

High- I_c single-coat YBCO films prepared by the MOD process

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Received 7 November 2011; accepted 23 November 2011

Abstract-- A single-coat $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) film of high critical currents (I_c) could be successfully fabricated by optimizing the viscosity of the coating solution in the metal-organic deposition (MOD) process. From a Ba-deficient coating solution (Y: Ba: Cu = 1: 1.5: 3) having the viscosity of 212 mPa·sec, 0.9 μm -thick single coat YBCO film with the I_c value of 289 A/cm-width ($J_c = 3.2 \text{ MA/cm}^2$) at 77 K was achievable on the SrTiO_3 (STO) substrate, which was superior to that of our previous report for 0.8 μm -thick single coat YBCO film from a stoichiometric coating solution (Y: Ba: Cu = 1: 2: 3) on the LaAlO_3 (LAO) substrate. This result might be attributed to denser and more homogeneous microstructure in the case of the YBCO film from the Ba-deficient coating solution.

1. INTRODUCTION

The MOD process is known to be cost-effective for the fabrication of YBCO coated conductors (CCs) which are attractive for various electric power applications [1-3]. Gupta *et al.* [4] first reported that the metal trifluoroacetate (TFA) precursors were suitable for avoiding the formation of BaCO_3 during the pyrolysis stage and thus YBCO films with high critical current density (J_c) over 1 MA/cm^2 at 77 K in self-field could be produced by the TFA-MOD method [5]. Thereafter, numerous literature [6, 7 and references therein] have reported MOD-processed YBCO films with even higher J_c values.

The TFA-MOD process had several drawbacks, including a long duration period (typically over 10 h) at the pyrolysis stage (normally up to 400°C) and a limited thickness (normally up to $\sim 0.5 \mu\text{m}$) of a single-coat YBCO film due to a serious crack formation [6] during the pyrolysis stage. By employing a fluorine-reduced precursor solution, the pyrolysis stage could be greatly shortened within 3 h [8, 9]. The cracks generated during the pyrolysis stage made it hard to produce high- I_c YBCO films since they were maintained after the firing stage. Thus, a multi-coating method has been developed to increase the film thickness of YBCO by several groups [10, 11], which is, however, inappropriate for a high throughput process of long-length CCs. An alternative approach is to increase the thickness of the single-coat YBCO film. Up to now, only two groups reported a successful fabrication of single-coat

high- I_c YBCO films, including our group [8] and American Superconductor Co. (AMSC) [11-13]. Our group reported a single-coat 0.8 μm -thick YBCO film having I_c of 212 A/cm-width at 77 K [8], and AMSC reported a single-coat 1.2 μm -thick YBCO film exhibiting I_c of 445 A/cm-width at 77 K [13].

In this study, at first, we carefully investigated the critical processing parameters leading to high- I_c YBCO films by the single dip coating method. Then, we tried to produce high- I_c YBCO films from the Ba-deficient coating solution since the YBCO films from the Ba-deficient coating solution were reported to exhibit higher J_c values compared with that from the stoichiometric one [14-17].

2. EXPERIMENTAL

The fluorine-reduced coating solutions were prepared by mixing two different solutions which had been prepared independently. For the solution containing Y and Cu components, Y and Cu acetylacetonate were totally dissolved in the propionic acid with pyridine. This solution was dried at 80°C to form a dark green gel, and dissolved again in methanol. For the solution containing Ba component, Ba-acetate was dissolved in TFA with distilled water, dried at 80°C to form Ba-TFA, and then dissolved again in methanol. The final coating solution was prepared by mixing these two different solutions. The cation ratios of the coating solutions were adjusted to have Y: Ba: Cu = 1 : 2 : 3 (stoichiometric coating solution) and 1 : 1.5 : 3 (Ba-deficient coating solution).

The coating solutions were dip-coated on the LAO and STO substrates with the withdrawal speed of 32 mm/min, and subsequently pyrolyzed up to 500°C with a heating rate of $3^\circ\text{C}/\text{min}$. As-pyrolyzed films were fired to grow YBCO films at 825°C for 2 h in 4.2 % humid atmosphere containing 300 ppm Ar/ O_2 and finally oxygenated at 450°C for 1 h in a pure oxygen gas atmosphere.

The viscosity of the coating solution was measured by a rotational rheometer. The phases and crystallographic orientations of the YBCO films were characterized by x-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation. Surface morphology and film thickness of the films were analyzed by scanning electron microscopy (SEM). The standard four-point probe method was employed for the transport

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measurements including superconducting transition temperature (T_c) and I_c at 77K in self-field using the voltage criterion of 1 $\mu\text{V}/\text{cm}$.

