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Physica C 351 (2001) 175–181

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**PHYSICA** C

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# Continuous deposition of ex situ YBCO precursor films on rolling-assisted biaxially textured substrates by electron beam evaporation

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Received 7 April 2000; accepted 5 October 2000

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## Abstract

A reel-to-reel electron beam evaporation system has been developed to continuously deposit Y–BaF<sub>2</sub>–Cu precursor for ex situ YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (YBCO) processed films. The quality of a YBCO film on biaxially textured, oxide buffered, Ni tape strongly depends on the condition of the precursor deposit. For continuous precursor deposition, a uniform cation stoichiometry (i.e., Y:Ba:Cu = 1:2:3) over the entire length of precursor film is essential. Rutherford backscattering spectrometry studies indicated that the partial pressure of water vapor during the deposition has a significant effect on cation deposition rates and the oxygen content in the precursor film. The oxygen content of the precursor is increased and the precursor stability upon exposure to air is improved by introduction of water vapor during precursor deposition. High quality precursor films with a thickness of 300 nm have been deposited on lengths of rolling-assisted, biaxially textured substrates in the reel-to-reel electron beam evaporation system. In this paper, long length precursor deposition processing will be discussed. Properties of some post-annealed YBCO films will also be presented. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* High-*T<sub>c</sub>* superconductors; Continuous deposition; Biaxial texture; Ex situ YBCO precursors; E-beam evaporation

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## 1. Introduction

Since the discovery of high temperature superconductivity (HTS) in 1986, significant progress

has been made towards fabricating long, flexible HTS wires and cables with high critical current densities ( $J_c$ ) for various electrical industry applications. One of the most successful approaches to date is the so-called oxide-powder-in-tube (OPIT) process to produce high critical current density, polycrystalline, silver-sheathed Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> (Bi-2212) and Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> (Bi-2223) tapes [1–3]. Although thousands of meters of OPIT Bi-2212 and Bi-2223 tape have been fabricated, the intrinsic properties of Bi-based compounds (i.e., the

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temperature dependence of the irreversibility field) limit Bi-based HTS tapes to applications either in low magnetic fields and high temperatures ( $>75$  K) or in higher magnetic fields and low temperatures ( $<40$  K). Compared with Bi-based compounds,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) compounds have extraordinarily high critical current density at high temperature ( $>75$  K) in the presence of magnetic fields that are usually required for electric power applications including motors, generators and magnets [4]. However, high  $J_c$  values can only be obtained for YBCO films that are oriented with a high degree of crystalline texture both normal to and within the basal plane. A biaxial textured substrate is essential for the preparation of textured YBCO films. One approach, known as the rolling-assisted biaxially textured substrate (RABiTS) process, uses a biaxially textured Ni tape prepared by cold rolling and annealing as a template to deposit both buffer layers and superconductors. High critical current densities greater than  $10^6$  A/cm<sup>2</sup> have been demonstrated for short lengths of deposited YBCO conductor made by the RABiTS approach [5–8].

A successful RABiTS architecture for short samples is  $\text{CeO}_2/\text{YSZ}/\text{CeO}_2/\text{Ni}$  [9–13]. Although meter lengths of RABiTS substrates have been prepared [14,15], one meter lengths of high  $J_c$  YBCO conductors have not yet been produced by the RABiTS approach. Obviously, a continuous process is required for any large-scale production of superconductor tapes. Starting with rolled Ni tapes, four additional steps must be performed in a continuous fashion: annealing the Ni to obtain the cube texture, depositing suitable epitaxial buffer layers, depositing YBCO precursors, and post processing to form YBCO films. One approach for growing YBCO in a continuous mode is the ex situ  $\text{BaF}_2$  precursor process [16]. This involves coating Y– $\text{BaF}_2$ –Cu precursors on epitaxial substrates at room or near room temperature, then annealing or converting precursors to YBCO films at high temperatures.

