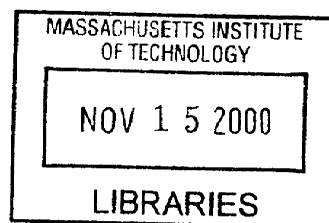
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ABSTRACT

YBa₂Cu₃O_{7-x} (YBCO) thin films were prepared on lanthanum aluminate (LAO) single crystals and buffered (5000 Y₂O₃, 500 CeO₂) Ni-single crystal substrates by metal organic deposition (MOD) process. Glassy films were converted to epitaxial YBCO films, by heating in wet atmosphere of N₂/O₂ mixture. A novel technique was used to determine the rate of conversion of films from glassy state to crystalline YBCO films. In this approach, the concentration of residual fluoride in the partially converted films was examined using fluoride ion selective electrode. Results obtained by this method were compared to results obtained by such methods as X-ray analysis and in-situ resistivity measurements. Analysis of data obtained by different methods showed that fluoride concentration measurement method is a fast and very accurate method.

The influence of different factors on conversion rate was investigated by this approach, including high and low vapor pressure of water in the processing atmosphere, temperature and influence of substrate material on conversion.

A simple model was proposed to describe the growth of crystalline YBCO film for diffusion controlled and reaction controlled growth kinetics. Results obtained by in-situ resistivity measurements were compared to results predicted by the model. The obtained data fits the model that describes interface reaction limited growth kinetics.

Thesis Supervisor: Michael J. Cima

Title: Sumitomo Electric Industries Professor of Engineering

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Chapter 1

Introduction

The discovery of superconducting cuprates in late 1980's resulted in a wide spread of research in this area. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) is one of the mostly investigated high temperature superconducting materials, because it is relatively easy to prepare as a pure phase material. It was one of the first superconductors, that had a superconducting state transition temperature above 77 K. ($T_c=93$, for $x=0.07$) For $x < 0.6$ YBCO crystallizes with orthorhombic structure as shown on figure 1.1. For $x=0.6$, YBCO has non-superconducting tetragonal structure. YBCO can be used in different applications, such as superconducting wires, transformers, electric motors and many other. These applications require high critical current densities.

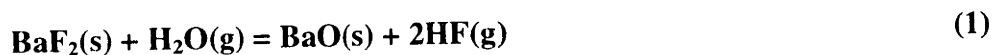
Thin films of YBCO can support very high current density (J_c) (1). Recent studies of YBCO showed results of J_c greater than 4.0 MA/cm^2 at 77 K. These results have increased the interest in the research of different techniques of deposition of thin films of high temperature superconductors (HTSC).

There are many different methods of thin film deposition. Most of the approaches can be separated into *in situ* and *ex situ* methods. Deposition and crystallization of the film occurs simultaneously for *in situ* methods at a heated substrate. Crystallization in *ex situ* methods occurs during separate heat treatment.

The *ex situ* method that was used in this study is called metal organic deposition (MOD). This method was first developed by Gupta *et al.* (3,4). Metal trifluoroacetate (TFA) precursors are used for preparation of superconducting oxide films. The TFA precursor is spin coated to a lattice-matched substrate material. TFA salts decompose to a barium, yttrium, and copper oxyfluoride material during low temperature heat treatment at temperatures below 400 °C.

This method has many advantages. It is easy to control stoichiometry of deposited films, it does not require vacuum, and it is relatively easy to deposit films on large areas which is particularly important for large scale production. YBCO films prepared by MOD method have excellent electrical properties (1). One of the disadvantages of this approach is high porosity of films that is associated with high relative volume change (~20%) during high temperature decomposition.

TFA precursors solve problem of formation of BaCO₃ during decomposition, because BaF₂ is a more stable compound (14). BaF₂ is removed at high temperatures by the introduction of water vapor. Decomposition according to the reaction



Decomposition of BaF₂ occurs during high temperature heat treatment at the temperature range of 700-800 °C. Crystalline YBCO that formed grows epitaxially on the substrate at this temperature.

Epitaxial growth of YBCO can result in two different types of crystallographic orientation: a-axis and c-axis grains orientation. It was demonstrated in many studies that c-axis orientation is the preferred one (1,5,9,14). A-axis grains form high angle grain boundaries which exhibit weak-linked electrical behavior. Increasing number of a-axis grains, substantially decrease the J_c of a film. Films with c-axis grains have very good electrical properties.

There are several parameters that influence structure of thin films. One of the most important parameters is PO_2 . Feenstra *et. al.* in their work (5) showed that films grown at the conditions close to the stability line of YBCO (below this line YBCO decomposes into Y_2BaCuO_5 , $BaCu_2O_2$, and $YBa_3Cu_2O_{6+y}$) result in c-axis films (see Figure 1.2). These are conditions with low PO_2 and relatively low temperatures. Processing of thin films with thickness < 500 nm using these conditions will result in films of c-axis orientation and high J_c .

It was shown in earlier studies that J_c decreases rapidly with increasing thickness of the film. One of the most important reasons for low electrical properties of thick films is the high content of a-axis grains.

Only thick films can be used in electrical applications due to economic reasons. It is important to be able to grow films of thickness larger than 1 micron. Water vapor partial pressure during the high temperature decomposition (1) was demonstrated to be an important factor, in controlling the content of a-axis grains in thick films of thickness >1 micron. This study showed that using different partial pressures of water vapor could help solve the problem of contamination of thick films by a-axis grains. It was also shown that partial pressure significantly influences growth rate of YBCO films, and a theory

consistent with observation was proposed. Unfortunately, no results were presented, that quantitatively show the growth rate dependence on water vapor partial pressure in the processing atmosphere. In this work, the influence of partial pressure of water in the processing atmosphere on the growth rate of TFA-derived YBCO films was made.

YBCO films deposited on metal substrates are now being extensively studied. Ni is one of the mostly investigated metal substrates for deposition of superconducting films. Deposition of YBCO directly on Ni is impossible due to reaction between film and substrate and formation of a scale of NiO due to diffusion of oxygen through the film. Contamination of YBCO by Ni ions is also not favorable, due to decrease in T_c of YBCO (6). Deposition of epitaxial buffer layers is a common solution of these problems (7). Y_2O_3 and CeO_2 are commonly used materials for buffer layers, that is why they were chosen as a buffer materials in our study.

The substrate material has a significant impact on final structure orientation, and growth kinetics of YBCO films. Films grown on $SrTiO_3$, for example, have smaller density of a-axis grains than films on $LaAlO_3$ (9). Nieh *et. al.* observed similar effect of substrate on the density of a-axis grains on the films prepared by “barium fluoride” process on $SrTiO_3$, $LaAlO_3$, and $LaGaO_3$. It was also observed that changing the orientation of the substrate also changes its growth kinetics. A-axis grains have higher growth rate (10), because unit cell builds faster along ac- or cb-planes than along ab-plane.

We investigated, as a part of our study, the influence of substrate material on kinetics of growth of YBCO thin films deposited on single crystal $LaAlO_3$ and buffered Ni substrates.

P. McIntyre in his studies investigated the nucleation and growth kinetics of TFA-derived YBCO thin films (9,17). His work was based on TEM and X-ray analysis observations of partially converted quenched films. A mechanism based on partial melting of the intermediate material was described, and experimental results that indicate a liquid phase that is stable under the conditions used in the high temperature heat treatment were presented. It was shown by TEM observations that YBCO crystals nucleate at the substrate surface and then coalesce into a continuous film, that covers the substrate surface completely. Growth of the c-axis oriented YBCO in the upward direction is a much slower process than lateral growth along the substrate/film interface. Investigation of the growth kinetics at this stage were conducted using X-ray analysis of partially converted films, quenched after different stages of completeness. Volume fraction data were determined by comparing the integrated intensities of {102} reflections of c-axis oriented films to the intensity of fully converted film at the same processing conditions. Two temperatures of growth were investigated and activation energy was calculated based on growth rates calculated from X-ray analysis results. The technique used in these studies allowed investigation of samples converted to less than 60%. This restriction was due to reaction of YBCO with humid furnace atmosphere. Activation energy calculated in the study as it was pointed out by the author was not very accurate, due to the fact that only two annealing temperatures investigated and was only a rough estimate. These facts show that a more intensive study was needed for better understanding of the conversion kinetics of TFA-derived YBCO films and influence of different factors on growth process.

Different experimental techniques such as TEM observations, X-ray analysis, and resistivity measurements had been used for investigating of growth kinetics of thin films (1,9,13). In our study a novel technique was used for investigation of the TFA-derived YBCO films growth kinetics. This technique is based on measurements of concentration of residual BaF_2 in processed films by fluoride ion selective electrode. Partially converted films were dissolved in an acidic solution of known volume. Concentration of fluoride in the solution was measured using Orion® selective electrode. Given the fluorine content and the volume of the films, the fluorine concentration can be determined. This technique has significant advantages over standard methods. It does not require difficult procedure for preparation of samples for investigation. It provides a fast analysis, and has a high accuracy. Results that were obtained by using this new method were also compared to results that were received by using X-ray analysis and *in situ* resistivity measurements.

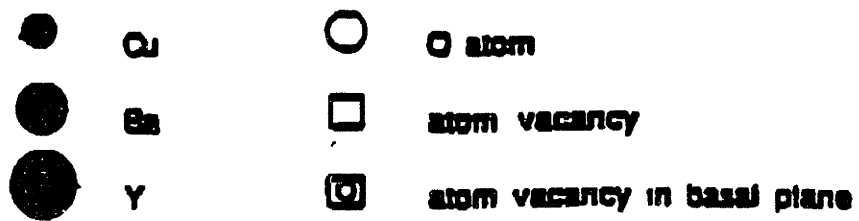
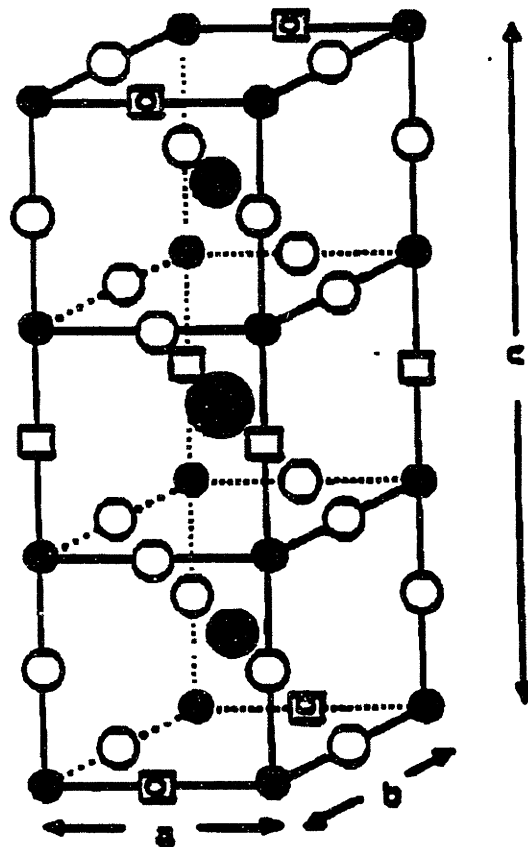


Figure 1.1. Crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ from (18)

