

Kinetics of $\text{YBa}_2\text{Cu}_3\text{O}_7$ film growth by postdeposition processing

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(Received 8 July 1999; accepted for publication 8 February 2000)

The *ex situ* growth of thick textured $\text{YBa}_2\text{Cu}_3\text{O}_7$ films on SrTiO_3 substrates was investigated in order to find the factors, which influence growth kinetics. It was found that the growth rate of $\text{YBa}_2\text{Cu}_3\text{O}_7$ films remains constant during heat treatment and is proportional to the square root of the H_2O partial pressure in the processing atmosphere. Using transmission electron microscopy, we observed that the growth of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ films proceeds from a thin, ~ 7 -nm-thick, layer of liquid located at the growth front. Chemical analysis of this layer and the adjacent material suggests that decomposition of an oxifluoride compound in the precursor film occurs at the liquid layer-precursor film interface. The rate of this decomposition reaction defines the growth rate of $\text{YBa}_2\text{Cu}_3\text{O}_7$. Using a simple model we show that rate of this reaction is limited by the out-diffusion of the decomposition product HF. © 2000 American Institute of Physics. [S0003-6951(00)03014-X]

The development of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) coated tapes on a flexible textured metallic substrate has gained significant attention.^{1,2} Recently, it has been demonstrated that precursor films grown by vapor deposition can be fabricated into 2–5- μm -thick textured YBCO films on SrTiO_3 , using *ex situ* processing,^{3,4} with J_c of $> 2 \times 10^5$ A/cm² at 1 T (perpendicular field) at 77 K.^{5,6} This translates to approximately 10^6 A/cm² in self-field. Somewhat worse, but still encouraging results were obtained for 5 μm YBCO on (RABITS) substrates with $J_c = 0.7 \times 10^5$ A/cm² at 77 K and 1 T, $H \parallel c$.⁷

The *ex situ* process, also known as the BaF_2 process, consists of preparing a precursor film, a mixture of fine grain Y, Cu, and BaF_2 in the correct stoichiometric ratio and subsequently processing the film in a controlled-atmosphere furnace to convert it to a *c*-axis textured YBCO film. As described previously in greater detail,⁵ the precursor films were deposited by the evaporation of Y and Cu using electron beam guns and by thermally evaporating BaF_2 . The deposition rate was ~ 14 nm/s as calculated from the thickness of the processed YBCO films and polished [100] SrTiO_3 were used for the substrates. The processing was performed in a quartz tube and the processing atmosphere was synthesized by mixing certified gases using electronic mass flow controllers. The humidity of the reaction atmosphere was controlled such that water vapor partial pressure varied from 25 to 200 Torr. After processing the completed films were annealed at 500 °C in one atmosphere of pure oxygen for $\frac{1}{2}$ h in order to fully oxygenate the YBCO.

In order to quantify the YBCO growth rate during the *ex situ* processing of the precursor films, the film electrical conductance was measured while the heat treatment was in progress. Since crystalline YBCO is highly conducting compared to the precursor, which is an insulator, the conductance of the film increases sharply as soon as the YBCO layer begins to form. During growth the conductance, $\sigma(t)$, increases in proportion to the YBCO thickness and becomes constant when the conversion reaction is complete. The data

interpretation is straightforward: the linear time dependence of $\sigma(t)$ is due to the constant synthesis growth rate of YBCO. The plateau region indicates completion of the process, with the insulating precursor having been fully converted to YBCO.