3. RESULTS AND DISCUSSION

To optimize the thickness of the single-coat YBCO film without cracking, we first measured the viscosity values of the stoichiometric coating solution with increasing its holding time up to 12 h at 80°C within an oven. The initial viscosity value of the coating solution was 2.7 mPa-sec. The viscosity variation of the coating solution with the holding time at 80°C is shown in Fig. 1. In this figure, one can see that as the holding time increases, the viscosity of the coating solution drastically increases and finally reaches at 254 mPa-sec after 12 h.

Each coating solution of its own viscosity was dip-coated on the LAO (001) substrates, and subsequently pyrolyzed up to 500°C within 3 h. Cross-sectional images of as-pyrolyzed films are shown in Fig. 2(a)-(e). As expected, the thickness of as-pyrolyzed films is increased with increasing the viscosity of the coating solution. In the case of 1.9 μm thickness, however, cracks are observed on the surface of the film as shown in Fig. 2(f). From these results, the critical thickness of as-pyrolyzed films for avoiding the crack formation is between 1.6 and 1.9 μm , which correspond to the viscosity values of 212 and 254 mPa-sec, respectively. The cracks most probably originate from an excessive drying stress caused by the shrinkage during the pyrolysis heat treatment [6].

As shown in Fig. 2(d), 1.6 μm -thick as-pyrolyzed film was obtained from the stoichiometric coating solution with the viscosity value of 212 mPa-sec. After the firing heat treatment of this film, 0.8 μm -thick YBCO film could be fabricated on the LAO (001) substrate, indicating that 50 % reduction in thickness occurred during the firing stage. With the same viscosity of 212 mPa-sec for the Ba-deficient coating solution, we could fabricate 0.9 μm thick YBCO film on the STO (001) substrate. The SEM micrographs of this sample are represented in Fig. 3(a) and (c). For a comparison, SEM micrographs of 0.8 μm -thick YBCO film from the stoichiometric coating solution,

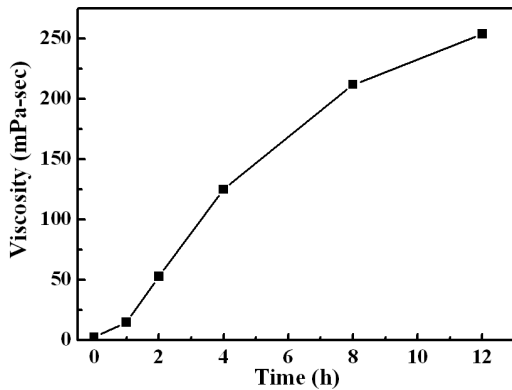


Fig. 1. Viscosity of the coating solution as a function of the holding time at 80°C.

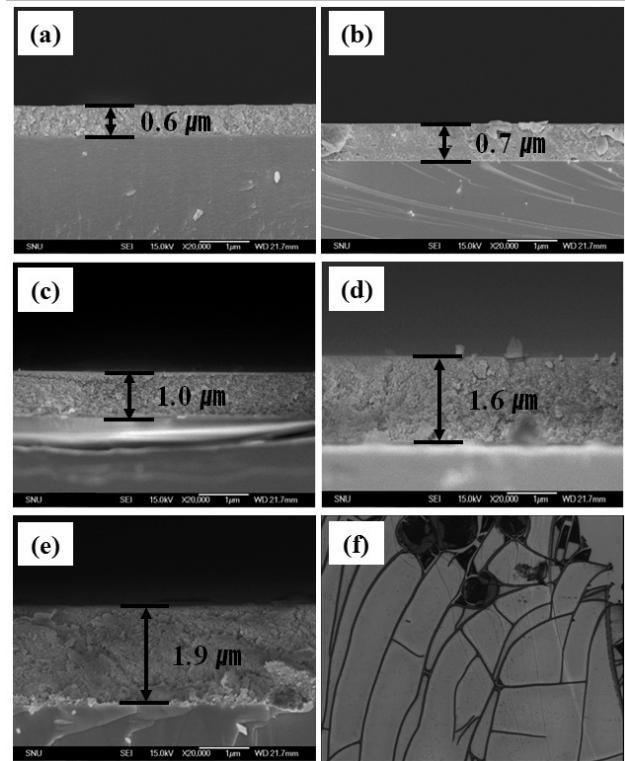


Fig. 2. SEM cross-sectional images of as-pyrolyzed films at 80°C for various holding periods: 1 h (a), 2 h (b), 4 h (c), 8 h (d), and 12 h (e). (f) is a plan-view of the sample (e) with an optical microscope (200 times magnification).