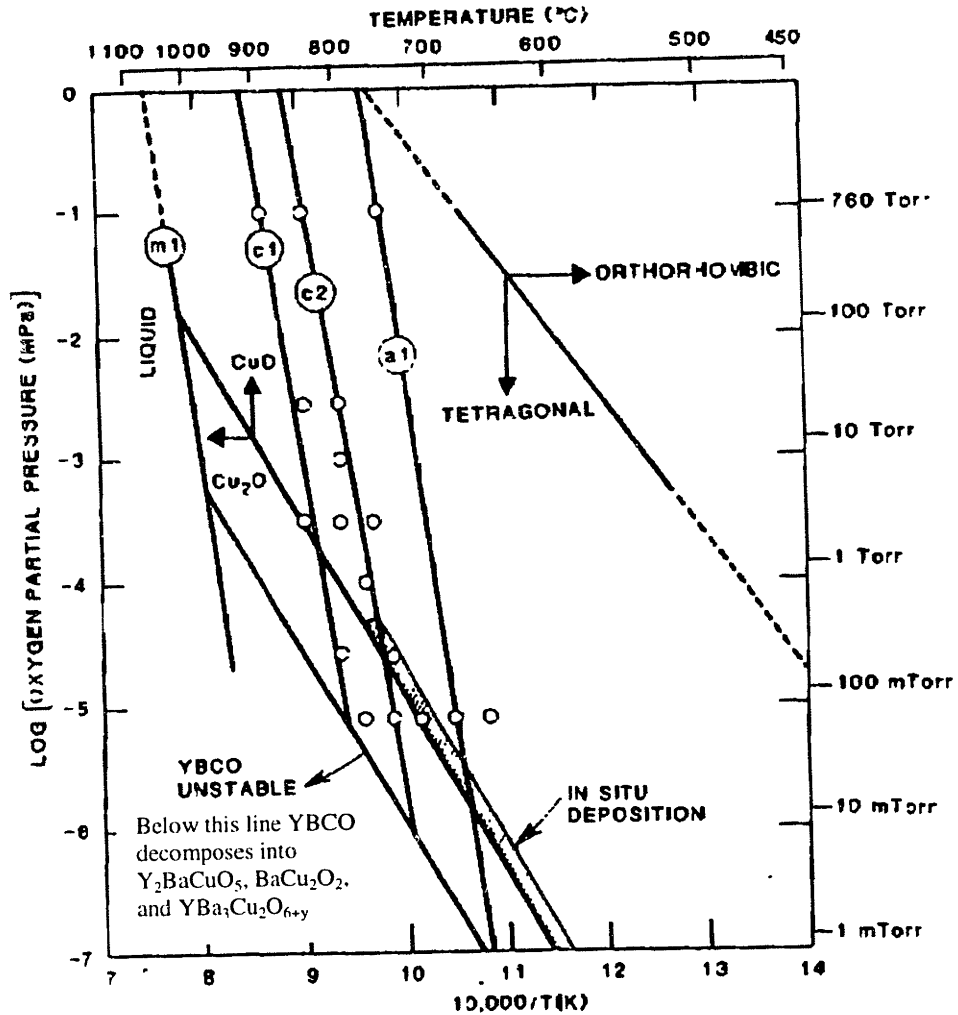


Figure 1.2. Oxygen partial pressure vs temperature diagram showing annealing conditions explored in (5) in relation to YBCO stability line, melting line m1, tetragonal to orthorhombic transition line and CuO-Cu₂O-O₂ equilibrium/Hammond-Bormann line, indicating conditions for optimal *in situ* film growth. Annealing conditions yielding films of comparable epitaxial and structural properties are connected by straight lines denoted by c1, c2, and a1, respectively. Predominantly c-oriented films were obtained between c1 and c2.

Chapter 2

Experimental Procedure

Processing

A metal trifluoroacetate precursor for spin coating was prepared by reacting yttrium, barium, and copper acetates and trifluoroacetic acid in water. Acetates were added in stoichiometric cation ratio of 1:2:3 respectively. Product was then dried to a semisolid state, and then redissolved in methanol. The methanol solution was spin-coated on to a lattice-matched substrate using photoresist spin coater. Spin coating was done in a particulate containment hood with the humidity substantially lower than 50 % RH. Circular wafers of LAO were received from commercial vendor (8). The wafers were diced into smaller (6.0 mm X 6.0 mm) square pieces using diamond-impregnated wire blade. We used square (001)-oriented LaAlO_3 (LAO) single crystal substrates and (100) oriented circular nickel single crystal substrates of approximately 6-mm diameter. Substrates were cleaned using ultrasonic bath in three successive solutions of chloroform, acetone and methanol. Substrates were investigated after cleaning under optical microscope at 40-X and wiped with methyl alcohol. Spin coating was performed at approximately 4000 rpm and an acceleration time of 0.4 s. The temperature in the hood during spin coating was in the range of 23-31 °C. Samples were then placed in processing zone of the furnace. Epitaxial buffer layer was deposited prior to spin coating procedure on nickel substrates. The buffer layer is necessary to prevent reaction between substrate material and YBCO coating during high temperature conversion. The buffer

was deposited in e-beam chamber, and consisted of two layers - 5000 Å of Y_2O_3 and 500 Å CeO_2 .

All heat treatments described in this work were conducted in quartz tubes heated in CM 2200 horizontal furnaces. Samples were introduced into the furnace on a quartz plate. The temperature of samples was measured using K-type thermocouple sealed in a high-purity alumina tube. The tip of the alumina tube was placed a few millimeters behind samples (downstream).

A horizontal split type furnace was used for heat treatments of samples. Flow rate of oxygen in the furnace was controlled by manual flow meters and regulated gas pressure. The low-temperature heat treatment consisted of the following segments as. Sample temperature was increased to 195 °C in 1 hr., then increased to 220 °C at a ramp rate of 0.05°C/min., and finally heated to approximately 400 °C in 40 min., after this heating segment active heating was stopped. The furnace was then cooled in stagnant, humid oxygen. The temperature profile for this heat treatment is shown on Figure 2.1. Gas was switched from dry to moist during the initial heating segment. Moist atmosphere during initial heating segment was used to suppress volatilization of copper. Switching from dry to moist oxygen was made at approximately 13 min. of the first segment. Water vapor was introduced into the furnace by bubbling a gas through water. The water reservoir was kept at room temperature. Gas was saturated to approximately 95-100 % RH. A volumetric flow rate of 10 +/- 1 scfh was used for the dry O_2 , and volumetric flow rate of 10 +/- 1 scfh was used for the moist O_2 .

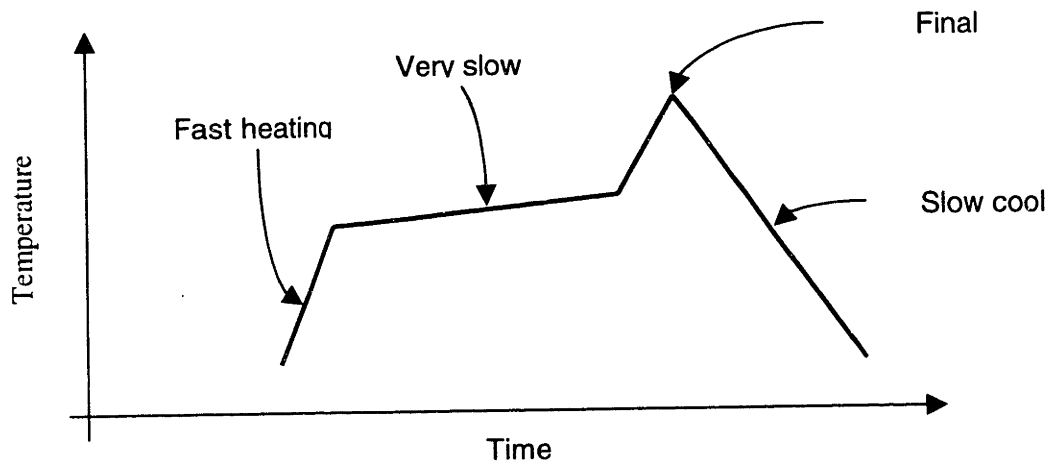


Figure 2.1. Heating profile for low temperature heat treatment.

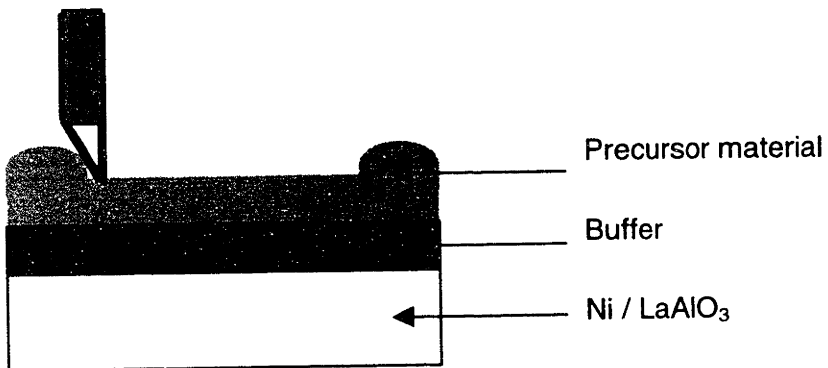


Figure 2.2. Thick edges of precursor material was mechanically removed prior high temperature anneal.

All samples were prepared by mechanically removing edges of films in order to reduce variations of thickness of films in the center and the edges. Variations in thickness of films were due to spin coating (see Figure 2.2).

A special set up and procedure were developed for samples used in the kinetic studies (see Figure.2.3). The furnace was preheated to the temperature of the high temperature anneal. Humidified gas was passed through the furnace at rate of 3 l/min. Moisture was introduced to the furnace atmosphere only approximately 10 minutes prior introduction of a sample. The samples at the beginning of the heat treatment were placed in the cold part of the furnace on quartz plate attached to the K-type thermocouple. This thermocouple was used for monitoring temperature of samples. Samples were quickly introduced in to the hot zone after the heat treatment temperature was reached and stabilized in the hot zone of the furnace. The samples reached temperature within approximately 5 minutes. Specimens were held for varying annealing times and then quenched by pushing samples from hot zone to the cold zone. The moisture was turned off prior to the quenching of samples and dry gas was flowing though the furnace. Samples were moved to the upstream end of the furnace for quenching. Moisture levels of 0.6-1.2 % RH (~21 °C dew point), were used for low moisture conditions and 95-100 % RH for high moisture conditions. Oxygen level in the furnace was prepared by using electronic mass flow controllers and mixing ultrahigh-purity nitrogen with oxygen/nitrogen mixture of known concentration. Insertion of samples to the hot zone and quenching to the cold zone was made without breaking sealing. This prevented back-mixing of furnace atmosphere with laboratory atmosphere.

