Ex-situ Post-deposition Processing for Large Area $Y_1Ba_2Cu_3O_7$ Films and Coated Tapes

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***Abstract*— *Ex-situ* post-deposition reaction processing is considered a promising alternative to *in-situ* physical vapor deposition techniques for coated $Y_1Ba_2Cu_3O_7$ conductor development. It was reported recently, that attempts at *ex-situ* processing of long $Y_1Ba_2Cu_3O_7$ precursor tapes resulted in an inhomogeneous growth rate over the tape length and rather poor properties for the whole sample. We performed a set of experiments in order to clarify the mechanisms for the *ex-situ* processing of large area films and estimate properties of long coated conductors manufactured by the *ex-situ* technique. It was found that rate limiting step of *ex-situ* growth of $Y_1Ba_2Cu_3O_7$ is removal of the reaction product, hydrofluoric acid, by both gas diffusion and convection in the reaction atmosphere. We report on a quantitative model that well describes the observed growth rates for films with various areas.**

***Index Terms*—Barium fluoride process, coated conductors, YBCO.**

I. INTRODUCTION

Barium fluoride reduction is an *ex-situ* process for the production of bi-axially aligned $Y_1Ba_2Cu_3O_7$ (YBCO) films on epitaxial substrates [1]-[4]. The process has several advantages over in-situ techniques, since it separates deposition and epitaxial growth into two steps. The precursor film is a microcrystalline mixture of BaF_2, Cu and Y. Depending on the deposition technique the Cu and Y may be present in metallic form or in the form of oxides, but it is essential that Ba be in form of barium fluoride. During the heat treatment several complex reactions take place and YBCO forms as a product. In simplified form the reaction pathway may be written as follows:

$$Y + BaF_2 + Cu \rightarrow CuO + (Y,Ba)(F,O)_2 + O_2 + H_2O \rightarrow YBCO + HF \quad (1)$$

The presence of two gas phases, H_2O and HF are important factors, which determine properties of this heterogeneous reaction [5]. Specifically, decomposition of yttrium-barium oxy-fluoride in water vapor and the release of HF turn out to be a rate-limiting step of reaction (1) [6].

Application of the process for coated conductor production seems promising, but several problems need to be solved. First, an *ex-situ* reactor, which allows for the simultaneous parallel processing of tapes up to 1 km long, has to be designed. Second, reproducible growth of several microns thick bi-axially aligned YBCO layers has to be mastered. These two issues are far from being solved. In this paper we address the first one. We analyze two quite different *ex-situ* reactor designs and estimate the maximum capacity of each one.

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II. EXPERIMENTAL

Precursor films of the approximate stoichiometric cation composition Y:Ba:Cu = 1:2:3 were deposited on 3×10 mm^2 (100) $SrTiO_3$ substrates without external heating in a vacuum chamber. The Y and Cu were deposited using Temescal 14 kW electron beam guns and a 300 W thermal evaporation source was used to deposit the BaF_2. The deposition rate was 14 nm/s as calculated for the thickness of annealed YBCO films. The background pressure in the chamber was 1×10^{-6} Torr during deposition and the deposition rates of the individual sources were controlled by Inficon quartz crystal deposition rate monitors [7].

In this study we analyzed two types of *ex-situ* reactors: an atmospheric and a partial pressure one. The atmospheric reactor basically consists of a quartz tube inside a tubular furnace. The procesing atmosphere was synthesized by mixing certified gases using electronic mass flow controllers. The total gas flow was fixed at 200 cm^3/min and was humidified by bubbling through a heated water bath. The humidity was measured with a thin film polymer capacitive sensor and active feedback was used to stabilize the water vapor partial pressure by varying the water bath temperature. In the atmospheric reactor the pressure inside the tube is equal to the atmospheric pressure, ~760 Torr.