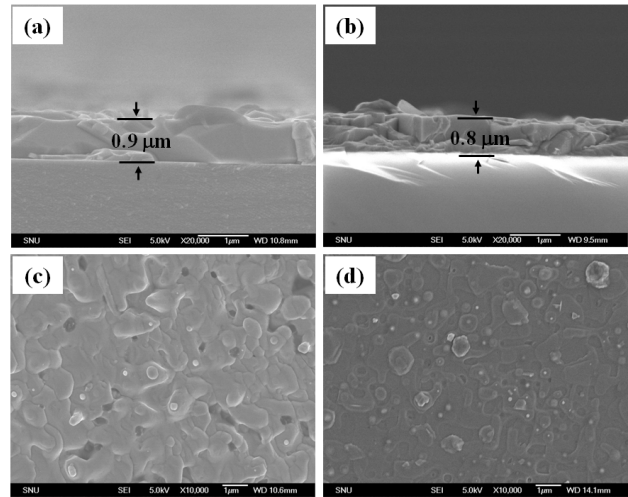


Fig. 3. SEM cross-sectional images of the YBCO films from the Ba-deficient coating solution (a) and the stoichiometric one (b). (c) and (d) are plan-view images of (a) and (b) samples, respectively. The micrographs (b) and (d) are from our previous report [8].

which were presented in our previous report [8], are also shown in Fig. 3(b) and (d). Compared with the YBCO film from the stoichiometric coating solution, the YBCO film

from the Ba-deficient coating solution exhibits a quite different surface morphology as shown in Fig. 3(c) and (d), which is probably due to larger amount of the liquid phase pushed to the top surface of the YBCO film in the case of the YBCO film from the Ba-deficient coating solution.

The XRD θ - 2θ diffraction pattern of the YBCO film from the Ba-deficient coating solution is represented in Fig. 4(a). For a comparison, the XRD pattern for the YBCO film from the stoichiometric coating solution is also represented. Both YBCO films are strongly c -axis oriented. In the YBCO film from the Ba-deficient coating solution, small peaks of the BaCuO₂ and CuO phases are detectable. These second phases are considered to exist at the film surface, which is in good agreement with the surface morphology shown in Fig. 3(c). Several groups [14, 15] reported that the secondary phases existing within the YBCO matrix from the the Ba-deficient coating solution were Y₂Cu₂O₅ and CuO by the TEM analyses. Although not presented, Y₂Cu₂O₅ nanoparticles trapped in the YBCO matrix were also observed by TEM in our samples. However, the Y₂Cu₂O₅ phase peak is unobservable in Fig. 4(a) because the amount of the Y₂Cu₂O₅ particles is small.

Fig. 5 shows the I - V curves of the YBCO films at 77 K in self-field. Both YBCO films exhibited almost identical $T_{c,zero}$ value of ~ 90 K. As shown in Fig. 5(a), 0.9 μm -thick YBCO film having the I_c value of 289 A/cm-width ($J_c = 3.2$ MA/cm²) at 77 K in self-field was achieved from the Ba-deficient coating solution. This result is superior to that of 0.8 μm -thick YBCO film exhibiting the I_c of 212 A/cm-width ($J_c = 2.65$ MA/cm²) at 77K in self-field from the stoichiometric coating solution in Fig. 5(b).

Other researchers [14-16] have reported similar results to ours, and tried to explain the reason for the difference in J_c values by analyzing microstructure with TEM. Nakaoka *et al.* [14] reported the effect of the composition of the coating

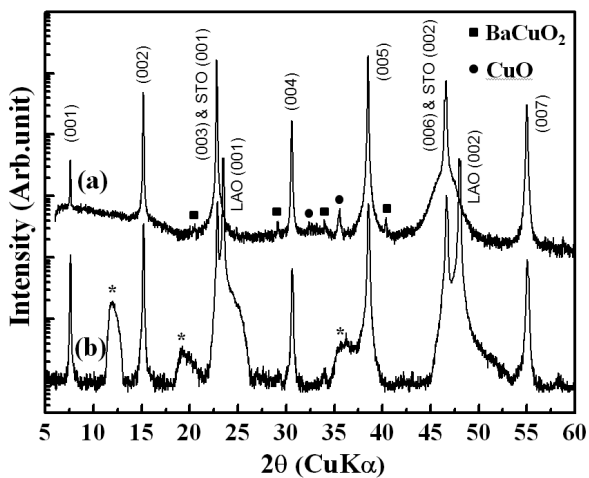


Fig. 4. XRD θ - 2θ diffraction patterns of the YBCO films from the Ba-deficient coating solution (a) and the stoichiometric one (from ref. [8]) (b). The peaks marked with the asteroids are originated from the LAO substrates.