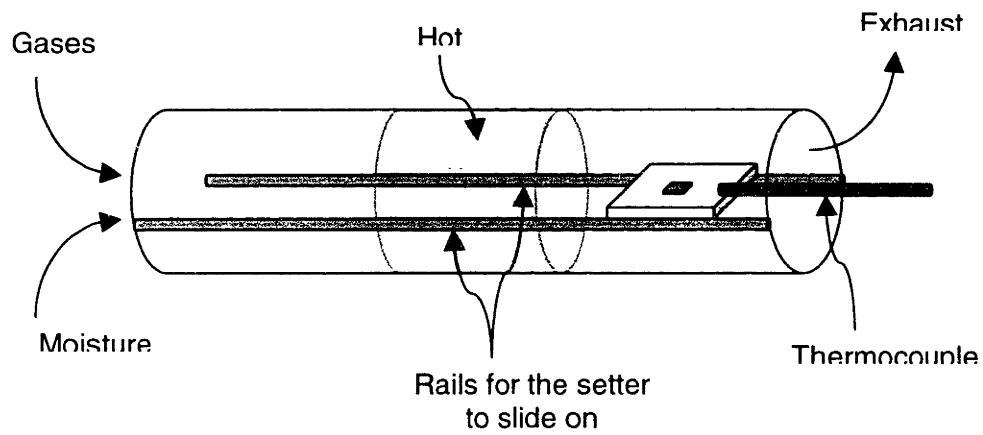


Figure 2.3. Quenching set-up.

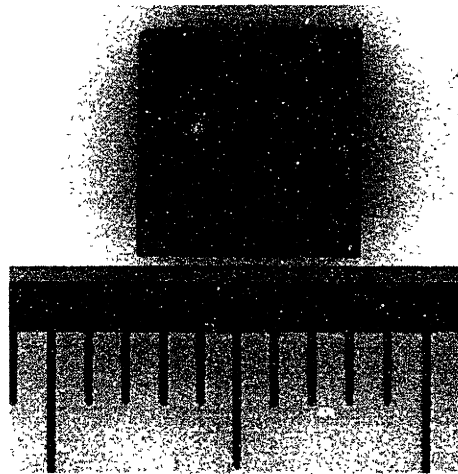


Figure 2.4. Picture of a sample made with a scanner. Resolution of 600 dpi..Scale bar was placed for calibration of surface measurements.

Fluoride concentration measurements

The fluoride ion concentrations of quenched samples were determined using an Orion® 96/09-combination fluoride selective electrode as a function of time that samples spent at temperature. Pictures of all samples were taken (see Figure 2.4), using scanner with resolution of 600 dpi. Surface area of the films was digitally measured using ImageTool™ software. Samples were dissolved in 15 ml of nitric acid solution of 3.25 pH for 48 hours. Solutions were buffered to 5.30 pH for measurement with low level Tisab after complete dissolution of films. All measurements were made according with procedure described in the manual of the electrode. Separate calibration curve was made using solutions of known concentrations (see Figure 2.5) for each series of measurements. The moles of fluorine per cm² were calculated using fluoride electrode measurements and the volume of the solution in which films were dissolved.

Data that we obtained by using fluoride measurements was also compared to X-ray analysis data. X-ray data was collected using Rigaku RU-200 rotating anode X-ray source diffractometer. We used accelerating voltage of 50 kV and emission current of 200 mA in this work. Theta-two theta scans were made in a range of 5-100 °.

In situ resistivity measurements

In situ resistivity measurements were made on samples during conversion of glassy oxyfluoride films into crystalline YBCO films. The schematic of the setup that has been used for this experiment is shown on Figure 3.6.

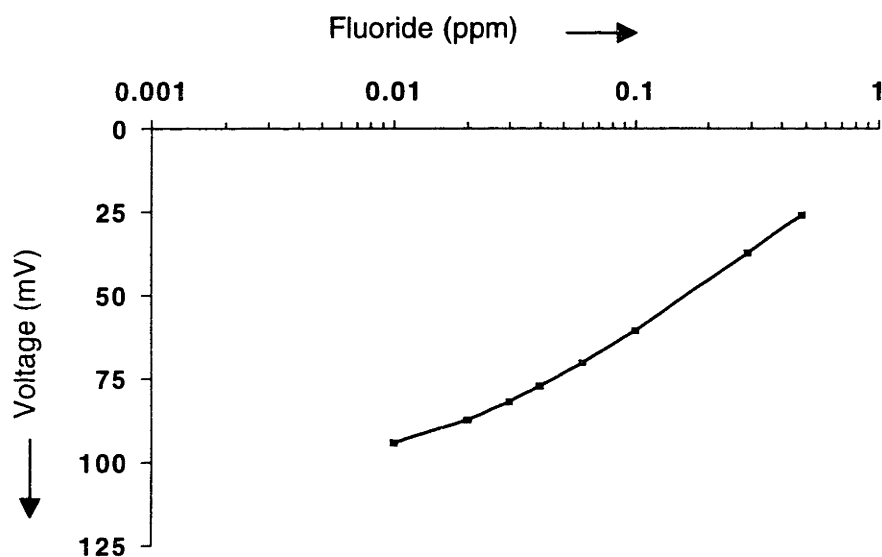


Figure 2.5 Calibration curve for Fluoride measurements.

Small silver pads were evaporated on the oxyfluoride films. Evaporation was made in Denton DV-502A vacuum evaporator. Samples were placed on inconel plate that was attached to an alumina tube.

Two nichrome wires were spring loaded on top of two silver pads at sample surface. Electrical circuit that was made is shown on Figure 4.3(b). K-type thermocouple was placed right behind the sample. Thermocouple was placed into high-purity alumina protection tube. Analog chart recorder Linseis TYP 7045 was used for collecting data from thermocouple, voltage source and voltage across resistor. It was particularly important to have a stable voltage source, for those purposes Keithly 487-picoammeter/voltage source was used. The same kind of furnace and gas supply setup was used as the one described above.

Chapter 3

Results

Effect of different processing parameters on growth kinetics of TFA-derived YBCO films were investigated in this study. We investigated particularly the influence of PH_2O , PO_2 , temperature, and substrate material. Table 3.1 shows the conditions that were investigated.

Moisture level	Temperature, $^{\circ}\text{C}$	PO_2 , ppm	Substrate material	Time for full conversion, min
1.2 % RH	785	1000	LAO	180
100 % RH	785	1000	LAO	15
100 % RH	735	300	LAO	60
100 % RH	735	300	Ni	60
100 % RH	755	500	LAO	35
1.2/100 % RH	725	490	LAO	75
1.2/100 % RH	725	100	LAO	75

Table 3.1 Conditions investigated in the study

Fluoride concentration measurements

Influence of substrate material

Samples prepared on buffered Ni substrates and LAO substrates showed almost identical growth rate under equivalent high temperature anneal processing conditions (735^o C, 300 ppm O₂). (see Figure 3.1). In this figure the percentage of completeness was plotted as y-axis, that represents how much fluorine has been removed as compared to unprocessed film. The samples were fully converted in approximately 60 minutes in both cases. Note that on the plots for fluoride electrode measurements, the time-axis starts at -5 minutes. The time between -5 and 0 minutes represents the time that was required to heat-up the samples to the processing temperature.

Results on fluoride electrode measurements were compared to X-ray analysis data of samples that were prepared on buffered Ni substrate. X-ray analysis (see Figure 3.2) showed good correlation with data obtained by fluoride electrode measurements. Figure 3.2 (a) shows an X-ray pattern, that was obtained from the sample quenched after 15 minutes at 735^o C. As indicated, the BaF₂ (111)-peak can be clearly seen. The sample that was quenched after 40 minutes at 735^o C does not have residual BaF₂ according to X-ray analysis suggesting that the film was fully converted to crystalline YBCO. The small discrepancy between fluoride measurements and X-ray analysis can be seen. We believe that this difference is due to higher sensitivity of the first method.

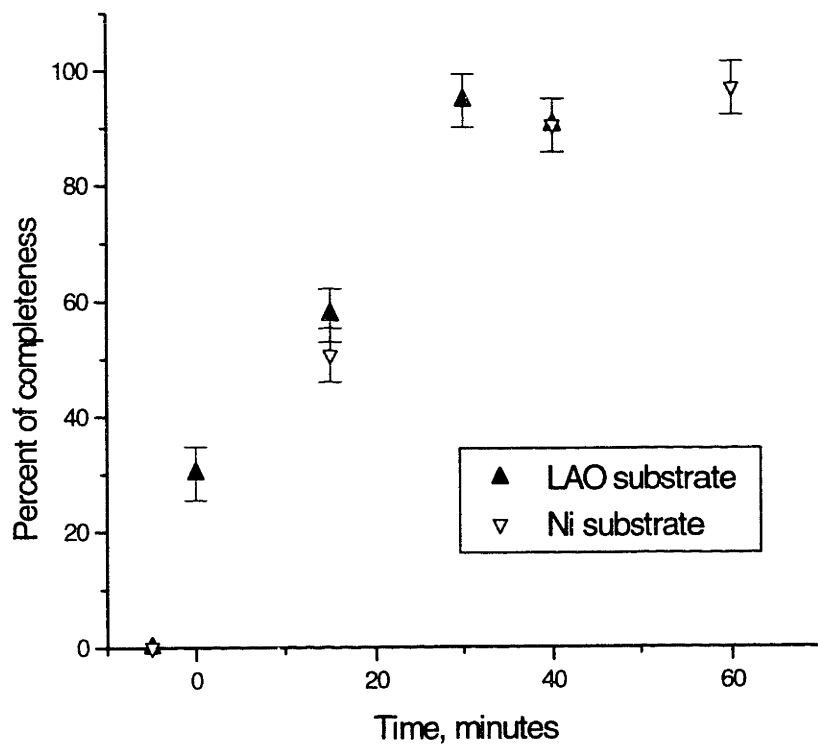
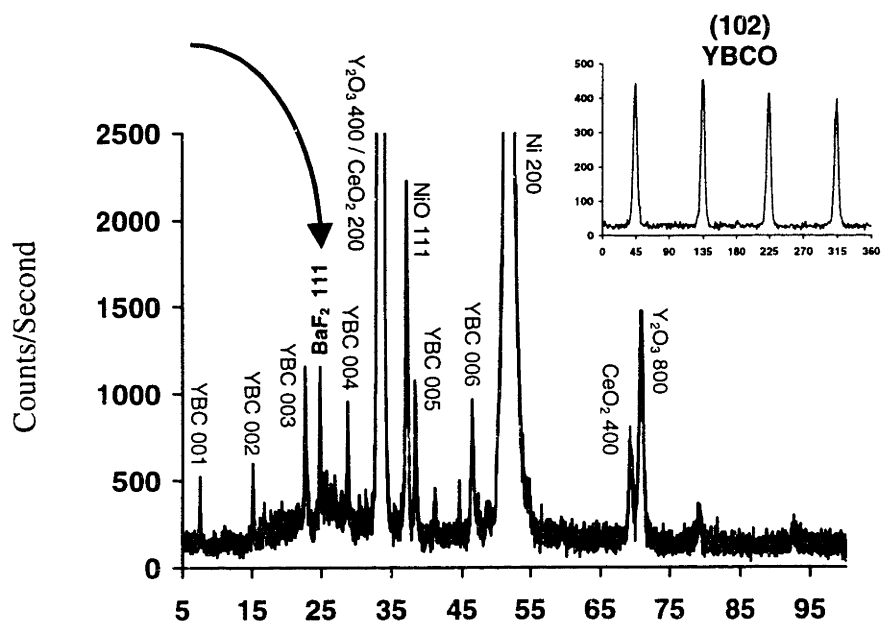
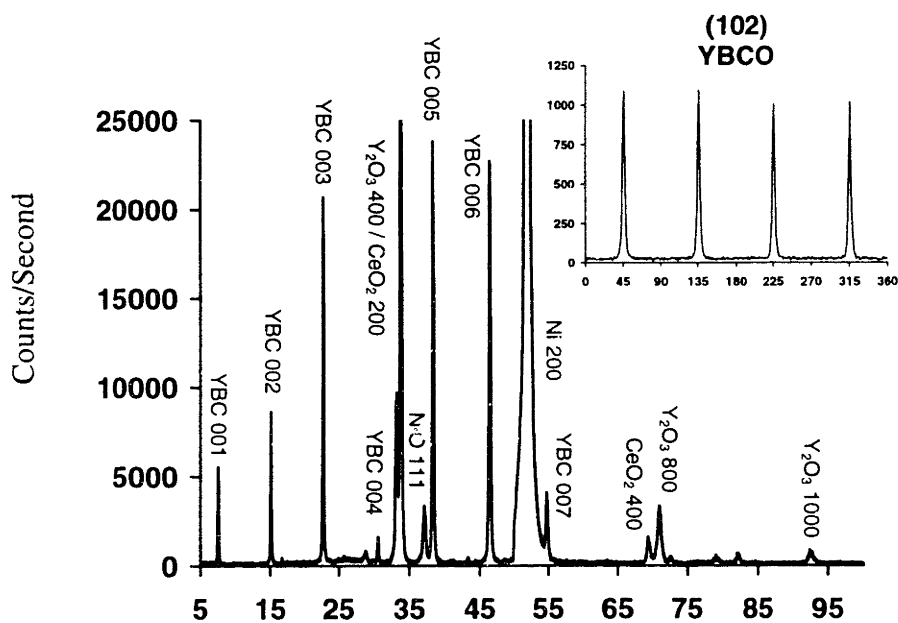


