Modification and Conversion of E-beam Co-evaporated Precursors for Fabricating High Critical Current $YBa_2Cu_3O_{7-\delta}$ Films

Yifei Zhang, Ron Feenstra, Claudia Cantoni, David K. Christen, and Dean J. Miller

***Abstract*—*Ex situ* conversion of *e*-beam co-evaporated precursors was studied in an effort to fabricate high critical current YBCO films using the BaF_2 process. It was shown that an intermediate oxygenation annealing prior to the conversion modifies the precursor crystallinity and promotes *c*-axis epitaxial growth while randomly-oriented film formation is suppressed. With the modified precursors, a critical current density (J_c, 77 K & 0 T) of 2.1 MA/cm^2 measured by SQUID magnetometry was obtained in 1.8 μm thick YBCO films. This corresponds to an estimated transport critical current I_c of about 500 A/cm-width. The mechanism of the pre-annealing effect was investigated by characterization of the precursors, quenched films, and fully converted films using XRD, SEM, and TEM. Cross-sectional TEM was used to study the early nucleation of YBCO film at the precursor/substrate interface. The significant effect of the precursor modification indicated that, in addition to optimizing conversion processing parameters, modifying the precursor is an effective way to achieve the desired epitaxial film structure and to obtain higher critical currents, I_c.**

***Index Terms*—critical current density, epitaxial growth, nucleation, YBCO film.**

I. INTRODUCTION

GREAT achievements have been made during the last decade in the development of the technology for fabricating $YBa_2Cu_3O_{7-\delta}$ (YBCO) coated conductors for energy efficient electric-power applications. Biaxially textured substrate templates can now be fabricated using techniques such as RABiTS (Rolling Assisted Biaxially Textured Substrate) or IBAD (Ion Beam Assisted Deposition). The properties of YBCO films made by either *in situ* or *ex situ* methods have been significantly improved and interim performance requirements have been met, to some extent, by laboratory short samples as well as long-length pilot wires. Efforts being made in industries include scaling up the process to fabricate long tapes that are readily available for practical applications. The goal, for example, is to produce 1,000 m tapes with critical current I_c (77 K, self-field) reaching 1,000 A/cm-width [1].

In the process of scaling-up for practical production, many technical challenges still exist. The main challenges include (1) finding simpler, therefore more economical ways of making substrate/buffer template, (2) improving the existing techniques or developing new deposition methods to achieve higher throughput of YBCO film, (3) realizing end-to-end property uniformity in long length, and (4) attaining critical currents that scale with film thickness.

The thickness dependence in properties has been widely observed for YBCO films made by different techniques. Typically, with an increase of film thickness the critical current density (J_c) decreases. Although the mechanisms underlying the phenomenon are still under investigation, characterization of thick films has revealed that structural degradation plays a role in the property deterioration [2-4]. Through-thickness structural variation found in thicker films includes deviation in YBCO orientation, secondary phase formation, porosity, *etc*. Therefore, the phase integrity and texture quality of thicker films are generally not as good as those of thinner films (<1μm). The through-thickness structural variation such as the deviation of YBCO orientation from the *c*-axis texture suggests that film thickness may have effects on the YBCO nucleation and growth in *ex situ* films.

Fabrication of YBCO films by *ex situ* techniques involves deposition of a precursor film on a biaxially textured template by solution coating, as in the TFA-MOD method, or by co-evaporation, as in the BaF_2 process. The epitaxial YBCO film is then formed during a high-temperature processing of the precursor. The conversion is normally carried out in a wet oxygen ambient. Using *e*-beam co-evaporation, it is relatively easier to deposit dense, homogeneous and thick precursors than using TFA-MOD.

In principle, the thermodynamics and kinetics of the conversion reaction and YBCO formation are determined by the processing conditions and the structure and chemistry of the precursors. Since the YBCO structure and properties are very sensitive to the conversion condition, most studies have focused on the effects of the processing parameters during the conversion, such as temperature, oxygen partial pressure, water partial pressure, *etc*. While optimization of processing condition appears to be very important for evident reasons, the

---

Manuscript received 25 August 2008. This work was sponsored by the U.S. Department of Energy, Office of Electricity Delivery and Energy Reliability and Basic Energy Sciences as part of a DOE program to develop electric power technology. The work at Oak Ridge was performed under contract No. DE-AC05-00OR22725 with UT-Batelle, LLC. The work at Argonne was performed under contract W-31-109-ENG-38.