The partial pressure reactor had the same geometry as the atmospheric one. An mechanical rotary vane pump and a liquid nitrogen cold trap were used to pump efficiently both non-condensable gases and water vapor from the reactor tube. By adjustment of the gas flow rate and the pumping speed the total pressure inside the partial pressure reactor tube was varied from 100 mTorr to 30 Torr. Gases were supplied into the reactor by electronic mass flowmeters and a stainless steel vessel filled with water served as a water vapor source. Active feedback was used to maintain constant water vapor pressure in the vessel. Water vapor entered the reactor through a variable orifice. A capacitance diaphragm gauge determined the absolute value of water vapor pressure with

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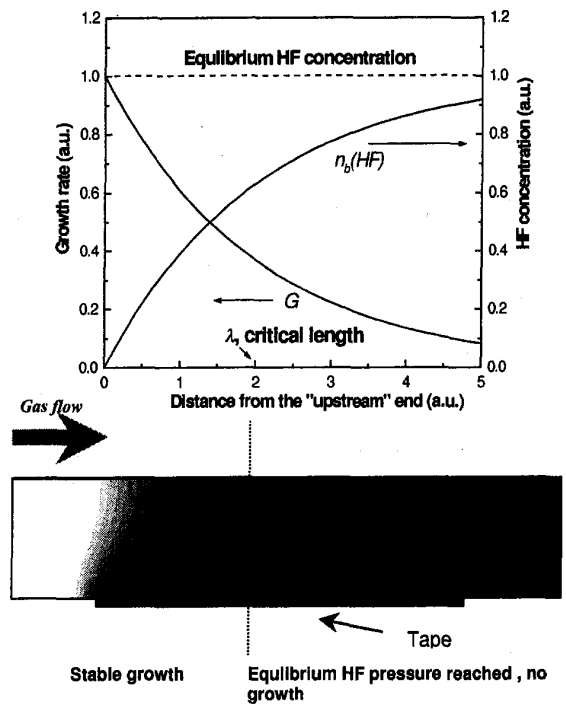

Fig.1 Results of numeric simulation of HF transport during processing of a tape in an atmospheric reactor. Darker shade means higher HF pressure. Upper graph shows variations of the growth rate and avarage HF concentration in the reactor obtained from an analytical solution of (4) .

accuracy 5%. We also routinely checked the gas content in the reactor by means of a quadrupole mass spectrometer.

In both reactors the oxygen partial pressure was maintained at level of 100 mTorr.

III. Atmospheric Reactor

In the atmospheric reactor a mixture of inert gas and oxygen is humidified and then passed into the reactor at atmospheric pressure. Such a simple design allowed achieving good properties for short samples, where both single crystal and buffered metallic tapes were used as the substrates. However, attempts to process 10 to 100 cm long samples in the atmospheric reactor resulted in a very inhomogeneous growth rate from one end of the sample to the other [8], [9]. One possibility for the occurrence of such an inhomogeneity is due to water vapor starvation of the growing tape. This model assumes that a boundary layer forms at the tape surface and convective gas exchange at sections of the tape located "downstream" is much lower than that of the "upstream" part. A simple estimate shows that due to very high water vapor pressure and low growth rates, typically found in an atmospheric reactor, the supply of water vapor by diffusion only is more than enough to support stable growth. It is more likely that removal of HF, which is produced as a result of barium oxy-fluoride decomposition as a part of reaction (1), causes problems with growth homogeneity. In our earlier publications [5], [6] we developed a model of the *ex-situ* growth kinetics. The following assumptions are used in our model:

1) Reaction (1) is in a state of dynamic equilibrium at the growth front and the partial pressure of HF, p_i(HF), at the YBCO-precursor interface is related to the water vapor partial pressure, $p(H_2O)$, (due to high $p(H_2O)$ values we neglect it's spatial variations) by the equilibrium condition:

$$p_i(\mathrm{HF})/\,[p(\mathrm{H_2O})]^{1/2} = K \qquad (2)$$

where K is the equilibrium constant of reaction (1). Equation (2) gives an explanation to an earlier observation of a square root growth rate (G) dependence on $p(H_2O)$. If the growth rate is limited by HF removal from the film surface, a simple argument shows that $G \propto p_i$(HF) but from (2) $G \propto p(H_2O)^{1/2}$ in agreement with the experimental results [5]. Our estimates show that the equilibrium constant K is quite small, for instance at a typical value $p(H_2O)$ = 20 Torr the equilibrium HF partial pressure is only about 13 mTorr.