The critical current density of a YBCO film on RABiTS strongly depends on precursor quality or deposition conditions. For continuous precursor deposition, a uniform cation stoichiometry (i.e., Y:Ba:Cu = 1:2:3) over the entire length of pre-

cursor film is essential. In addition, a high quality precursor film should be free of delamination or cracks and chemically stable upon exposure to air. Our studies indicate that the partial pressure of water vapor during precursor deposition has significant effects on cation deposition rates and the oxygen content in the precursor film. Introduction of water vapor during the deposition increases the oxygen content of the precursor, and the precursor stability following exposure to air is also improved. A reel-to-reel electron beam coevaporation system has been developed to continuously deposit Y– $\text{BaF}_2$ –Cu precursors on RABiTS. High quality precursor films with a thickness of 300 nm have been deposited on meter lengths of RABiTS in a continuous mode. A critical current density as high as 500,000 A/cm<sup>2</sup> in self-field at 77 K has been achieved for YBCO films on short segments (5 cm long, 1 cm wide, 300 nm thick) of these precursor films.

In this paper, long length precursor deposition processing by electron beam coevaporation will be discussed. Properties of some post-annealed YBCO films will also be presented.

## 2. Experimental

The precursor tapes were deposited by coevaporating Y,  $\text{BaF}_2$  and Cu in a reel-to-reel electron beam evaporation system, which had been described elsewhere in more detail [14]. Deposition rates for the three cation materials were measured by three identical Leybold Inficon XTC/2 quartz crystal monitors (QCM). Each monitor was aimed at the center of its corresponding source. To prevent cross talk from other sources, each monitor was equipped with a  $\sim 25$  cm long shielding tube. There was also a tungsten cap with perforated holes covering the  $\text{BaF}_2$  source to avoid decomposition of  $\text{BaF}_2$  arising from direct electron beam bombardment. A cm wide, 50  $\mu\text{m}$  thick Ni tape was mounted on two reels – one driven continuously by a stepper motor and one tensioned by a variable torque motor. The travel speed of the tape could be varied from 5 to 2500 cm/h. The integral reel-to-reel system has the capability of processing up to two meters of buffered tape

without breaking vacuum to refill the crucibles. Overnight pumping yielded a base pressure of  $1 \times 10^{-7}$  Torr. The partial pressures of  $\text{H}_2\text{O}$  and  $\text{O}_2$  were controlled by precision leak valves, and the partial pressures of  $\text{H}_2\text{O}$ ,  $\text{H}_2$  and  $\text{O}_2$  were monitored by a SRS 100RGA mass spectrometer. The long length RABiTS tapes used for precursor deposition were prepared by sputtering [15], and had an architecture of  $\text{CeO}_2/\text{YSZ}/\text{CeO}_2$  on rolled Ni. Long-length precursor tapes were ex situ converted to YBCO in a furnace under 1 atm pressure of  $\text{O}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$  [16–18].

### 3. Results and discussion

#### 3.1. Cation rate control

During precursor deposition, the QCM deposition rates were set to yield a film cation ratio Y:Ba:Cu=1:2:3, as determined by Rutherford backscattering spectrometry (RBS). However, these QCM rates strongly depended on the residual gas pressure of the vacuum chamber. As the partial pressure of  $\text{H}_2\text{O}$  or  $\text{O}_2$  changed, the QCM deposition rates required to achieve the 1:2:3 ratio would also change. In order to understand such changes, a series of precursor samples were deposited on rolled Ni tapes under different  $\text{H}_2\text{O}$  partial pressures. All these samples had the 1:2:3 cation stoichiometry as determined by RBS measurements. Fig. 1 shows a plot of Y, Ba QCM deposition rate changes relative to the Cu rate as a function of  $\text{H}_2\text{O}$  pressure. The QCM rate change for Y was pronounced while the QCM rate change for  $\text{BaF}_2$  was negligible. This was probably because Y was more reactive with water vapor than  $\text{BaF}_2$  or copper. For example, in order to maintain the correct 1:2:3 cation stoichiometry, the QCM Y rate relative to the QCM Cu rate at a  $p(\text{H}_2\text{O})$  of  $1 \times 10^{-5}$  Torr should be 36% more than that at a  $p(\text{H}_2\text{O})$  of  $5 \times 10^{-7}$  Torr. It seems that because yttrium oxide forms more readily on the QCM at higher  $p(\text{H}_2\text{O})$ , the sensitivity of the QCM (Z-ratio, density) to the effective deposition rate of Y increases. In order to maintain precursor stoichiometry during the long period of precursor