Figure 3.1. Influence of substrate material on conversion kinetics (0.35 microns film thickness)



(a)



(b)

Figure 3.2. X-ray patterns of quenched samples with Ni substrate: (a)- 15 minutes quenching time; (b)- 40 minutes quenching times

Influence of partial pressure of H₂O

Two different conditions were investigated in our study. 1.2% RH was selected for low moisture level and 100 % RH for full moisture level. Smith and Cima also investigated these conditions in one of their papers (1) and that would allow us to compare it with our results. Moisture level in the processing atmosphere had a tremendous effect on the rate of growth of films. Going from 100 % RH to 1.2 % RH changed time of full conversion almost 12 times, and increased from approximately 15 to approximately 180 minutes. (See Figure 3.3). It is hard to tell exact times of conversion from these results. More accurate analysis would require more samples per each curve, especially for slower low moisture conversion.

Influence of partial pressure of oxygen

Influence of partial pressures of oxygen was investigated for two values of partial pressure. Figure 3.4 shows fluoride electrode measurements of films that were fired at 725 °C at 15 minutes with 1.2% RH and 1 hour and 45 minutes with 100 % RH. PO₂ levels that were investigated were 100 ppm and 490 ppm. One can see that partial pressure of oxygen didn't change kinetics of conversion of YBCO films. Both films were fully reacted after approximately 100 minutes total time after 700 °C was reached.

Influence of temperature

Temperature during conversion is another factor that strongly influences growth rate of TFA-derived YBCO films (9). Three different temperatures were investigated under the same level of moisture in the processing atmosphere and one temperature at so called Low/High conditions (15 min. with 1.2 % RH, and 1 hour 45 minutes with 100 % RH). Increase in temperature had a very significant impact. Films grown at 785 °C at 100 % RH showed much faster conversion rate. With the reaction being complete in 15 minutes. Films converted at 755 °C were fully converted after approximately 35 minutes. Films that were grown at 735 °C exhibited the lowest conversion rate under the same level of humidity (100 % RH) in the processing atmosphere, and were converted in approximately 60 minutes. The lowest investigated temperature was 725° C. Conditions for that temperature were not fully equivalent to previous. Conversion was carried out at 1.2% RH during first fifteen minutes, and only after that first segment 100 % RH was applied. Full conversion was reached after 90-95 minutes taking into account this first segment. This result is in a good agreement with general trend of increasing time with decreasing temperature.

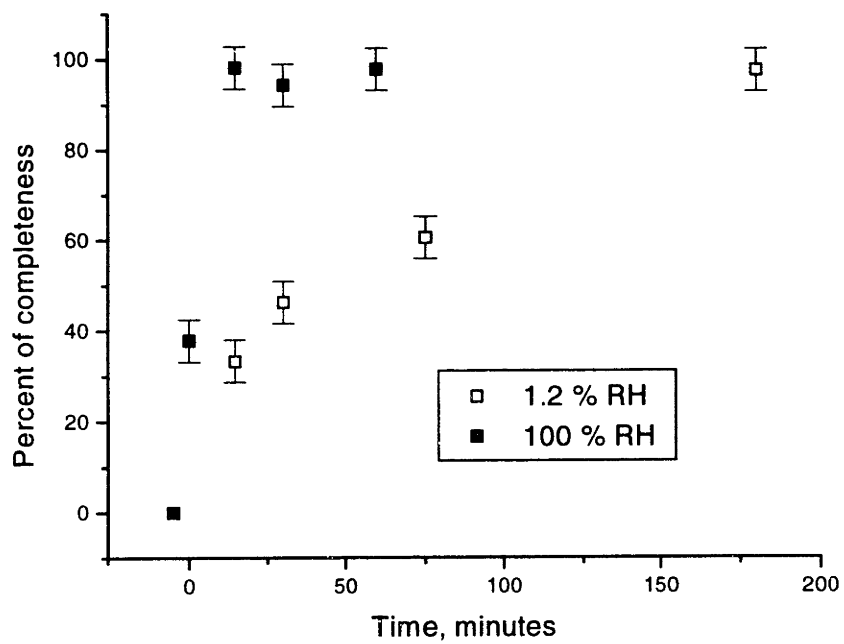


Figure 3.3. Influence of partial pressure of water on conversion kinetics. Both series of samples were prepared at 785 °C, 1000 ppm of oxygen. (0.35 microns film thickness)

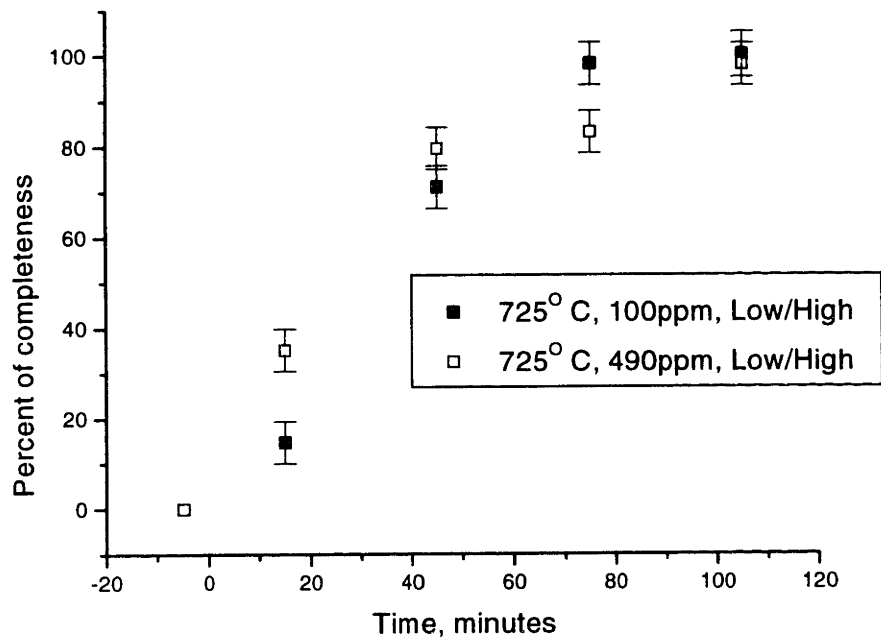


Figure 3.4. Influence of Oxygen partial pressure on conversion kinetics. Samples were prepared at 725^o C, 100 ppm of oxygen for one series of samples and 490 ppm for another. First 15 min of conversion was made at “Low” moisture condition (1.2 % R.H.), and rest of heat treatment was at “High” moisture (95-100 % R.H.) (0.35 microns film thickness)

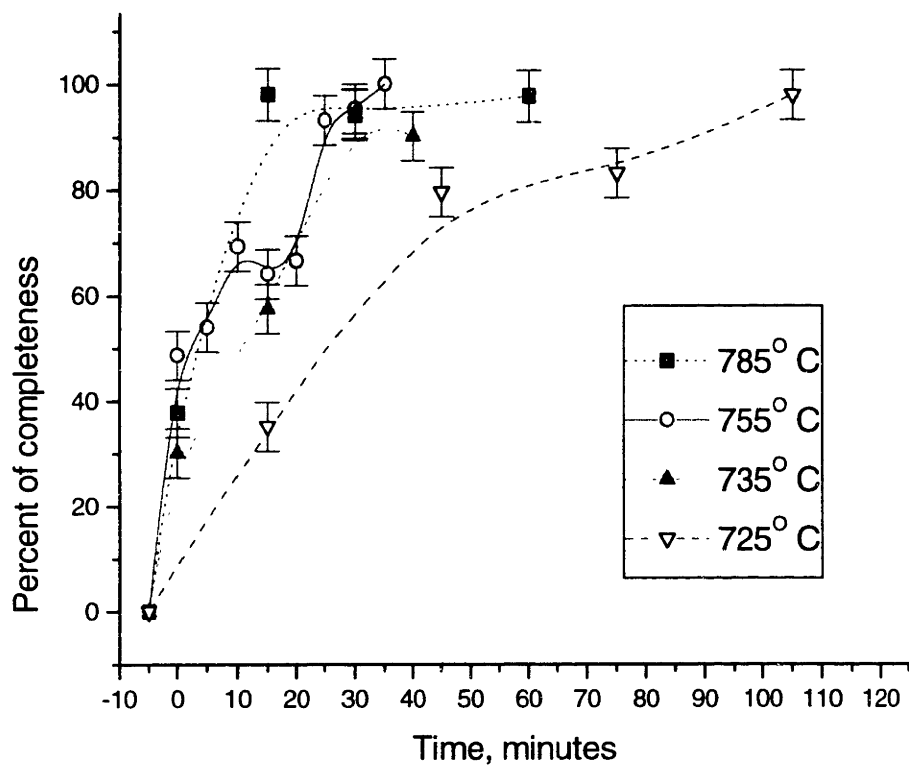


Figure 3.5 Influence of temperature on kinetics of conversion. (0.35 microns film thickness)

***In situ* resistivity measurements**

In situ resistivity measurements were conducted as a part of the growth kinetics study. This kind of measurements is very attractive, as only one measurement to get a complete growth curve. McIntyre (9) showed that TFA-derived YBCO films nucleate at the substrate and grow upwards. Based on this result it was assumed that YBCO grows layer by layer in an upward direction which permitted us to observe the growth of YBCO by measuring the resistance of the growing film. Figure 4.3 shows a schematic of a circuit that was assumed to be present in the film when voltage is applied to the top of the film. The total resistance of the film decreases as the YBCO grows, because thickness of TFA film decreases. Resistance stops changing after YBCO layer stops growing while on the graphs it will be represented by a flat part of a curve. We could not measure resistance directly on a film because we did not have a constant current source. This problem was solved by making a circuit that is shown on Figure 3.5. One can measure the voltage across the external resistor of known resistance (see appendix A) from which we can get the resistance of the film.