Y. Zhang, R. Feenstra, C. Cantoni, and D. K. Christen are with the Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA (phone: 865-574-6264; fax: 865-574-6263; e-mail: zhangyf@ornl.gov).

D. J. Miller is with the Argonne National Laboratory, Argonne, IL 60439 USA (e-mail: miller@anl.gov).

effects of the precursor itself on the conversion have drawn little attention, especially in the case of the BaF_2 process. When thicker precursors cannot be simply converted under the same conditions used for thinner ones, the thickness emerges as a new parameter. The suggestion is that the precursor itself may need to be changed to cope with the thickness dependence issue. It is possible to make thicker precursors also "conversion-friendly" by modifying their structure and chemistry [5, 6], which requires an understanding of what the important precursor characteristics are and how they affect the conversion.

Precursor modifications can be implemented not only during the deposition, but also afterwards. In this study, an intermediate oxygenation annealing at 500 °C was given to the precursor after the deposition and prior to the high-temperature processing. The modified and as-deposited precursors were converted under the same conditions, and the results were compared for evaluating the effects of the precursor modification. The precursors and converted films were characterized to study the effects of the pre-annealing. The emphasis in this report is on the precursor structure, while the changes in precursor chemistry will be addressed elsewhere.

II. EXPERIMENTAL

YBCO precursors were deposited on CeO_2 buffered single crystal (100) YSZ substrates (Crystal GmbH) by *e*-beam co-evaporation of Y, BaF_2 and Cu at a deposition rate of about 1 nm/sec. The oxygen pressure used during the deposition was about 5×10^{-6} Torr, and the substrate temperature was 100 °C. The CeO_2 buffer layer of 100~200 nm thick was deposited using rf magnetron sputtering from a commercial CeO_2 target (Plasmaterials) with the substrate temperature at 740 °C.

The precursor pre-anneals were done in a quartz tube furnace, under 1 *atm* pressure and various flowing gas ambients. The high-temperature conversion processing was carried out in a low-pressure rf furnace system in which the oxygen partial pressure (P_{O2}) and water partial pressure (P_{H2O}) were carefully controlled [7]. The system features a greatly reduced total pressure (P_{tot}), at levels between 50 to 200 mTorr, which is the sum of P_{O2} and P_{H2O}. A combination of a low total pressure and relatively higher water partial pressure facilitates a faster conversion of the precursors. Quenching of a sample was conducted by simply dropping it from the hot zone into the room temperature space.

The critical current densities of the fully converted films were measured by a Quantum Design MPMS 7 SQUID magnetometer, where the magnetic field was applied perpendicular to the film surface. The J_c values were determined according to the Bean critical state model, $J_c = 20\Delta M/[aV(1-a/3b)]$, where ΔM is the magnetic moment hysteresis (emu), V is the volume of the film, and $a \leq b$ are the lateral dimensions of the sample. All J_c values reported in this paper were obtained by magnetometer measurements.

XRD was used to study the early crystallization in the pre-annealed precursors. The phase composition and texture quality of fully converted films were also investigated by XRD. The film surface morphology was inspected by SEM as an indicator of YBCO orientation. Cross-sectional TEM was used to characterize the structures of the films at different states.

III. RESULTS AND DISCUSSION

A. YBCO Film Properties

High J_c (2.5~3.5 MA/cm^2) YBCO films can be readily made from our *e*-beam co-evaporated precursors with thickness below 0.5 μm. However, in order to avoid formation of randomly-orientated YBCO components, the conversion rates were limited to 0.1~0.2 nm/sec. While the *c*-axis YBCO nucleates epitaxially at the precursor/substrate interface, the randomly-oriented YBCO could nucleate homogeneously within the precursor. The as-deposited precursors are in a meta-stable state featuring a pseudo-amorphous structure. At the high-temperature processing condition, there is a large thermodynamic driving force for the precursor to transform into more stable phases. Randomly-oriented YBCO may nucleate when the nucleation barrier is overcome. The competition between heterogeneous epitaxial *c*-axis nucleation & growth and homogeneous random nucleation becomes more prominent for thicker precursors when the conversion inevitably needs longer time.