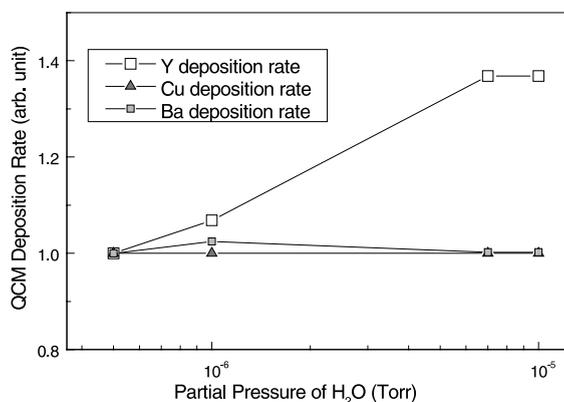


Fig. 1. Deposition rate registered on QCM as a function of water vapor pressure. These rates are required to maintain a cation composition of Y, Ba and Cu = 1:2:3.

deposition, the water vapor pressure needs to be constant.

Water vapor can be replaced by  $\text{O}_2$  during precursor deposition. The advantage of using  $\text{O}_2$  is that the total chamber pressure for a given oxygen activity would be much lower than that by using water vapor. For high rate deposition where high oxygen activity is required for rapid oxidation, this would be a significant advantage. However, high  $\text{O}_2$  partial pressures might lead to oxidation of the electron beam filaments, sources, and the nickel substrates.

Using QCM to maintain stable, controlled co-evaporation rates from three sources over long periods of deposition time is experimentally challenging. In addition to the constant supply of  $\text{H}_2\text{O}$  or  $\text{O}_2$ , the sources need to be evaporated uniformly during the deposition. The type of crucible liner for each target material, the sweep pattern of the electron beam over the source, and changes in shape of a solid source at high temperature would all contribute to the QCM rate changes. Despite these challenges, many RABiTS lengths up to 1 m long have been coevaporated with precursors by our reel-to-reel electron beam system using QCM control. For a typical 70 cm long, 1 cm wide and 300 nm thick Y– $\text{BaF}_2$ –Cu precursor tape, the cation deviations from end to end for Y, Ba and Cu were  $\pm 3\%$ ,  $\pm 3\%$  and  $\pm 2\%$ , respectively.

### 3.2. Oxygen content in precursor films

Precursor samples were deposited on vitreous graphite substrates to examine the composition of O, F, Ba, Cu and Y individually by RBS. The combined deposition rate was 0.7 nm/s with a  $p(\text{H}_2\text{O})$  of  $1 \times 10^{-5}$  Torr. Fig. 2 shows an RBS measurement on such a precursor film. Results from the simulation [20, 21] in Fig. 2 indicated that while the composition of Y, Ba and Cu was 1:2:3, F was about 4, and O was 3.0. For a precursor film deposited under  $1 \times 10^{-6}$  Torr water vapor pressure, O was only 2.4 while the other elements were almost the same. With lower O content, precursor films were more susceptible to changes in color or even delamination upon exposure to air. It seems that due to the lower initial oxygen content, precursors tend to absorb more oxygen upon exposure to air, which in turn might cause a severe anisotropic volume change along the depth of the precursor film. Our experimental results show that precursor films would delaminate if they were deposited at a  $p(\text{H}_2\text{O})$  of less than  $1 \times 10^{-6}$  Torr or a  $p(\text{O}_2)$  of less than  $5 \times 10^{-7}$  Torr. Therefore, during precursor deposition, a  $p(\text{H}_2\text{O})$  of  $1 \times 10^{-5}$  Torr or a  $p(\text{O}_2)$  of  $5 \times 10^{-6}$  Torr was used to avoid delaminating of the precursor films.