Table 3.2 shows processing conditions for samples on which resistivity measurements were made. Conditions investigated by this method are similar to conditions that were investigated using fluoride electrode. All films were spun on LAO substrate and went through the same kind of low temperature process as samples that were used for fluoride electrode measurements.

Moisture level	Temperature, °C	PO ₂ , ppm	Substrate material
100 % RH	785	1000	LAO
1.2 % RH	785	1000	LAO
1.2/100 % RH	725	100	LAO

Table 3.2 Conditions for resistivity measurements

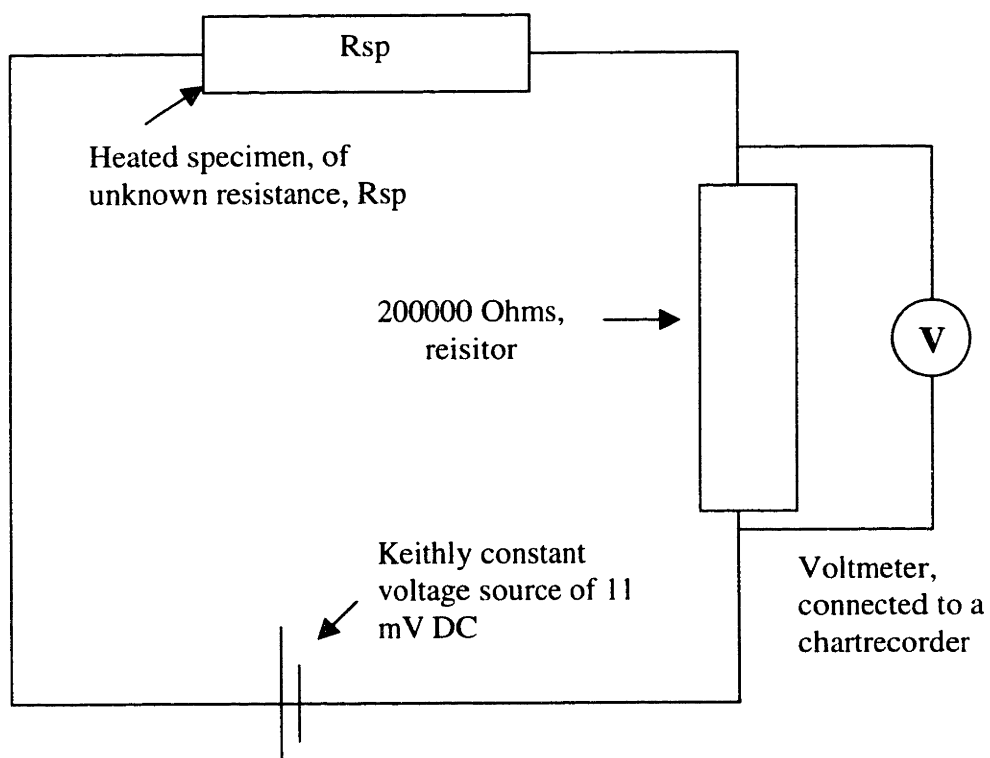


Figure 3.6. Schematic of a circuit used for *in situ* resistivity measurements.

Data that was obtained by this method generally showed good agreement with fluoride measurements results that were presented above. Samples during these measurements were not quickly heated up to the processing temperature, as in the quenching study, but were heated at a ramp rate of approximately $25^{\circ}\text{C}/\text{min}$ in the moist atmosphere. Figure 3.6 shows one of the heating profiles that were used in this study.

Figure 3.6 shows two curves that were measured on samples prepared at 785°C , 100 % RH, and 1000 ppm of O_2 . On both samples the reaction was completed in approximately 15 minutes, according to this curves after they reached 700°C . This result is in a very good agreement with result that was obtained from quenching studies. According to that result samples were also converted in 15 minutes under the same processing conditions.

Figure 3.7 shows curve that was measured at 785°C , 1.2 % RH, and 1000 ppm of O_2 . Moisture during this run was introduced into the furnace only after temperature of the sample reached 785°C . This curve is also in a good agreement with the result of quenching studies. Sample was converted in approximately 182 minutes after temperature of the sample reached 785°C . Samples fired at the same conditions were converted in approximately 180 minutes according to fluoride measurements.

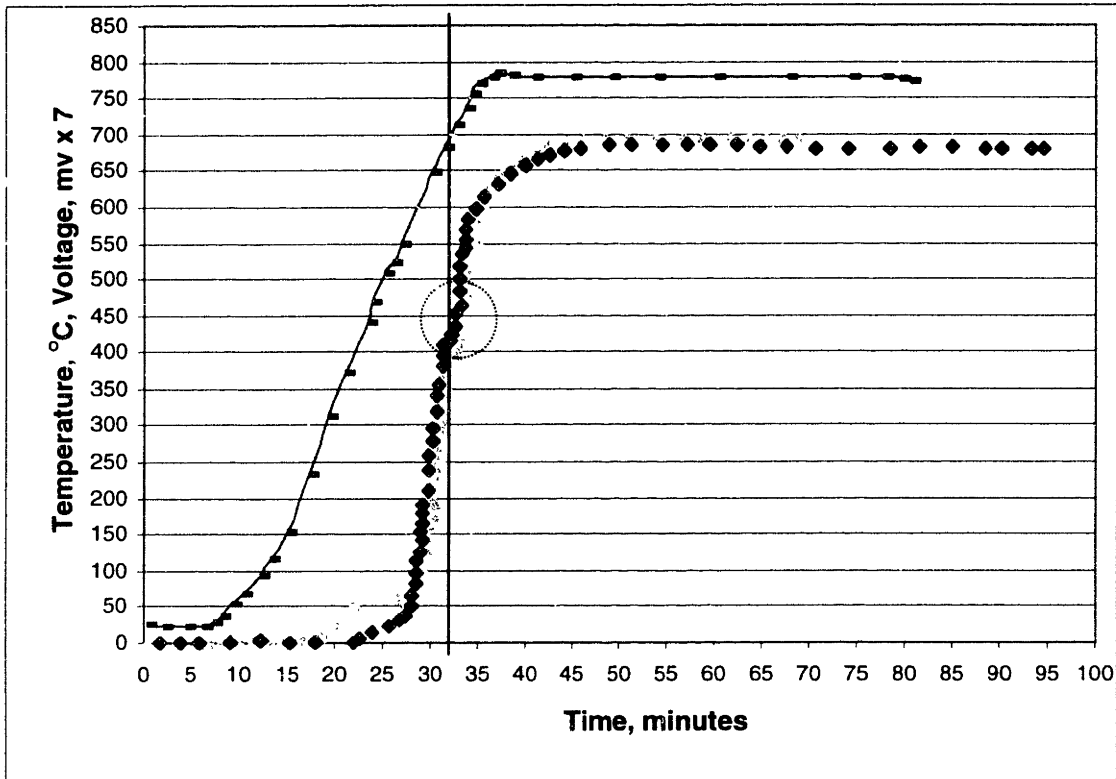


Figure 3.7 Influence of temperature on conversion kinetics. *In situ* resistivity measurements. Top curve is the heating profile used during this measurement. Region of changing slope is inside dashed circle. Vertical line shows that change of slope corresponds to 700 °C, on the temperature profile.

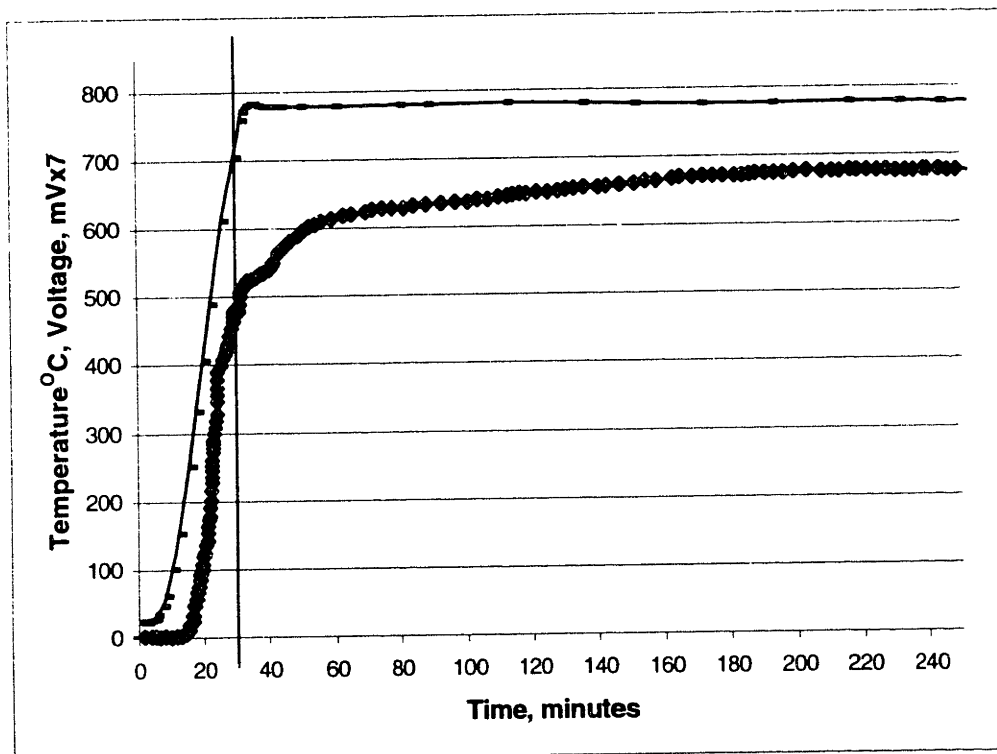


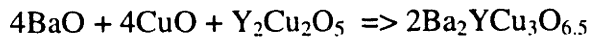
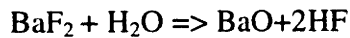
Figure 3.8. *In situ* resistivity measurements at 785 °C, 1000 ppm, 1.2 % R.H. Top curve is the heating profile used during the measurement. Vertical line shows time when moisture was introduced into the furnace after sample temperature reached 785° C.

Chapter 4

Discussion

Fluoride concentration measurements

It is well established that YBCO films growth proceeds by the advancement of interface between YBCO and precursor material from substrate to the top surface (9,13). The growth of the crystalline film is initiated by the reaction between BaF_2 and H_2O (1). In a subsequent reaction BaO reacts with Y_2O_3 and CuO and forms the crystalline YBCO



The growth front has a relatively sharp interface with precursor (9,13). One can measure the extent of growth by measuring the fluoride concentration in the film assuming that most of the fluorine in the film is presented as a BaF_2 . Selective fluoride electrode was used this study to measure concentration of fluoride in the known volume of solution in which half-converted films were dissolved. This method allows significant advantages over such methods as X-ray analysis or *in situ* TEM measurements. Primarily because of its high resolution and sensitivity. Very small concentrations of fluoride can be measured using fluoride ion selective electrode as it can be seen from the calibration curve (see fig.2.5). It is also a relatively simple kind of analysis as compared to TEM observations.