To suppress the randomly-oriented YBCO, the precursor needs to be relatively more stable. An intermediate temperature annealing was given to the precursors in order to adjust their thermodynamic state. A series of test anneals was conducted at various temperatures and in different gas ambients. It was found that annealing at 500 °C with pure oxygen could change the precursor conversion behavior. The main effects include: thinner (<0.5 μm) precursors, when pre-annealed, can be processed at faster conversion rates (0.7~1.2 nm/sec) while still achieving the same high J_c values equivalent to the un-pre-annealed films processed at slow rates; for thicker (0.5~1 μm) films, J_c's from the pre-annealed precursors are more than twice those for films converted from the as-deposited precursors. As an example, a 0.7 μm thick film (sample ID: S1) with a J_c of 2.7 MA/cm^2 (77 K, 0 T) is given in Table 1.

TABLE 1 PRE-ANNEAL SCHEMES FOR PRECURSORS AND J_c VALUES OF YBCO FILMS

Sample ID	Thickness (μm)	Pre-anneal Scheme	J_c (77 K, 0 T) (MA/cm^2)
S1	0.7	ann	2.7
S2	1.5	ann	0.2
B1	1.8	ann+ann	2.1
B2	1.8	ann+as	0.4
B3	1.8	as+ann	0.2
B4	1.8	as+as	0.1

When the pre-annealing experiments were extended to even thicker (1~2μm) films, the results indicated that the effect did not simply carry over. Conversion of the pre-annealed 1.5 μm thick precursors yields films with low J_c's. One example (sample ID: S2) is given in Table 1.

To understand how the effect is limited by the thickness, bi-layer precursors (total thickness=1.8 μm) were deposited with equal thicknesses of each individual layer. The bi-layer precursors (sample ID: B1~B4 in Table 1) were pre-annealed differently depending on whether there was one pre-anneal after the deposition of each individual layer. The pre-annealing scheme described in Table 1 for the bi-layer precursors is to be interpreted in the following way. The term "as + ann" for sample B3, for example, denotes that the precursor was not pre-annealed after the first layer's deposition but had a pre-anneal after the second layer's deposition. All the bi-layer precursors were then processed under the same conditions. The results given in Table 1 show that only the double-pre-annealed precursors (sample ID: B1) yielded high-J_c films (note that each J_c value listed here is an average from several samples identically processed.) The 2.1 MA/cm^2 J_c of the film measured by magnetometry corresponds to an equivalent transport critical current of about 500 A/cm-width. More importantly, the results indicated that the conversion is limited by precursor characteristics rather than by thickness.

B. *Structures of Fully Converted Films*

XRD and SEM were used to study the structure of fully converted films. The XRD θ~2θ diffraction patterns for each film with high-J_c show high intensity YBCO (00l) peaks, while patterns with low (00l) peak intensities always correspond to low-J_c films. YBCO (113) pole figure analysis further revealed the difference in texture quality of the different films. Film surface SEM images are consistent with the XRD data: in general, typical *c*-axis morphologies were observed for films with high J_c values while randomly-oriented YBCO, characterized by various needle-like features, emerged on the surfaces of low-J_c films. SEM surface images of sample B2 and B3, which both had low J_c values, are shown in Fig. 1 (a) and (b).

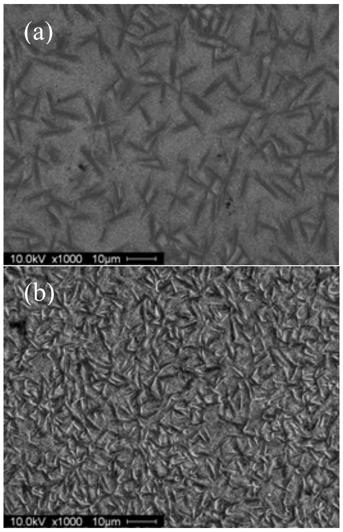

Fig. 1. SEM surface morphology images of (a) sample B2, and (b) sample B3.

The difference in the surface morphology between B2 and B3 indicates that although the films were converted under the same condition and both had low J_c's, their structural details are different. The bi-layer film B3 had a low J_c similar to the single-layer film S2, implying that when the thickness reaches 1.5 μm a single pre-annealing is not sufficient to suppress the formation of randomly-oriented YBCO. The surface image of B2 shows sparsely distributed "thick" random YBCO needles, differing from the densely distributed "thin" needles of B3 (and S2 as well, not shown here). This suggests that whether the single pre-anneal was given before or after the second layer's deposition had an effect on the kinetics of the randomly-oriented YBCO formation. Evidently, these changes resulted from modifications to the precursor structure and chemistry caused by the pre-annealing.