2) The rate of HF removal is limited by diffusion in the gaseous processing atmosphere. This means that resistance to HF transport in the precursor solid is much less than in the surrounding gas. As a consequence HF pressure at the film surface, p_s(HF), can replace the partial pressure at the growth interface, p_i(HF), in (2). We believe that this is true, at least for films thinner than 5 μm. The most compelling evidence is that the growth rate does not depend on the precursor film thickness, but depends on lateral width W of the film, that is $G \propto 1/W$. Our interpretation of this observation is that HF flow is determined by the pressure gradient in the gas phase which is approximately $p_s(\mathrm{HF})/W$.

The kinetics of *ex-situ* growth is reduced to a classic problem of mass transfer from a surface by diffusion and convection of the carrier gas. In a typical *ex-situ* reactor the gas velocity is quite low, flow is laminar and diffusion is the predominant mechanism of the HF transport from the film surface. In general form the average YBCO growth rate of a square precursor film with width W can be expressed through the following quantities [6]:

$$G \approx VDK[p(\mathrm{H_2O})]^{1/2} / kTS \qquad (3)$$

Where $V = 10^{-22}$ cm^3 is the volume of the YBCO unit cell, k is Boltzmann's constant, T = 735 °C (the processing temperature) and $D \approx 2.5$ cm^2/s (T = 735 °C, p = 760 Torr) is the diffusion constant of HF in the processing atmosphere. S is a tabulated sample shape factor which also depends on the gas flow rate F. It can be shown that for the case of a small sample or high gas flow, $F >> WD$, $S \approx W$. In the limiting case of a large sample or low flow rate $S \approx W^2D/F$.

A long tape is treated in a similar manner. An essential parameter in the long tape case is the HF background pressure, p_b(HF). Since the local growth rate is proportional to the pressure gradient, $G \sim [p_s(\mathrm{HF}) - p_b(\mathrm{HF})]$, the growth slows down considerably when $p_s(\mathrm{HF}) \approx p_b(\mathrm{HF})$. Three factors define the spatial distribution of p_b(HF):

a) HF production by the tape

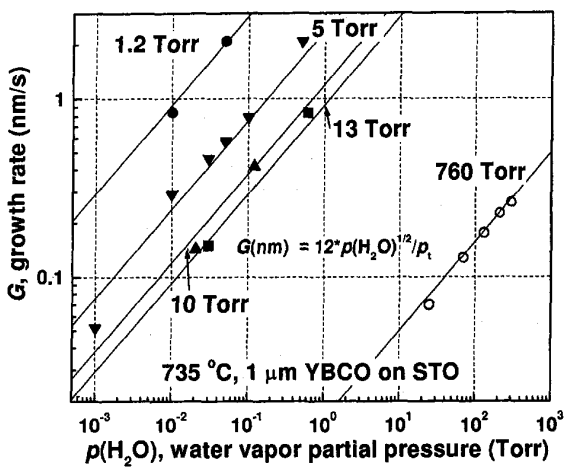

Fig.2. Growth rates of 1 μm films versus water vapor partial pressure at various total pressures. Solid lines are approximations by (6), where A = 12, $p(H_2O)$ and p_t are in Torr.