The major disadvantages of this method are requirements for clean glassware and possibility of formation of complexes that can influence results of measurements.

Influence of substrate material

The usage of flexible metal substrate is essential for future industrial applications of thin superconducting film coatings. Buffered single crystal nickel substrate was used in our study to simulate such substrate. Epitaxial buffer layers of 5000 Å Y_2O_3 and 500 Å CeO_2 were deposited on nickel substrates by e-beam evaporation.

The effect of substrate material on the growth kinetics of the thin films was investigated. Figure 3.1 shows two curves that were obtained by using fluoride selective electrode. X-ray diffraction patterns from nickel samples confirmed that the films had c-axis orientation (Figure.3.2). Growth rates of films on nickel and $LaAlO_3$ do not differ significantly according to that data. This result demonstrates that processing conditions determined for films grown on single crystal $LaAlO_3$ substrates can be used for films grown on buffered metal substrate. However these measurements can be only a rough estimate of kinetic behavior of such films. Only one curve was measured for YBCO films grown on nickel substrate samples. More accurate measurements are required for better understanding of growth kinetics of films prepared on metal substrate.

Influence of partial pressure of H_2O

The preparation of thick films is very important for industrial applications. Many research groups are working on the growth of thick YBCO films. Electrical properties of these superconducting films such as critical current density (J_c), decreases with increasing thickness (l) of film. One of the reasons for this degradation is the formation of a-axis grains. J_c values of a-axis oriented films are orders of magnitude lower than of

c-axis oriented films. Density of a-axis grains increases with increasing thickness of a film and it is one of the main focuses in research activities to solve that problem.

A method was proposed for preparation of thick films with low a-axis content in one of the recent studies (1). Initial part of high temperature heat treatment was conducted in this approach at low partial pressure of water (approx. 1.2 % RH) and high partial pressure of water (95-100 % RH) was used for the rest of heat treatment. Films prepared by this method showed critical current densities of more than 1 MA/cm² at film thickness of 1 micron. These studies show that growth rate is one of the most important factors that control a-axis density of thick films.

Partial pressure of water in the processing atmosphere greatly influences growth rate of TFA-derived YBCO (1) films during high temperature anneal. The part of this research was aimed at quantitatively determining how moisture influences growth rate of TFA-derived YBCO films.

Growth rate as a function of P_{H₂O} is shown in table 4.1. The growth rate was calculated as $U=h/t$, where h is thickness of film (0.35 micron in this study) and t is time required for complete removal of fluoride from the film. This table shows that increasing partial pressure approximately 83 times increased growth rate by a factor of 12. It has only two data points and cannot be used to predict growth the rate for different values of P_{H₂O}, it can give rough estimates of times necessary for full completion of the reaction at different vapor partial pressure conditions.

Partial pressure of water	Growth rate, (microns/minute)
1.2 % R.H.	0.0019
100 % R.H.	0.0233

Table 4.1. Growth rates as a function of P_{H_2O} at 785 °C, 1000 ppm.

Influence of partial pressure of oxygen

Influence of partial pressure of oxygen was investigated for two partial pressures, 490 and 100 ppm. Oxygen does not significantly influence the growth rate of YBCO films according to our measurements (see Figure 3.4). The same trend was observed by Solovyov *et al.* (13). Again only two partial pressures were investigated in our study. It should be noted that at high partial pressures of oxygen C-axis orientation of films changes at to a-axis and kinetics of YBCO growth will be different.

Influence of temperature

Another important factor that significantly influences the growth rate of YBCO thin films is temperature. Growth rate as a function of temperature is plotted on Figure 4.1. Four different temperatures were investigated (see Table 3.1). Growth rate was again calculated as $U=h/t$, where h is thickness of film and t is time required for complete removal of fluoride from the film as measured by the Fluoride selective electrode. Assuming a simple Arrhenius temperature relationship of the form

$$U = K \exp(-E_a/kT),$$

an activation energy for growth along the [001] axis can be calculated. The activation energy for this process was determined to be $E_a = 2.66$ eV using data shown on the Figure 4.2. Data shows very good fit to straight line in logarithmic coordinates.

Nucleation and growth kinetics of TFA-derived YBCO thin films were previously investigated by McIntyre *et al.* (9). Activation energy in that work was estimated to be ~ 5.3 eV. Such a big discrepancy can be explained by the fact that in his study only two annealing temperatures were used for calculation. Activation energy was calculated using 4 data points in our study, which increases the accuracy. Another reason for higher activation energy could be the fact that in McIntyre's study the samples were quenched downstream of the furnace and residual moisture was not completely purged during quenching. That means that during the quenching the films were still growing and that time was not included to the calculation of growth rate. The growth rate calculated in McIntyre's work as a result of that turned out to be higher than the actual value. We tried to prevent that problem by quenching samples upstream where most of the moisture was already removed by the dry gas that comes in to the furnace.

A larger number of samples were used to determine the kinetics of conversion at 755°C , 500 ppm of O_2 . Total of 8 samples was used for this curve (see Fig. 4.4 (a)). X-ray diffraction analysis was performed on each sample prior to dissolution in nitric acid solution for fluoride electrode measurements. Absolute intensity of the (200) BaF_2 peak was used as a measure of completeness of reaction in the X-ray analysis. Note that for samples prepared on nickel substrates we used (111) BaF_2 peak, and we can not use (200)-peak, because it is being overlaid by BaCeO_3 (002)-peak. For samples prepared on

LaAlO₃ we used the (200) BaF₂ peak because (111) BaF₂ peak is overlaid by LAO (012)-peak, especially when BaF₂ peak has low intensity and reaction is close to completeness.

Results of these measurements are shown on Figure 4.4. As one can see the results of X-ray analysis and fluoride measurements does not correlate with each other. Intensity of the BaF₂ peak increases at the beginning and drops only after 15 minutes. Smith *et al.* (1) observed the same behavior by *in situ* X-ray measurements. The increase in BaF₂ intensity can be attributed to the crystallization and growth of BaF₂ grains from, the amorphous TFA-film that goes in parallel with growth of YBCO film. That comparison shows that results of X-ray diffraction analysis can not be used as the only experimental technique to determine extend of the reaction BaF₂ with H₂O in TFA-derived YBCO films. X-ray analysis can be used as an additional type of measurements and as a qualitative measure in the investigation of kinetics of growth of TFA-derived YBCO films.

***In situ* resistivity measurements**

In situ resistivity measurements were performed on films grown under similar processing conditions as that investigated using fluoride electrode. It was determined by the cross-sectional TEM studies (9,11,12) that TFA-derived YBCO films epitaxially nucleates at the substrate. C-axis grains coalesce and rapidly cover the substrate surface. Subsequent growth occurs layer-by-layer perpendicular to the film/substrate interface. An electrical circuit can be used to model YBCO growth as shown

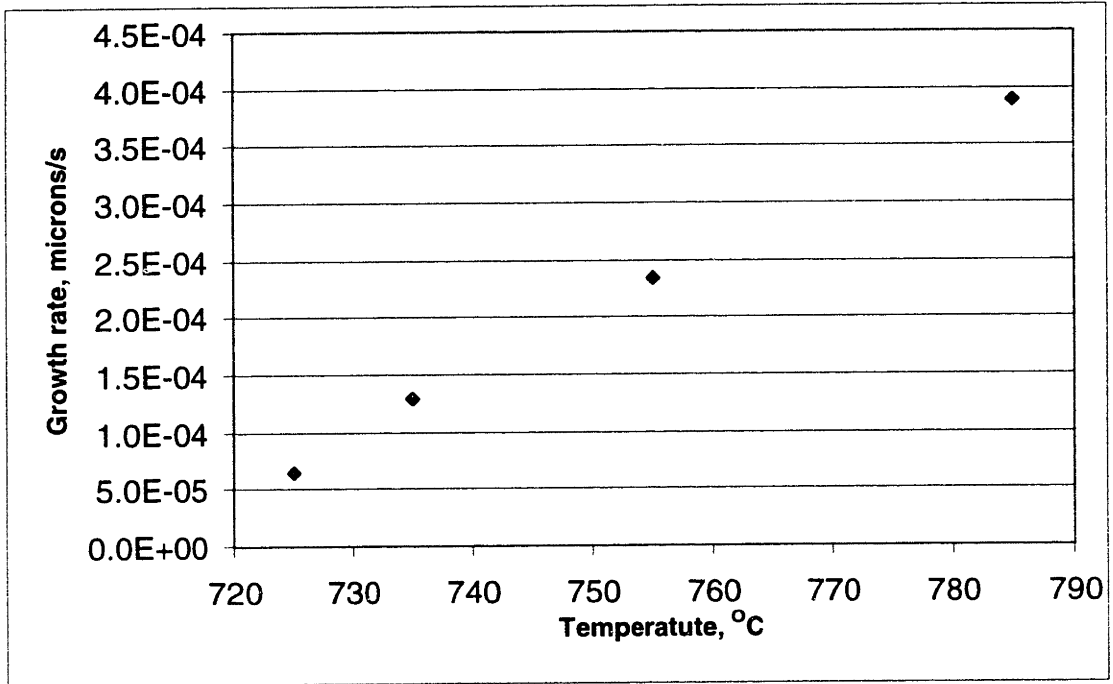


Figure 4.1 Growth rate as a function of annealing temperature.

(0.35 microns film thickness)

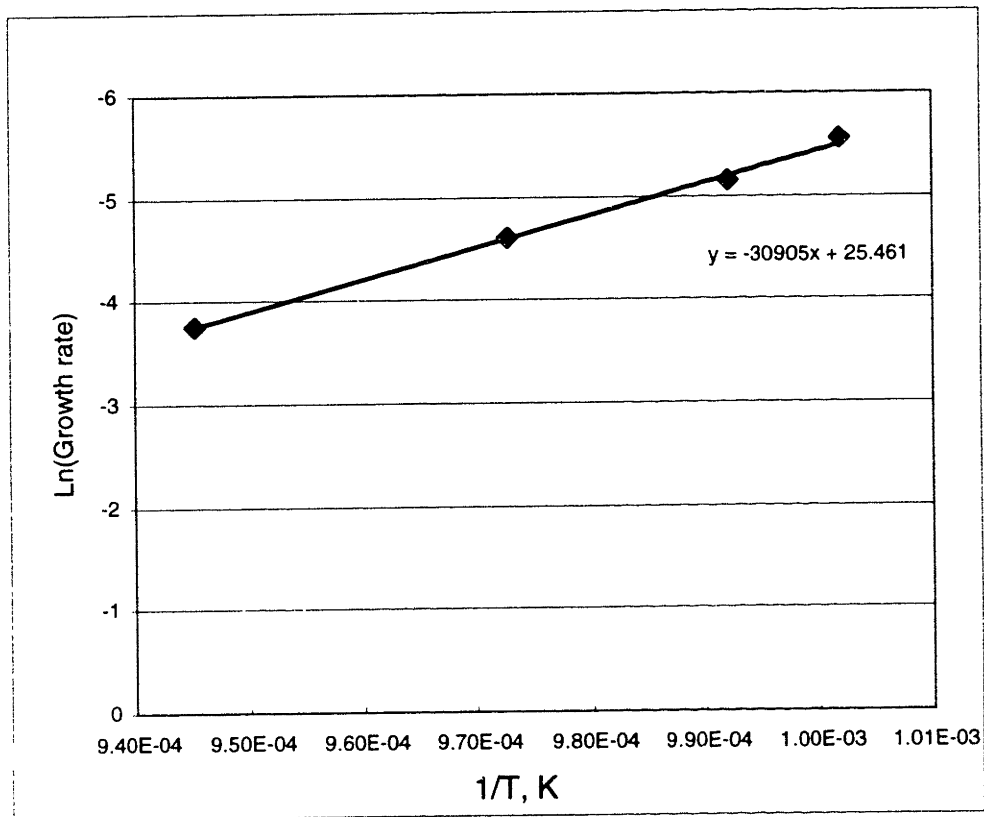


Figure 4.2. Calculation of activation energy. Logarithmic plot of growth rate as a function of $1/T$.

on Figure 4.3. The precursor material has much higher resistance than crystalline YBCO material. The growing YBCO layer consumes the precursor material and resistance decrease. Resistance stops changing and stays constant after growth is complete.