C. *Pre-annealed and As-deposited Precursors*

For precursors of the same thickness, the changes in their conversion behavior, *i.e.* the changes in their responses to the processing ambient in terms of phase nucleation and growth, are solely the results of the pre-annealing when the processing conditions were kept same. XRD and TEM were used to compare the precursors in order to pinpoint key factors that may dominate the precursor conversion behavior.

Shown in Fig. 2 are XRD θ~2θ scan patterns of two 0.7 μm thick precursors: one was pre-annealed and the other was in the as-deposited state. It can be seen that the as-deposited precursor was basically amorphous, showing no peaks other than those from the buffer and substrate. The pre-annealed precursor had crystallized BaF_2 and copper oxide CuO. Using the Sherrer equation, the size of the nano-crystallites can be calculated to be about 15 nm.

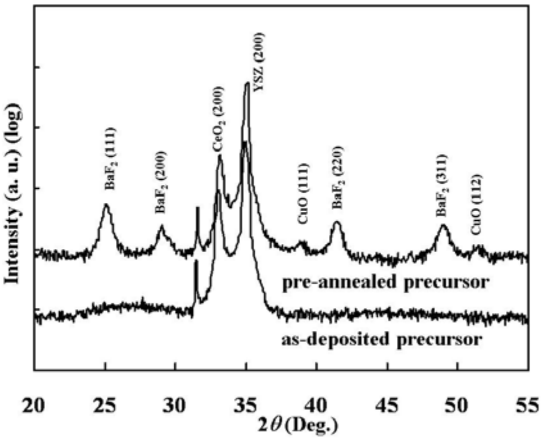

Fig. 2. XRD θ~2θ scan patterns of two 0.7 μm thick precursors, one was pre-annealed and the other was in the as-deposited state.

The formation of the nano-crystallites in pre-annealed precursors was further confirmed by TEM. The cross-sectional TEM image, Fig 3(a) shows the precipitates of the nano-crystallites in a pre-annealed precursor. In contrast, the TEM investigation did not find any crystallization in the as-deposited precursor, as shown in Fig 3(b). The essentially amorphous structure of the as-deposited precursors is one of the reasons why these precursors are more reactive or less stable. They are prone to structural changes under the processing condition at high temperature, making the homogeneous nucleation of random YBCO more liable.

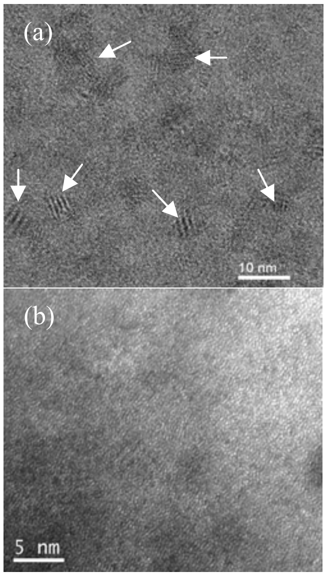

Fig. 3. Cross-sectional TEM images of (a) a pre-annealed precursor, and (b) an as-deposited precursor, both are 0.7 μm thick. The nano-crystallites are seen in the pre-annealed precursor, marked with the arrows, while the structure of the as-deposited precursor is basically amorphous.

D. Quenched Films

Characterization of quenched films is an effective way to investigate the early nucleation of YBCO films in the *ex situ* process. To find out whether the pre-annealing scheme had any influence on film nucleation, two samples were quenched from their processing temperature and then studied with TEM. The quenches were conducted 5 min after the samples reached the processing temperature. The two samples were both bi-layer 1.8 μm films. They were pre-annealed in the same way as B1 and B3, respectively, *i.e.*, one was double pre-annealed and the other had only one pre-annealing after the deposition of the second layer. The cross-sectional TEM images of the two quenched films are shown in Fig. 4(a) and (b).