The conductance versus processing time of 3- μm -thick YBCO films, processed at three different oxygen partial pressures P_{O_2} , is shown in Fig. 1. The YBCO growth is seen to be nearly linearly proportional to the period of heat treatment as has been previously observed in the reaction of chemically derived precursor films.^{4,8} It is also evident from Fig. 1 that the processing time, which we define as the crossover from the linear region of the $\sigma(t)$ curve to the plateau, does not depend on the oxygen partial pressure. That is, the growth rate for all three films is approximately equal. The square root of the growth rate versus water vapor pressure for seven YBCO films processed at 735 and 800 °C, $P_{\text{O}_2} = 100$ mTorr is shown in Fig. 2. This data set is composed of

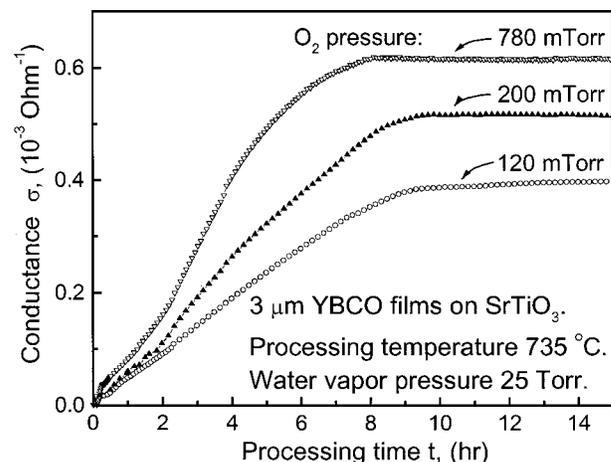


FIG. 1. Variations in the conductance of 3- μm -thick YBCO films grown at different O_2 partial pressures are presented. Note that the conductance of all three films increases almost linearly and reaches a plateau after 8 h of processing. This demonstrates that the YBCO growth rate is independent of the O_2 partial pressure.

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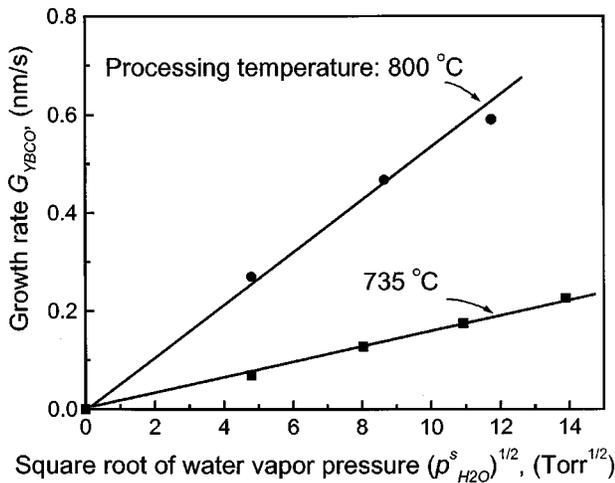


FIG. 2. The dependence of the YBCO growth rate on square root of H_2O partial pressure is shown for 3 and 5- μm -thick films processed at two different temperatures: 800 and 735 $^{\circ}\text{C}$. This demonstrates the square root dependence of the growth rate on the H_2O partial pressure. Solid lines represent a square root dependence.

3 and 5- μm -thick films and demonstrates that the growth rate of the YBCO films is proportional to the square root of the H_2O partial pressure in the processing atmosphere.

A cross-sectional transmission electron microscopy micrograph of a 3- μm -thick film is shown in Fig. 3. The film was removed from the furnace when the measured value of the conductance indicated that it was half processed. The micrograph reveals that the film consists of three regions, a c -axis oriented YBCO layer, a very thin ~ 7 nm amorphous layer, and untransformed material consisting of CuO grains and an oxifluoride compound. This is shown in Fig. 3(a) except for the CuO grains. Chemical analysis of these layers