b) Convection due to carrier gas flow
c) Diffusion

In order to simplify the problem the HF concentration gradients in the radial direction were excluded. Combining the three factors above we obtained the following one dimensional equation:

$$D\, d^2n_b/dx^2 - v dn_b/dx + D\,(n_s - n_b)/S_r = 0 \qquad (4)$$

Where $n_b(\mathrm{HF}) = p_b(\mathrm{HF})/kT$ is the background HF concentration at a distance x from the "upstream" end of the tape, S_r is the reactor cross-section, $v = F/S_r$ is the carrier gas velocity and $n_s(\mathrm{HF}) = p_s(\mathrm{HF})/kT$ is the equilibrium HF concentration at the tape surface, defined by (2). Results of a numerical solution of a two-dimensional version of equation (4) are shown in Fig. 1. The solution predicts that at some critical point the background concentration of HF n_b(HF) will become close to n_s(HF). Beyond this point the growth will virtually stop since there would be no pressure difference between the film surface and the flowing gas. An analytical solution of (4) gives the following functional dependence of the growth rate on distance, x:

$$G\,(x) = G(x=0)e^{-x/\lambda} \qquad (5)$$

The parameter λ in (5) defines the approximate reactor capacity, or maximum tape length, which can be processed in the reactor. λ values depend on the reactor geometry and the gas flow. There are two limiting cases: if gas flow is low, $F << DS_r^{1/2}$, then $\lambda = S_r^{1/2}$ .i.e. λ is equal to the reactor radius. In the limiting case of high gas flow, $F>>DS_r^{1/2}$, one finds $\lambda = F/D$. An estimate of λ demonstrates that a simple tubular atmospheric reactor is not suitable for the large-scale processing of coated tapes. For example, for our reactor F = 200 cm^3/min and λ = 7 cm. To process uniformly a 10 m tape in such a reactor one needs λ = 40 m and a gas flow of 600 l/min. Such a high gas flow poses technical problems and it is not clear that uniform growth could be achieved in any case, since, in derivation of (4), the gas flow was assumed to be low and laminar. An exact numerical solution of corresponding mass transfer equation is required.

IV. Partial Vacuum Reactor

In a partial vacuum reactor a pump is used to force gas transport through the reactor tube. The balance between pumping speed and gas flow defines the absolute pressure in the reactor. The HF diffusion constant in the processing atmosphere depends on the total pressure, p_t, as $D \propto 1/p_t$. It follows from (3) that the growth rate, G, should depend on p_t and $p(H_2O)$ as:

$$G = A[\,p(H_2O)]^{1/2}/p_t \qquad (6)$$

where A is a coefficient which can be easily inferred from (3). We carried out a set of growth runs in a wide range of conditions: total pressure was varied from 760 to 1.2 Torr and water vapor pressure from 150 to 10^{-3} Torr. The samples in each case were 1 μm precursor films on 3 × 10 mm^2 substrates and the processing temperature was 735 °C. The results are summarized in Fig. 2 where the growth rate, G, is plotted versus the water vapor pressure, $p(H_2O)$, for various total pressure values. Data for the atmospheric reactor are also presented as the curve corresponding to p_t = 760 Torr. Approximations to (6), where A = 12 and the pressures are in Torr, are shown as solid lines in the figure. It is clear that (6) well describes the growth kinetics.

It is evident from Fig. 2 that the partial vacuum reactor allows the achievement of very high growth rates at very low $p(H_2O)$ values. However, there are certain limitations on the growth rate as far as the superconducting properties are concerned. We found that for G > 10 nm/s, YBCO nucleates as a mixture of random and a-axis oriented phases. The J_c's of such samples were low. Stable c-axis growth was observed at G < 2 nm/s with J_c(0 T) ≈ 1 MA/cm^2 and J_c (1T, $H||c$) 1×10^5 to 2×10^5 A/cm^2 at 77 K. Much higher J_c's were measured at even lower growth rates. An obvious way to slow down the growth rate is to decrease $p(H_2O)$ and increase p_t. It turns out, however, that $p(H_2O)$ values less than approximately 10 Torr, are detrimental to c-oriented growth in films thicker than 1 μm. On the other hand, a partial vacuum reactor operated at high total pressure is converging towards an atmospheric reactor with all associated problems outlined in the previous section.