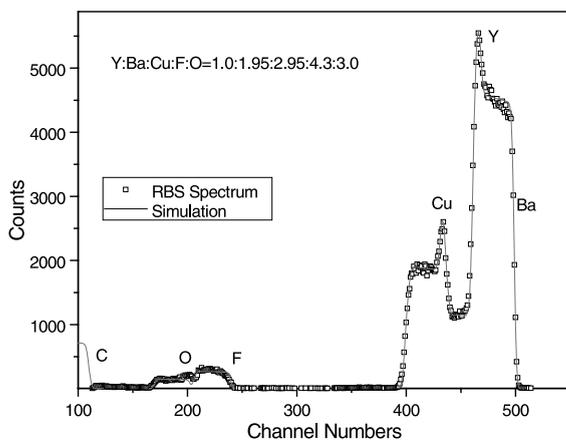


Fig. 2. A Rutherford backscattering spectrum of a Y–BaF<sub>2</sub>–Cu precursor film deposited on a graphite plate. The spectrum was measured with 2.3 MeV He ions at 160° detecting angle. The simulation was conducted by RBX program [21].

### 3.3. Substrate temperature during co-evaporation

Radiant heating from the three evaporation sources raised the precursor substrate temperature substantially above room temperature. To examine the effects of substrate temperature on precursor growth, a series of precursors were deposited on bare nickel at different substrate temperatures. Without substrate heating, precursor films were usually amorphous. An X-ray diffraction  $\theta$ – $2\theta$  scan showed only very weak BaF<sub>2</sub> peaks (Fig. 3). However, the intensity of BaF<sub>2</sub> (111) peaks increased dramatically as the substrate temperature increased. Fig. 3 suggests that at higher substrate temperatures, more crystalline BaF<sub>2</sub> formed in the precursor films. In order to further investigate the influence of crystalline BaF<sub>2</sub> on the YBCO growth, we deposited precursors on SrTiO<sub>3</sub> (STO) or CeO<sub>2</sub> coated YSZ single crystal substrates at different temperatures. These precursors were then post annealed to form YBCO at 740°C with  $p(\text{O}_2)$  of 100 mTorr and  $p(\text{H}_2\text{O})$  of 100 Torr [16,18]. Fig. 4 shows the critical current density ( $J_c$ ) for YBCO films at 77 K with and without heating to 400°C during the precursor deposition.  $J_c$  values were almost the same (1–2 MA/cm<sup>2</sup> at 0.1 T) for these two samples. In contrast, for the 500°C substrate temperature, the sample did not carry any current at 77 K and the surface color was partially brown after post annealing. This suggests that the formation of large

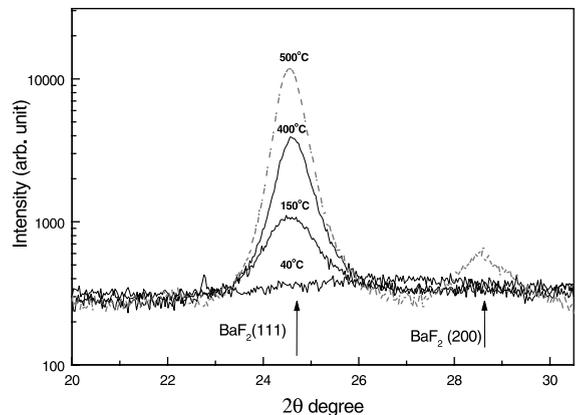


Fig. 3. X-ray diffraction  $\theta$ – $2\theta$  scans of precursor films formed at different substrate temperatures.

