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Dongqi Shi

University of Wollongong, dongqi@uow.edu.au

Lin Wang

University of Wollongong, lw997@uow.edu.au

Jung Ho Kim

University of Wollongong, jhk@uow.edu.au

Xuebin Zhu

University of Wollongong, xuebin@uow.edu.au

Min Liu

University of Wollongong, minliu@uow.edu.au

See next page for additional authors

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Authors

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YBCO Film With Sm Addition Using Low-Fluorine TFA-MOD Approach

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Abstract—Yttrium barium copper oxide (YBCO) film was synthesized by a metal-organic deposition (MOD) process with fluorine-free Y and Cu precursor. The precursor solution with Sm addition enabled further improvement of the thickness and uniformity of precursor films. The calcination and firing processes were studied, and the precursor film was successfully converted to dense and uniform YBCO film on LaAlO_3 (LAO) substrate after annealing in a wet Ar and O_2 atmosphere. The measured critical current density (J_c) value was about 80 A/cm-w (2.66 MA/cm²). The trifluoroacetate (TFA) reduced MOD process has the advantage that it has a larger tolerance for variations in the gas flow rate and path. The results on a Sm-YBCO film deposited on LAO with a CeO_2 buffer layer fabricated by MOD are also presented.

Index Terms—Coated conductor, fluorine, MOD, YBCO film.

I. INTRODUCTION

METAL-ORGANIC deposition (MOD) is a non-vacuum chemical solution deposition process capable of being scaled to industrial level applications with cost effectiveness. Recently, an MOD process for $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO)-based high temperature superconducting film has been developed very quickly [1]–[3], and YBCO thin films with high critical current density can be routinely fabricated by a MOD-TFA process using a trifluoroacetate (TFA)-based precursor solution [4]–[6]. The most important issues in the MOD-processing of YBCO coated conductor are synthesis of the MOD precursor solution and the heat-treatment process. The conventional MOD-TFA process using full metal-TFA salts in the precursor solution generates a large amount of HF gas during the calcination step.

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D. Shi, L. Wang, J. H. Kim, X. Zhu, Q. Li, R. Zeng, and J. Ahn are with the Institute of Superconducting & Electronic Materials (ISEM), University of Wollongong, Wollongong NSW 2522, Australia (e-mail: dongqi@uow.edu.au; lw997@uow.edu.au; jhk@uow.edu.au; xuebin@uow.edu.au; ql327@uow.edu.au; rzeng@uow.edu.au; ja970@uow.edu.au).

M. Liu is with The Key Laboratory of Advanced Functional Materials, Ministry of Education, Beijing University of Technology, Beijing 100022, China (e-mail: Lm@bjut.edu.cn;).

J. Yoo and Y. K. Kim are with the Korea Institute of Machinery and Materials (KIMM), Changwon, Kyungnam, 641-010, Republic of Korea (e-mail: yjm1682@kmail.kimm.re.kr; voice21@kmail.kimm.re.kr).

T. Yamashita, J. Barry, and R. Taylor are with Mesaplexx Pty Ltd., QLD 4113, Australia (e-mail: toru.yamashita@mesaplexx.com; john.barry@mesaplexx.com; richard.taylor@mesaplexx.com).

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As a result of this, a long processing time and special gas flow are required to fabricate large area crack-free precursor film, while the thickness of precursor film is limited to low values after single coating and calcination [7], [8]. This is a drawback for coated conductor and large area YBCO film for electronic applications. In order to overcome this problem, many efforts have been made to enhance the processing by modification of the precursor solution [9]–[14]. One of the approaches involves using reduced fluorine content in the precursor solution [13], [14].

In this report, the reduced TFA-MOD process was used to fabricate YBCO film. In order to enhance the viscosity of the solution, Sm was added using a chemical solution process.