We propose a solution for the problem of growth rate control in a partial vacuum reactor. It is possible to suppress the YBCO growth rate by means of mechanical restriction of HF diffusion from the film surface. Mechanical restriction can be achieved using a porous ceramic barrier, baffles, or some other mechanical arrangement. In this case the shape factor S in (3) is replaced by a parameter, l, which characterizes the permeability of the restriction. If $l>>W$, the HF pressure between the barrier and the film surface is approximately

equal to the equilibrium value p_s(HF). Provided that the gas exchange is fast enough so that the background HF pressure p_b(HF) << p_s(HF), the whole HF pressure drop occurs across the barrier. This technique allows one to adjust the growth rate G, the water vapor pressure $p(H_2O)$ and the total pressure p_t for optimal superconducting properties. In addition the HF pressure profile is determined by the barrier geometry and the film properties can be made homogeneous in directions both parallel and perpendicular to the gas flow. We have carried out a set of experiments using various types of restrictive geometries. Growth rates were varied from 0.1 to 2 nm/s using water vapor pressure from 5 to 22 Torr. The restriction allowed reduction of the growth rate by a factor of 10, compared to the growth rate of a sample with a free surface, see data in Fig. 2. It was found that at a water vapor pressure ~5 Torr and growth rates below 0.3 nm/s the critical current density increased considerably. A value of J_c (1 T, H||c) = 0.6 MA/cm^2 for a 1 μm thick film has been obtained.

It is instructive to compare the capacity of a partial vacuum reactor with an atmospheric reactor. We presume that a mechanical barrier to HF diffusion is used over the whole tape length. The HF transport in equation (4) is modified as follows:

$$D\, d^2n_b/dx^2 - v dn_b/dx + D\, l(n_s - n_b)/WS_r = 0 \qquad (7)$$

Here $v = F/S_r$ is the velocity of the gas and F is the pumping speed of the pump. W is width of the tape. The solution of (7) is similar to that of (4) and the critical tape length, λ, for the technologically important case of high pumping speed is:

$$\lambda = Fl/DW = Fn_s(\mathrm{HF})V/GW \qquad (8)$$

This expression allows the calculation of reactor capacities since it includes all known parameters. It is assumed that parameter l is adjusted to achieve desired growth rate G at given $p(H_2O)$ value.

For example consider a partial pressure reactor which operates at 20 Torr of water vapor, the same water vapor pressure used for processing in an atmosphere pressure reactor. At this pressure D (T = 735 °C, p_t = 20 Torr) ≈ 76 cm^2/sec and n_s(HF) = 5×10^{14} cm^{-3}. Taking G = 2×10^{-8} cm/s, W = 1 cm, $V = 10^{-22}$ cm^3 and F (T = 735 °C) ≈ 6×10^3 cm^3/sec (100 l/min pumping speed) we obtain $\lambda \approx 150$ m. Thus even a simple partial vacuum reactor allows processing of quite long tapes. Equation (8) shows that increasing pumping speed is the only way to achieve higher λ values. Indeed, the equilibrium HF concentration n_s(HF) is determined by the equilibrium condition (2). Since it is difficult to handle water vapor at pressures higher than the saturation pressure at the room temperature, the equilibrium HF concentration cannot exceed the value corresponding to $p(H_2O)$ = 20 Torr (n_s(HF) ≈ 5×10^{14} cm^{-3}). In addition it is not practical to make the growth rate less than 0.2 nm/s due to the long processing time required for the growth of the YBCO film. This leaves F as the only parameter which can be varied to increase λ.

V. Conclusion

We have estimated YBCO processing length capacity of two types of simple tubular *ex-situ* reactors. It was shown that the factor limiting the capacity of an *ex-situ* reactor is removal of HF produced by the decomposition of the BaF_2 in the precursor. A promising design for a high-capacity *ex-situ* reactor is a partial vacuum reactor combined with a method for restricting the diffusion of HF at the sample surface.

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