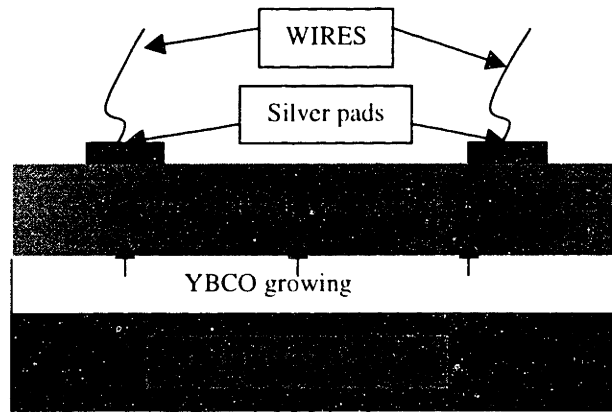
As it was shown in previous chapter this data showed good correlation with fluoride electrode measurements. Results obtained by both techniques show almost identical growth rates for samples fired at 785 °C, 1000ppm O₂ .

This technique, unfortunately, is difficult to use as a stand-alone measurement technique. The resistivity of samples, as it can be seen on the graphs 3.7 and 3.6, started to change earlier than expected, assuming that the precursor is an insulator and growing YBCO is a relatively good conductor. Resistance starts to drop as early as temperature reaches approximately 400°C. This change can be associated with coarsening of BaF₂ particles. As observed by *in situ* X-ray diffraction studies discussed earlier. In the *in situ* X-ray diffraction studies presented in the paper (1), there is an initial increase in the BaF₂ peak intensity; however the temperature at which the coarsening begins can not be accurately determined. Another explanation for that change can be that amorphous film has much higher conductance at higher temperatures.

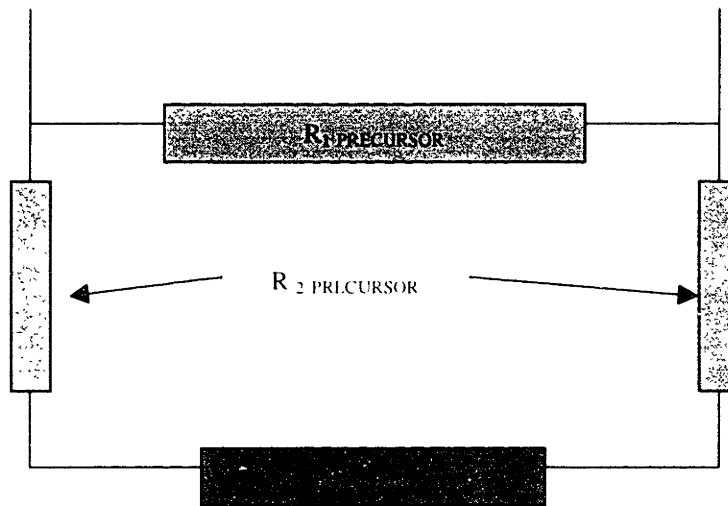
Another parameter that could possibly influence accuracy of our measurements is oxidation of nichrom wires that were attached to the surface of samples, however it is hard to estimate the influence of this factor, because oxide scale thickness and its conductivity was not measured. It is difficult to tell when exactly growth of YBCO crystalline film started.

Closer investigation of resistivity curves showed that around 700°C, the curves change their slope (see Figure 3.7). This observation is in a very good agreement with

thermodynamic stability data (5) that shows that the onset of YBCO formation occurs at this temperature at partial pressure of oxygen 1000ppm that was used during the run. This change of slope is very consistent, and is seen in three curves measured for films fired at 785 °C, 100 % RH, 1000ppm of oxygen. All three curves exhibited that change of slope at around 700°C. Similar observation can be made on other graphs but it is less explicit there as on previous graphs.

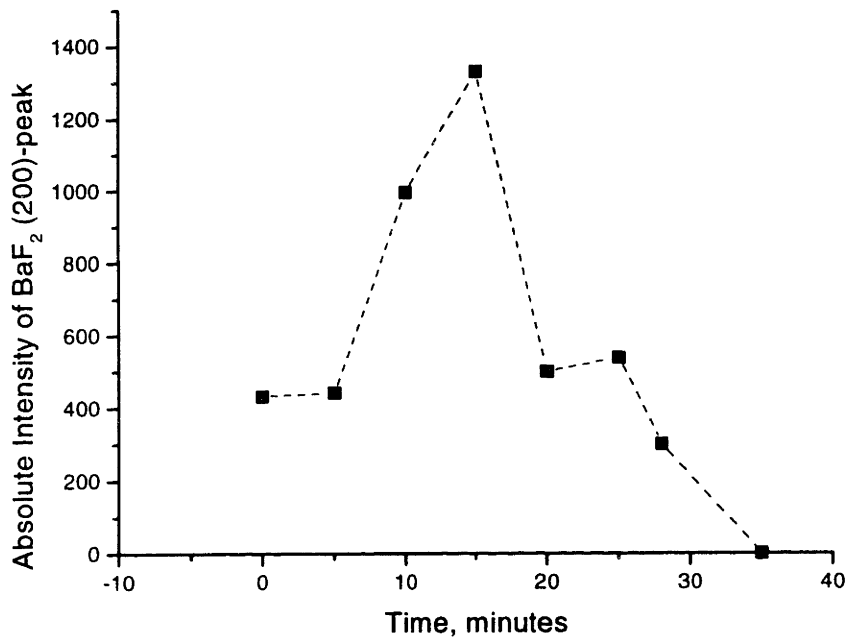


(a)

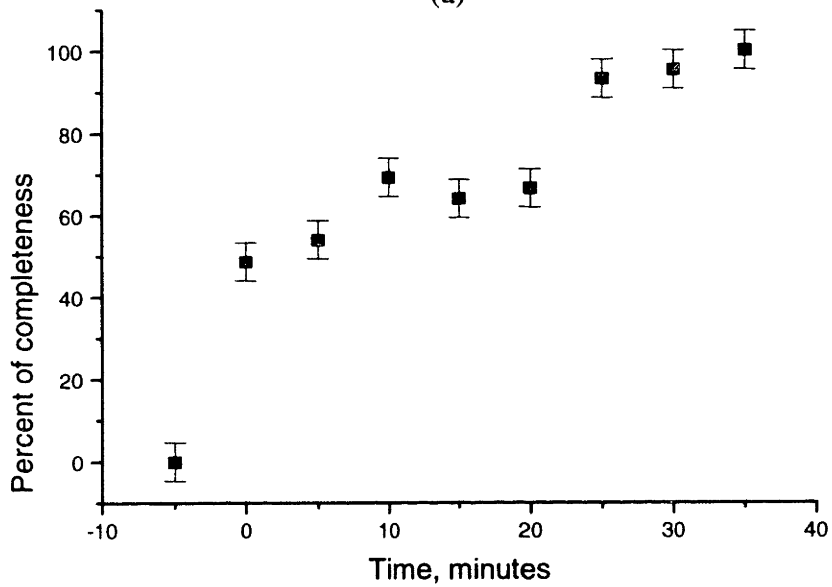


(b)

Figure 4.3. (a) Growth of crystalline YBCO, (b) growth-model circuit.



(a)



(b)

Figure 4.4. Kinetics of conversion of TFA-derived YBCO films prepared at 755^o C, and 500 ppm of O₂: (a) X-ray analysis, (b) fluoride electrode measurements

Modeling of YBCO films growth and comparison to experimental results

The growth of crystalline YBCO film can be modeled by using an electrical circuit that was described in previous section.

Resistance of the film according to our circuit model can be expressed by the following equation

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2 + 2 * R_3}$$

where R_1 - resistance of the precursor film parallel to the direction of growth, R_2 - resistance of precursor film perpendicular to the direction of growth, and R_3 – resistance of YBCO film as it is shown on figure 4.3(a). Resistance R_1 , R_2 and R_3 can be calculated as

$$R_1 = \frac{\rho_1 * w}{(l-x) * w},$$

$$R_2 = \frac{\rho_1 * (l-x)}{w^2},$$

$$R_3 = \frac{\rho_3}{x},$$

Where ρ_1 - resistivity of the precursor, ρ_3 - resistivity of the YBCO, l - total thickness of the film (0.35 microns), w -width of the film (5 mm) (see figure 4.4).

Resistivities of YBCO and precursor film were estimated as approximately 0.2 and $5 \Omega - CM$ respectively. These numbers were calculated using values of resistance measured during *in situ* resistivity measurements of the films. We can determine resistance of the film, using $x(t)$ for instantaneous thickness of growing YBCO film, as a

function of time. The relationship between x and t will be linear $x=Ut$, for interface attachment controlled growth and parabolic, $x=Kt^2$, for diffusion controlled growth.

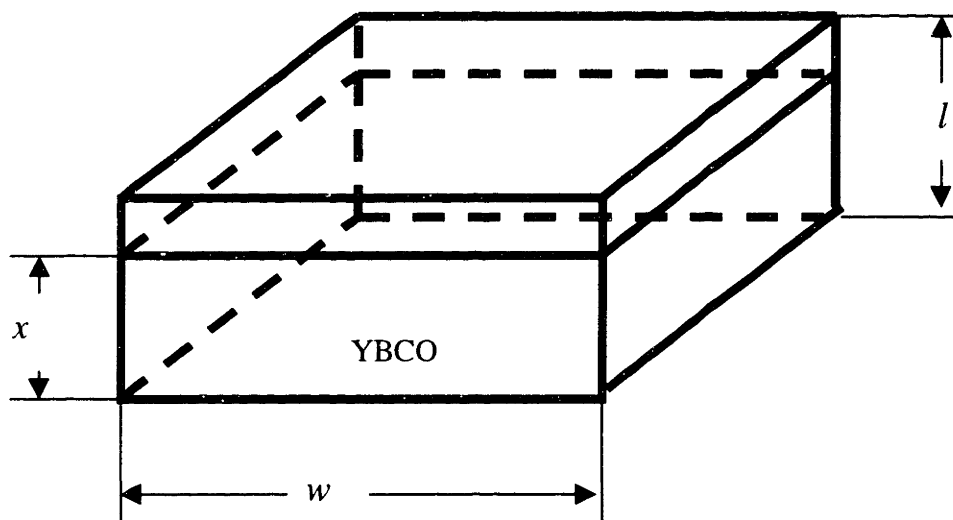


Figure 4.5. Dimensions of the sample.