II. EXPERIMENTS

The details of the synthesis of precursor solution have been reported elsewhere [15], [16]. In brief, fluorine-free yttrium and copper acetate-based metal salts were employed as yttrium and copper precursors. Those metal acetate-based salts were prepared by mixing metal acetate and suitable chelating agents. In addition to this, barium trifluoroacetate (TFA) salt was used as the barium precursor in the new precursor solution. The synthesized precursor solution was diluted with methanol and condensed to control the viscosity. The total content of fluorine in the precursor solution was only 30% of that for the conventional MOD-TFA precursor solution synthesized with metal-TFA salts (hereafter referred to as the all TFA solution). In addition to this, samarium precursor was added to the synthesized precursor solution. The amount of samarium in the precursor solution was less than 10%, and the viscosity of precursor solution was greatly improved by the samarium addition from 70 cP to 260 cP.

The Sm-YBCO precursor film was produced by spin coating on 10 mm × 10 mm single crystal LAO substrates. The gel films were treated through the standard two heating steps. First, they were decomposed to oxy-fluoride materials by increasing the temperature to 400 °C in a humid oxygen gas atmosphere from 200 °C. Then, the precursor films were heated to the maximum temperature (T_{max}) of 800 °C–820 °C in an Ar/ O_2 gas flow for 50 mins. In this work, the processing time is similar to the time of the standard TFA-MOD. The partial pressure of oxygen in the mixed gas was 1000 ppm, and the partial pressure of the water vapor ($P_{\text{H}_2\text{O}}$) was 5.5 vol%. After holding at T_{max} , the gas was switched to the dry mixture gas. The typical thickness of YBCO films is about 250 nm measured by stylus profilometer after chemical etching. X-ray diffraction (XRD) measurements were carried out to examine the phase composition of the YBCO films. X-ray pole figures were used to evaluate the out-of-plane

Fig. 1. XRD $\theta - 2\theta$ scan pattern of Sm-YBCO film on LaAlO_3 single crystal substrate.

Fig. 2. The pole figures of an Sm-YBCO film for the (103) plane and the (001) plane.

and in-plane textures of the YBCO films. DC four probe transport measurements were used to measure the critical current. The temperature and field dependences of the magnetic moment were investigated by employing a Quantum Design magnetic properties measurement system (MPMS) superconducting quantum interferometer device (SQUID) magnetometer with a maximum field of 5 T and temperature range $5 \text{ K} < T < 90 \text{ K}$.

The J_c values of the YBCO films in magnetic fields were determined by application of the Bean critical state model formula, $J_c(H) = 20\Delta m(H)/a(1 - (a/3b))$, where Δm is the vertical width of the magnetization hysteresis loop (emu cm^{-3}), and a and b (cm) are the cross-sectional dimensions of the sample perpendicular to the applied field, with $b \geq a$.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows a typical XRD pattern of Sm-YBCO film on LaAlO_3 (LAO) single crystal substrate. As shown in this figure, almost the same (0 0 l) reflections as for pure YBCO could be detected in the pattern of this film. However, there is a second phase peak at 32.26° (peak A). It may be a $\text{Ba}_2\text{Cu}_3\text{SmO}_7$ (101) peak (100% intensity at the powder diffraction).

Fig. 2 shows the pole figures, which indicate that the Sm-YBCO film has a biaxial texture with high pole symmetry, and no minor texture component is observed. The full width at half maximum values (FWHMs) of the in-plane and out-of-plane textures are 5.2° and 5.4° , respectively.

(a)

(b)

Fig. 3. AFM images of typical Sm-YBCO films on LAO substrate: (a) 2D deflection image; (b) 3D height image.

An atomic force microscope (AFM) image of the top of the Sm-YBCO sample is presented in Fig. 3. The film is dense, and there is no obvious porosity on the surface. However, outgrowths or particulates are evident on the surface. The AFM scan on this specimen indicates that the root mean square (R_{MS}) roughness over a $40 \mu\text{m} \times 40 \mu\text{m}$ area was about 107.4 nm, including the outgrowths, and was 54.7 nm over the same area if outgrowths are excluded.

Fig. 4 shows the critical temperature (T_c) and the critical current (I_c) plots of a typical Sm-YBCO sample with a thickness of 300 nm and a width of 7.1 mm. The V-I plot of the current measured in the specimen indicated that a 6.63 mm wide sample carried a critical current of 53 A at liquid nitrogen temperature, which is equivalent to a I_c of 80 A/cm-w and a J_c of 2.66 MA/cm^2 at 77 K and self-field. The T_c of the sample was 89 K as measured by MPMS.