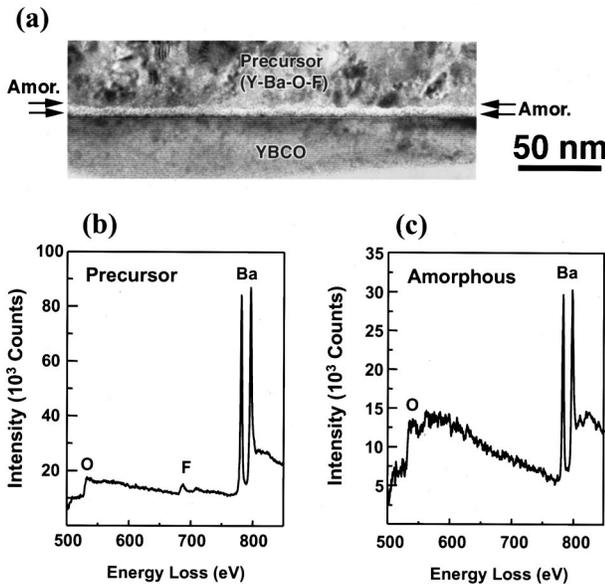
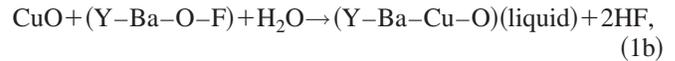
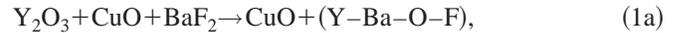


FIG. 3. (a) Transmission electron microscopy image of a half processed film demonstrating the presence of a thin ~ 7 nm thick amorphous region separating the transformed precursor and the YBCO growth front. (b),(c) EELS spectra from the precursor and the amorphous regions are compared. Note that both regions show the spectra for oxygen and Ba but the spectrum for F was not seen in the amorphous region suggesting that the decomposition of the fluoride takes place at the precursor-amorphous interface. The increased noise in the EELS signal for the amorphous layer as compared to the precursor material is due to the need for a smaller electron beam.

by electron energy loss spectroscopy (EELS) and energy dispersive x-ray spectroscopy, revealed the following: (1) The fluorine content in the precursor material adjacent to the amorphous layer, Fig. 3(b), was approximately equal to that of the precursor films prior to processing. (2) The fluorine is contained in an oxifluoride compound (Y-Ba-O-F) with a face-centered-cubic structure and a lattice parameter very close to that of BaF_2 as determined by electron diffraction analysis. (3) As shown in Fig. 3(c) there was no detectable fluorine in the amorphous (liquid) layer.

This suggests that the chemical reaction for the decomposition of the precursor material and the formation of YBCO can be written schematically as



In order to better understand the kinetics of the growth of YBCO in this process, particularly the observed square root dependence of the growth rate upon the partial pressure of H_2O , we proceed with the following assumptions. The YBCO growth rate is limited by the decomposition of the oxifluoride compound and the relevant chemical equilibrium is reaction (1b) given earlier. It is also assumed that the YBCO growth rate is independent of the oxygen partial pressure during processing. This is supported by the data in Fig. 1. Taking into account the slow YBCO growth rate the reaction is assumed to be only slightly shifted from equilibrium and standard chemical equilibrium theory can be applied.

If reaction (1b) is characterized by equilibrium constant K , then the partial pressures of H_2O and HF at the precursor-liquid phase interface, $p_{H_2O}^i$ and p_{HF}^i , are given by

$$p_{HF}^i / (p_{H_2O}^i)^{1/2} = K, \quad (2)$$

where the superscript “ i ” denotes the partial pressure at the interface. We also assume there is no absorption or release of HF or H_2O in the precursor and that the gradients of the partial pressures, p , across the precursor thickness are constant (linear isotherms). Then, the fluxes for H_2O and HF at the interfaces, F_{H_2O} and F_{HF} , respectively, are expressed as

$$F_{H_2O} = D_{H_2O} (p_{H_2O}^s - p_{H_2O}^i) / d, \quad (3)$$

$$F_{HF} = D_{HF} (p_{HF}^s - p_{HF}^i) / d, \quad (4)$$

where the superscript “ s ” designates the partial pressure at the surface of the film and d is the thickness of the remaining precursor material. D_{H_2O} and D_{HF} are the diffusion constants (cm^2/s) for H_2O and HF and are defined as $D = P/S$ where P is the permeability (moles/Torr cm s) and S is the solubility (moles/Torr cm^3). The pressure is given by $p = C/S$ where C is the concentration (moles/ cm^3) in the precursor material.⁹ The partial pressure of HF at the film surface is assumed to be much less than the HF partial pressure at the interface and is set equal to zero, i.e., $p_{HF}^s = 0$. The YBCO growth rate, G_{YBCO} , is proportional to the rate of the decomposition of the Y-Ba-O-F compound which is in turn is controlled by the flux of H_2O or HF . From Eqs. (2)–(4) we find