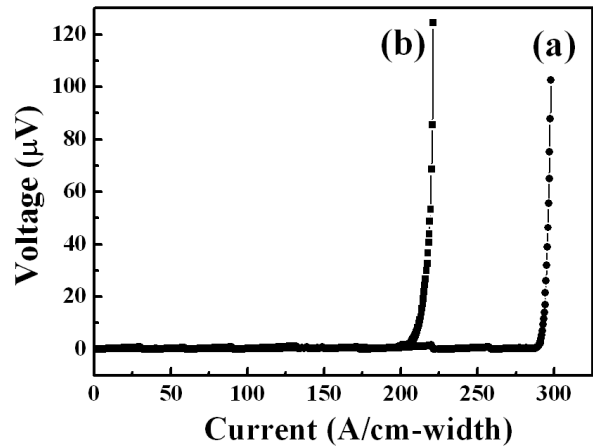


Fig. 5. The I - V curves at 77 K in self-field for the YBCO films from the Ba-deficient coating solution (a) and the stoichiometric coating solution (from ref. [8]) (b).

solution on the microstructure and superconducting properties of YBCO films prepared by a modified TFA-MOD process. Among various molar ratios of Y: Ba: Cu = 1: 1-3: 3 for the coating solution, they could prepare the YBCO film possessing the highest J_c value of 3.5 MA/cm² (77 K, self-field) from a Ba/Y ratio of 1.4-1.6. On the basis of TEM observations, it was suggested that the J_c improvement in the YBCO films obtained from the coating solutions containing the Ba/Y ratio of 1.4-1.6 was mainly attributed to a reduced porosity in films and thus denser microstructures in comparison with YBCO films from the Ba/Y ratio of 2.0. Matsuda *et al.* [15] reported the microstructure evolutions of YBCO films with the Ba/Y ratio of 1.4 and 2.0. According to their report, the YBCO growth rate from the precursor solution with the Ba/Y ratio of 1.4 was uniform along the ab -plane while the YBCO growth rate from the Ba/Y ratio of 2.0 was non-uniform along the ab -plane, and thus the YBCO growth front along the c -axis direction was not flat but bumped, suggesting higher probability to trap the second phases within the YBCO matrix. In agreement with this result, Tada *et al.* [16] also reported that larger amount of a Ba-F rich phase was trapped in the YBCO film from the Ba/Y ratio of 2.0 (i.e., the stoichiometric coating solution), leading to a J_c reduction, in comparison with the YBCO film from the Ba/Y ratio of 1.5 (i.e., the Ba-deficient coating solution). Therefore, according to these reports from other researchers, it can be summarized that the J_c improvement in the YBCO film from the Ba-deficient coating solution is attributed to denser microstructure with a reduced porosity and also to improved film homogeneity. In our results, it is speculated that these factors are responsible for the J_c improvement in the YBCO sample from the Ba-deficient coating solution. For the clarification of our results, however, *in-plane* texture analysis by XRD and pinning characterization by $J_c(B, T, \theta)$ measurements are required in addition to microstructure analysis by TEM, which are under progress.

4. SUMMARY

To optimize the thickness of a single-coat YBCO film, we have systematically investigated the relationship between the viscosity values of the stoichiometric coating solution, which were controlled by changing the holding time up to 12 h at 80°C, and the thickness of as-pyrolized films. From the microstructure analyses of as-pyrolized films, we confirmed that the critical thickness of as-pyrolized films for avoiding the crack formation was between 1.6 and 1.9 μm , which correspond to the viscosity values of 212 and 254 mPa·sec, respectively. With the viscosity of 212 mPa·sec, 0.9 μm -thick YBCO film having the I_c value of 289 A/cm-width ($J_c = 3.2 \text{ MA/cm}^2$) at 77 K in self-field was achievable from the Ba-deficient coating solution with the cation ratio of Y: Ba: Cu = 1 : 1.5 : 3, which was superior to that of our previous report for 0.8- μm thick YBCO film exhibiting the I_c of 212 A/cm-width ($J_c = 2.65 \text{ MA/cm}^2$) at 77K in self-field from the stoichiometric coating solution with the the cation ratio of Y: Ba: Cu = 1 : 2 : 3. This result might be attributed to denser microstructure with a reduced porosity and also to improved film homogeneity in the case of the YBCO film from the Ba-deficient coating solution. Further study on *in-plane* texture by XRD and pinning characterization by $J_c(B, T, \theta)$ measurements in addition to microstructure analysis by TEM is required for a full clarification of the J_c improvement in the YBCO film from the Ba-deficient coating solution.

ACKNOWLEDGMENT

This work was supported by a grant from the Center for Applied Superconductivity Technology under the 21st Century Frontier R&D program funded by the Ministry of Education, Science and Technology, Republic of Korea.

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