Fig. 5 shows J_c - B properties of Sm-YBCO films at different temperatures. The magnetic field was applied parallel to the c-axis of each film. Sm-YBCO films show that J_c can not remain constant at the low applied magnetic field of 0.1 T, which

Fig. 4. I_c measurements of a typical Sm-YBCO/LAO sample, with the YBCO thickness 250 nm. The width of the sample was 6.1 mm. The inset shows T_c as determined from the magnetic moment versus temperature.

Fig. 5. Field dependence of the J_c at different temperatures for Sm-YBCO/LAO with the field parallel to the c -axis.

means there is not a single vortex pinning regime. However, it can be said there is some evidence of a vortex bundle regime up to 50 K. Fig. 6 shows the flux pinning force density calculated from $F_p = J_c(B) \times B$, while the maximum pinning force density at 50 K is about $10 \text{ GN} \cdot \text{m}^{-3}$ over a broad magnetic field range from 1.2 T to 3.1 T. From the above data, Sm addition has not achieved any flux pinning enhancement, and further process optimization will be continued.

For the ordinary TFA-MOD process, a uniform gas flow rate is critical to obtaining large area YBCO films. In this experiment, it is easy to obtain $30 \text{ mm} \times 30 \text{ mm}$ uniform YBCO film using just end to end gas flow inside a quartz tube, due to the minor amount of HF gas in the reduced TFA-MOD process.

Sm-YBCO film also was deposited on CeO_2 buffered LAO substrate. The CeO_2 buffer layer was deposited using a MOD process with cerium acetate and propionic acid as precursor chemicals. The cation concentrations were 0.05–0.1 M for the seed layer and 0.2 M for the film. The details of the CeO_2 MOD deposition will be reported elsewhere. This work was mostly intended to test the quality of the CeO_2 buffer layer fabricated by the MOD process, which will be transferred

Fig. 6. The pinning force density at different temperatures, with the field parallel to the c -axis.

Fig. 7. XRD $\theta - 2\theta$ scan pattern of Sm-YBCO film on LaAlO_3 single crystal substrate.

onto Ni-alloy substrate. Fig. 7 shows the XRD pattern of the Sm-YBCO/ CeO_2 /LAO, which shows the pure YBCO (001) peaks and the pure c -axis orientation of the CeO_2 film. Fig. 8 contains the XRD pole figures of the Sm-YBCO/ CeO_2 /LAO, which imply good in-plane and out-of-plane alignment. However, the FWHMs of the in-plane and out-of-plane textures are larger than on LAO. Fig. 9 shows the I_c plots of a typical sample of a Sm-YBCO/ CeO_2 /LAO sample with a thickness of 300 nm and a width of 6.26 mm. The current measured in the specimen indicated that sample carried a critical current of 27 A at 77 K and self-field, which is equivalent to an I_c of 43 A/cm-w and J_c of 1.4 MA/cm^2 .

IV. CONCLUSION

In summary, an F-free Y and Cu precursor solution was synthesized for MOD YBCO film in order to reduce the fluorine content. Sm addition was used to modify the viscosity of the solution. A crack-free Sm-YBCO film was fabricated through spin coating and a two-step heating process. The Sm-YBCO film on LAO substrate using the F-free Y and Cu precursor solution shows a critical current of 80 A/cm-w and a critical current density of 2.66 MA/cm^2 after a single coating. In addition

Fig. 8. The pole figures of Sm-YBCO film for the (103) plane and the (001) plane.

Fig. 9. I_c measurements of a typical Sm-YBCO/CeO₂/LAO sample at 77 K and self-field with an YBCO thickness of 250 nm. The width of the sample was 5.9 mm.

to this, Sm-YBCO film was fabricated on CeO₂ buffered LAO substrate, in which the CeO₂ buffer layer was deposited by the MOD method. Further optimization of the precursor solution and of multi-coated film is in progress.

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