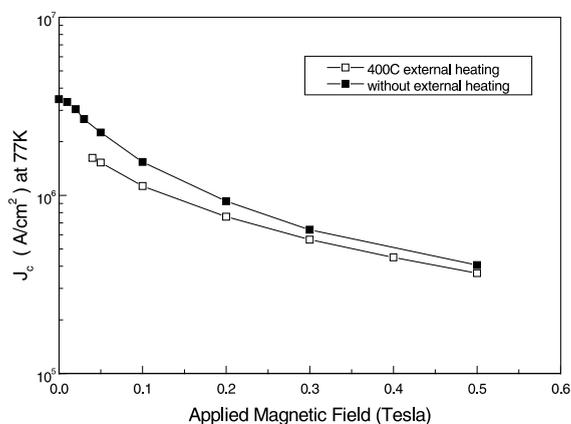


Fig. 4. Critical current density measurements at 77 K for the  $\text{CeO}_2$  coated YSZ single crystal substrates with 400°C external heating and without external heating during the precursor deposition. The field was parallel to the  $c$ -axis of the single crystal samples.

amounts or large sizes of crystalline  $\text{BaF}_2$  inhibits YBCO growth during annealing.

### 3.4. Long length YBCO tapes on RABiTS

To ultimately demonstrate the quality of long-length precursors on RABiTS tapes, high  $J_c$  YBCO superconductors must be grown. This requires both high quality precursor deposition and high quality precursor conversion to YBCO. We have deposited long-length precursors on RABiTS. These RABiTS tapes were obtained under

reel-to-reel moving tape condition and had an architecture of  $\text{CeO}_2/\text{YSZ}/\text{CeO}_2/\text{Ni}$ ; the thicknesses of the layers were 27, 800 and 27 nm, respectively. The precursors were deposited using a water vapor pressure of  $1 \times 10^{-5}$  Torr, an effective YBCO deposition rate of 0.7 nm/s and a tape speed of 35 cm/h. RBS measurements showed the composition ratios were  $\text{Y}:\text{Ba}:\text{Cu} = 1.03:2.06:3.00$ . The thickness, length and width of the YBCO tape were 310 nm, 70 and 1 cm, respectively. Then, the long-length precursor tape was ex situ annealed in a quartz tube furnace in a gas mixture of  $\text{H}_2\text{O}$ ,  $\text{O}_2$  and  $\text{N}_2$  under 1 atm total pressure [18]. Due to the short isothermal region (only 30 cm) and non-uniformity of gas flow along the length of our ex situ reaction furnace [19], the precursor tape was cut into short pieces for annealing in a stationary mode. Fig. 5 shows the XRD texture measurements of a 10 cm length of YBCO film. XRD in-plane  $\phi$ -scan (103) and out-of-plane  $\omega$ -scan (006) of the 10 cm long YBCO tape were  $(10.0 \pm 0.2)^\circ$  and  $(8.0 \pm 0.2)^\circ$ , respectively, indicating the excellent uniformity of the texture along the YBCO tape. The  $J_c$  measurements were made on a 5 cm long YBCO tape at 77 K in self-field. There were eight voltage measurement probes along the 5 cm length of YBCO tape; each was 0.5 cm from the next. Current probes were on both ends of the 5 cm tape. In order to reduce the heating during the measurement, each current lead was coated with silver on an area 0.5 cm long and 1 cm

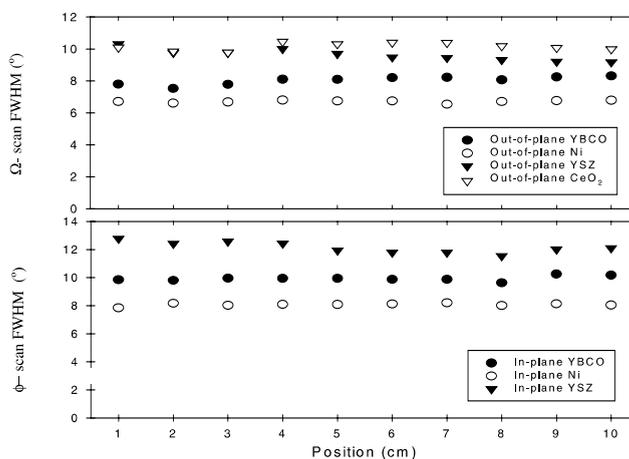


Fig. 5. In-plane  $\phi$  scans and out-of-plane  $\omega$  scans along a 10 cm length of YBCO tape.