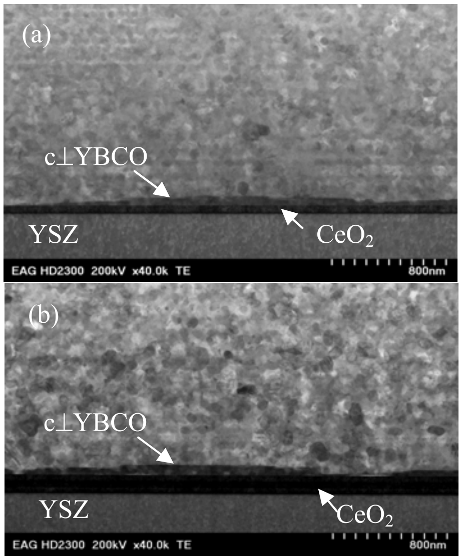

Fig. 4. Cross-sectional TEM images of the quenched bi-layer films for which (a) the precursor was double pre-annealed, and (b) the precursor was pre-annealed only once after the second layer's deposition.

For both the films, *c*-axis YBCO nuclei were seen at the precursor/substrate interface and no substantial difference in nucleus orientation and/or nucleation density is observed. Away from the interface, on the other hand, more prominent structural change can be seen in Fig. 4(b) for the precursor that had only one pre-anneal, while the double-pre-annealed one had less crystallization at the moment of the quench.

IV. CONCLUSION

The oxygen pre-annealing is an effective way to modify the precursor such that in the high temperature conversion of the precursor the *c*-axis YBCO formation is promoted and the randomly-oriented YBCO is suppressed. Nano-crystallites formed during the pre-annealing are presumably one of the reasons that are accountable for this effect. The beneficial effect appears to be limited to precursor thicknesses below 1 μm when the single layer films were processed. The reason for this limitation needs to be further investigated. It was demonstrated that 1.8 μm YBCO films with J_c (77K, 0T) > 2 MA/cm^2 could be reproducibly fabricated from bi-layer precursors when the intermediate temperature pre-annealing was given after each layer's deposition. It is evident that in addition to optimizing processing condition, the modification of the precursors can help improve the *ex situ* process for effectively fabricating high I_c YBCO films.

Preliminary investigation shows no significant difference in the heterogeneous YBCO nucleation at the precursor/substrate interface for the bi-layer precursor having double pre-annealing and the precursor having only one pre-annealing. Further investigation on YBCO nucleation, including homogeneous nucleation which leads to the formation of randomly-oriented YBCO, is required.

REFERENCES

[1] http://www.oe.energy.gov/hts_02.htm

[2] S. I. Kim, A. Gurevich, X. Song, X. Li, W. Zhang, T. Kodenkandath, M. W. Rupich, T. G. Holesinger, and D. C. Larbalestier, "Mechanisms of weak thickness dependence of the critical current density in strong-pinning *ex situ* metal-organic-deposition-route $YBa_2Cu_3O_{7-x}$ coated conductors," *Supercond. Sci. Technol.,* vol. 19, pp. 968-979, Aug. 2006.

[3] Q. X. Jia, H. Wang, Y. Lin, Y. Li, C. Wetteland, G. W. Brown, M. Hawley, B. Maiorov, S.R. Foltyn, L. Civale, P. N. Arendt, and J. L. MacManus-Driscoll, "Microstructural Evolution with the change in thickness of superconducting films," *IEEE. Trans. Appli. Supercon.*, vol. 17, pp. 3243-3246, Jun. 2007.

[4] V. F. Solovyov, H. J. Wiesmann, and M. Suenaga, "Critical current densities and the structural quality of 3- and 4-μm-thick superconducting $YBa_2Cu_3O_7$ layers synthesized using the *ex situ* process," *J. Appli. Phys.*, vol. 102, pp. 053902, Sep. 2007.

[5] R. Feenstra, A. A. Gapud, F. A. List, E. D. Specht, D. K. Christen, T. G. Holesinger, and D. M. Feldmann, "Critical currents I_c (77 K) > 350 A/cm-width achieved in ex situ YBCO coated conductors using a faster conversion process," *IEEE Trans. Appl. Supercond.*, vol.15, pp. 2803-2807, Jun. 2005.

[6] Y. Zhang, R. Feenstra, and D. K. Christen, "X-ray photoelectron spectroscopy study on e-beam co-evaporated precursors and their post-deposition conversion," in *MRS Conf. Proc.*, 2005, vol. 868E, p. C7.9.

[7] Y. Zhang, R. Feenstra, J. R. Thompson, A. A. Gapud, T. Aytug, P. M. Martin, and D. K. Christen, "High critical current density $YBa_2Cu_3O_{7-\delta}$ thin films fabricated by *ex situ* processing at low pressures," *Supercond. Sci. Technol.*, vol.17, pp.1154-1159, Jul. 2004.