Plots of resistance as a function of time are shown on figure 4.6. for both types of growth. Graph 4.6 shows that experimental data has good correlation with the curve, calculated using assumption of interface controlled growth, however because resistivity of precursor and YBCO were calculated, based on *in situ* measurements beginning and end-points of the calculated curve were preset to match to the values of experimental curve. A more important factor, is that experimental curve has the same shape as a calculated one. Other researchers (9,13) also obtained similar results, that were suggesting interface controlled growth regime for *ex situ* films.

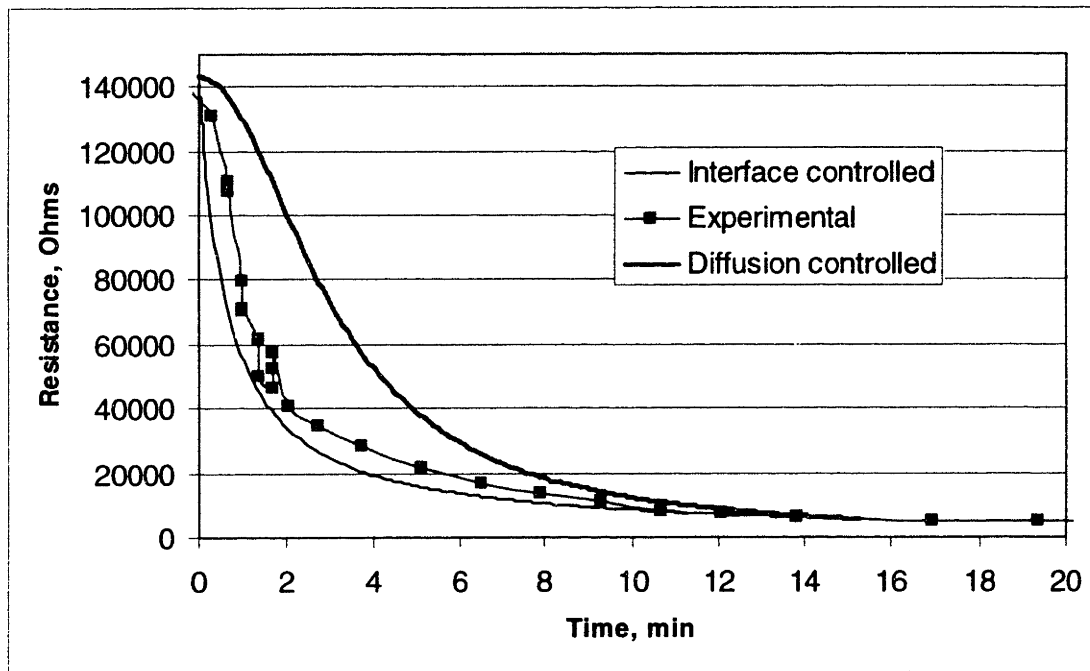


Figure 4.6. Modeling curves of interfaced controlled and diffusion controlled growth compared to experimental curve.

Chapter 5

Conclusions

A novel technique for the investigation the kinetics of growth of the TFA-derived YBCO films was developed and used in this study. The technique is based on measuring concentration of residual fluoride in the film by using selective fluoride ion electrode. This method was shown to be a fast, accurate and easy way for studying growth kinetics of TFA-derived YBCO films.

This method was used for studying influence of different parameters such as PH_2O , PO_2 temperature, and substrate material on growth kinetics of the films.

Partial pressure of moisture in the processing atmosphere during high temperature anneal of TFA-derived YBCO thin films has a significant effect on growth rate of the films with the growth rate of the thin films increasing with partial pressure of moisture.

Partial pressure of oxygen doesn't have a significant influence on the growth rate of YBCO thin films.

Temperature is another factor that strongly influences growth rate of YBCO thin films. Growth rate increases with increasing temperature. The growth rate has an Arrhenius temperature relationship, with activation energy of $E_a=2.66$ eV.

Two types of substrates were investigated in this study: LAO and buffered single crystal Ni. Substrate materials that were studied did not influence the growth kinetics of YBCO thin films.

Results obtained by the fluoride measurements were compare to the X-ray analysis data. It was demonstrated that X-ray analysis can not be used as the only

experimental tool for the investigation of growth kinetics of the films due to crystallization and coarsening of the BaF_2 grains that result in increasing intensity of the BaF_2 peak.

In situ resistivity measurements on TFA-derived thin films were shown to be a reliable method for studying growth kinetics of the films. Results obtained by this method showed good correlation with fluoride electrode measurements. A model developed to simulate the growth kinetics of YBCO films. The experimental results were compared to the modeling results. The growth rate of TFA-derived YBCO thin film exhibits an interface controlled growth regime in the experimental regime studied.

Appendix A: Resistance calculation for in-situ resistivity

measurements.

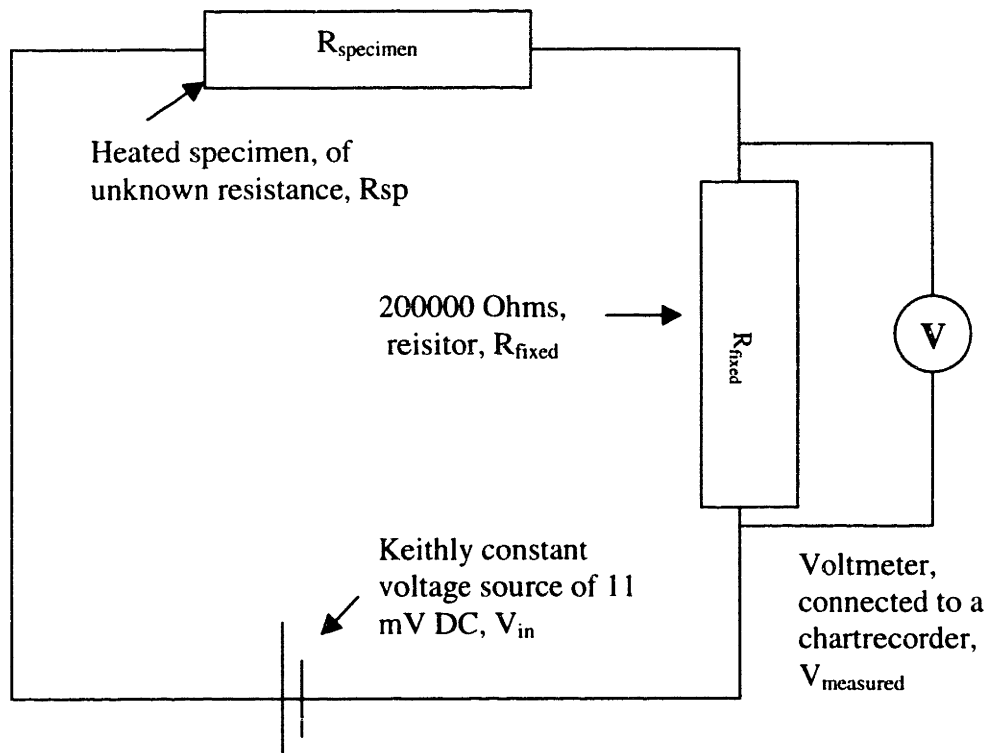
$$V_{in} = (V_{specimen} + V_{measured})$$

$$V_{in} = I * (R_{specimen} + R_{fixed})$$

$$I = V_{measured} / R_{fixed}$$

$$V_{in} = V_{measured} / R_{fixed} * (R_{specimen} + R_{fixed})$$

$$R_{specimen} = V_{in} / V_{measured} * R_{fixed} - R_{fixed}$$



Bibliography

1. Smith J. A., Cima M. J., Sonnenberg N., IEEE Transactions on Applied Superconductivity. v 9 n 2 II 1999. p 1531-1534
2. Larbalestier, Physics Today, 44, 74 (1991)
3. A. Gupta, R. Jagannathan, E.I. Cooper, and E.A. Geiss, in Chemistry of High-Temperature Superconductors II, edited by D.L. Nelson and T.F. George (American Chemical Society, Washington, D.C., 1988), p. 265.
4. A. Gupta, E.I. Cooper, R. Jagannathan, and E.A. Geiss, J.I. Landman, and B.W. Hussey, Appl. Phys. Lett. 52, 2077 (1988)
5. Feenstra R, Lindemer T.B., Budai J.D., Galloway M.D., J. Appl, Phys. 69: (9) 6569-6585 May 1, 1991
6. Boyce J.B., Bridges F., Claeson T., et al. Supercond. Sci. Technol. 4: S343-S345 1991
7. Cui, X. List, F A. Kroeger, D M. Goyal, A. Lee, D F. Mathis, J. Specht, E D. Martin, P M. Feenstra, R. Verebelyi, D T. Christen, D K. Paranthaman, IEEE Transactions on Applied Superconductivity. v 9 n 2 II 1999. p 1967-1970
8. Applied Technologies Enterprise, Irmo, SC
9. P.C. McIntyre, M. J. Cima, A. Roshko, J. Appl. Phys., 77 (10), 15 May 1995
10. C. W. Nieh, L. Anthony, J. Y. Josefowicz, and Krajenbrink, Appl. Phys. Lett. 56, 2138 (1990)
11. P.C. McIntyre, Sc.D. thesis, Department of Materials Science and Engineering, M.I.T., 1993
12. P. C. McIntyre and M.J. Cima, in Evolution of Surface and Thin Film Microstructure, edited by H.A. Atwater, E. Chason, M.A. Grabow, and M.G. Lagally, Mater. Res. Soc. Symp. Proc. Vol 280 (MRS Pittsburgh, PA, 1993), p.371
13. V. F. Solovyov, H.J. Wiesmann, Li-jun Wu, M. Suenaga and R. Feenstra, IEEE Transactions on Applied Superconductivity, v 9, n 2, June 1999
14. M. J. Cima, P. C. McIntyre, J. A. Smith, B. P. Chang, R.B. Hallock, XII Winter Meeting on Low Temperature Physics. Superconducting Ceramics. World Scientific. 1991, pp.13-23. Singapore.

15. M.G. Norton, C. B. Carter, *Scanning Microscopy*, Vol.6,n 2, 1992, pp.385-398
16. E. K. Hollman, D.A. Plotkin, S. V. Razumov, A. V. Tumarkin, *Physica C*, 296, 1998, pp. 37-42
17. P.C. McIntyre, M.J. Cima, *J. Mater. Res.*, Vol.9, Sep. 1994, pp. 2219-2230.
18. T. R. Dinger, T. K. Worthington, W. J. Gallagher, and R. L. Sandstorm, *Phys. Rev. Lett.*, 58 [25], pp. 2687-2690 (1987).

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