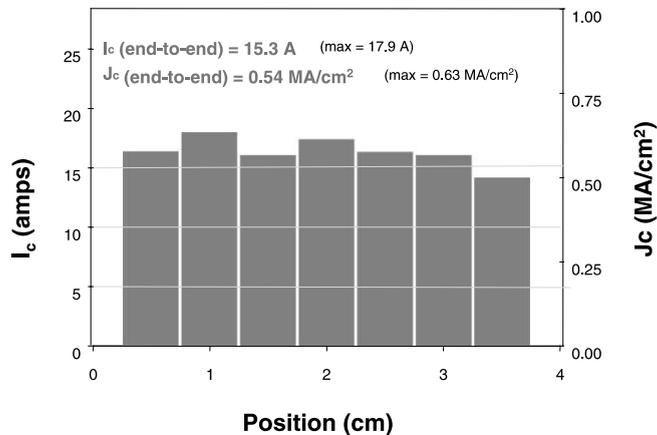


Fig. 6. Critical current density measurements for 3.5 cm of a 5 cm long YBCO tape at 77 K and in self-field. Gauge length is 0.5 cm.

wide. Therefore the  $J_c$  measurements were performed on only the central 3.5 cm of the 5 cm long YBCO tape. The entire tape and measurement block were immersed into a liquid nitrogen Dewar. From end to end,  $J_c$  at 77 K in self-field was determined to be 0.54 MA/cm<sup>2</sup> using a 1  $\mu$ V/cm criterion. Fig. 6 shows the  $J_c$  measurements on each 0.5 cm region of the tape. The standard deviation of  $J_c$  was less than  $\pm 7\%$ . These results suggest that the quality of the YBCO precursor tapes deposited by continuous electron beam coevaporation was excellent and adequate to produce high- $J_c$  YBCO superconducting tapes. This is the first time  $J_c$  of more than 0.5 MA/cm<sup>2</sup> has been reported for a 5 cm length of YBCO tape using the RABiTS approach. However, with the present conversion furnace, YBCO on RABiTS longer than 5 cm had much lower  $J_c$  after ex situ annealing process. That is mainly due to the non-uniformity of gas flow along the length and the short isothermal region of the furnace. For precursors longer than 5 cm, present conversion furnace needs to be modified in order to have an ex situ annealing process uniformly along the length. Therefore, the precursor conversion at this time limits the process to make long YBCO tape.

Efforts are underway to fabricate thicker and longer Y–BaF<sub>2</sub>–Cu precursor tapes with uniform stoichiometry along the length. In addition, a reel-to-reel ex situ reaction furnace is under construction using transverse gas flow to enable conversion of long lengths ( $\sim 1$ – $2$  m) of precursor tape

on RABiTS to high quality YBCO superconductors.

#### 4. Conclusion

We have developed a reel-to-reel electron beam coevaporation vacuum system to continuously deposit Y–BaF<sub>2</sub>–Cu precursors on long length RABiTS tapes. Experimental results showed that the quality of precursors strongly depends on the deposition conditions. A constant supply of O<sub>2</sub> or H<sub>2</sub>O is essential to obtain a uniform cation stoichiometry for thick or long length precursors.  $J_c$  measurements indicate that the long length precursors are compatible with the ex situ YBCO annealing process, and resulted in high  $J_c$  YBCO superconducting films.

#### Acknowledgements

The authors would like to thank R.A. Hawsey for his support. X. Cui and B.W. Kang would like to acknowledge the support from Oak Ridge Associated Universities. This work was conducted in part under a CRADA with 3M/Southwire/LANL funded by the US Department of Energy, the Office of Energy Efficiency and Renewable Energy, and the Office of Science. Oak Ridge National Laboratory is managed by Lockheed Martin Energy Research Corporation for the US Depart-

ment of Energy under contract no. DE-AC05-96OR22464.

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