$$\begin{aligned}
 G_{\text{YBCO}} &\propto F_{\text{H}_2\text{O}} \\
 &= -2F_{\text{HF}} \\
 &= 2KD_{\text{HF}}(\sqrt{p^* + p_{\text{H}_2\text{O}}^s} - \sqrt{p^*})/d,
 \end{aligned} \quad (5)$$

where $p^* = (D_{\text{HF}}K/D_{\text{H}_2\text{O}})^2$. Consider the following limiting cases of Eq. (5)

(a) $p_{\text{H}_2\text{O}}^s \ll p^*$

$$G_{\text{YBCO}} \propto \frac{D_{\text{H}_2\text{O}}}{d} p_{\text{H}_2\text{O}}^s \quad (6)$$

(b) $p_{\text{H}_2\text{O}}^s \gg p^*$

$$G_{\text{YBCO}} \propto \frac{2KD_{\text{HF}}}{d} \sqrt{p_{\text{H}_2\text{O}}^s}. \quad (7)$$

In the first case the water vapor pressure is low and the reaction rate at the interface is limited by the supply of water. The growth rate depends linearly upon the diffusion constant for water, $D_{\text{H}_2\text{O}}$, and the water vapor partial pressure, $p_{\text{H}_2\text{O}}^s$. In the second case the water vapor pressure is high enough so that the removal of HF limits the interface reaction and subsequent growth rate. For the experiments reported here the growth rate of YBCO is proportional to the square root of the water partial pressure in the processing atmosphere as shown in Fig. 2. We conclude therefore that the water vapor pressures used, 25–200 Torr, are high enough to satisfy the second case. The growth rate is also proportional to the equilibrium rate constant K for the decomposition of the fluoride and the HF diffusion constant, D_{HF} . This suggests methods for increasing the YBCO growth rate. For example it may be possible to increase D_{HF} by altering the chemical makeup of the precursor material or affecting the microstructure of the precursor film. Faster growth rates than presented here have been achieved in a similar process involving a chemically derived precursor.⁸ These precursor films are known to be highly porous perhaps allowing easier out-diffusion of HF.

One difficulty with this analysis is that the growth rate is inversely proportional to the thickness, d , of the unreacted precursor film. This thickness, d , decreases as the YBCO film grows and the model presented should take into account a moving boundary. This then predicts the growth of a film being proportional to a square root of the processing time in

contrast to the observed linear time dependence of $\sigma(t)$. Here, we speculate on possible sources of this contradiction. One possibility is that the precursor film is infused with percolating channels separated by an average distance d_{ch} . The density and cross-sectional area of the channels need only be sufficiently large that the gas-phase diffusion of water and HF in the channels is much faster than their diffusion in the precursor. In such a case, one can show that the pertinent diffusion distance is the approximate distance between the channels, d_{ch} . Then Eqs. (3) and (4) are still valid with d replaced by $\sim d_{\text{ch}}$ and the growth rate Eqs. (5)–(7) remain the same with the precursor film thickness d replaced by $\sim d_{\text{ch}}$. In such a model, the growth rate becomes constant. Another possibility is that the gas-phase diffusion of HF at the film surface, rather than solid-state diffusion in the precursor, controls the growth rate. In this case the growth rate will obviously be independent of the thickness of the film and remain constant for the duration of the heat treatment. These possibilities will be further investigated in order to clarify the limiting mechanism for the growth of a YBCO layer in this *ex situ* reaction process.

This work was carried out under auspices of in part Division of Materials Sciences, Office of Basic Energy Sciences, and Office of Energy Efficiency and Renewable Energy, U.S. Department of Energy under Contract No. DE-AC02-98CH10886.

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