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Effect of F/Ba ratio of precursor solution on the properties of solution-processed YBCO superconducting films

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ABSTRACT

$YBa_2Cu_3O_{7-x}$ (YBCO) thin films (with thickness of 220–230 nm) and thick films (with thickness of 1.1–1.2 µm) were prepared using low fluorine solutions with different F/Ba ratios (F/Ba=1–4.5). The effect of F/Ba ratio on the properties of the films was systematically investigated. The results showed that films derived from solutions with F/Ba < 2, regardless of whether they were thin or thick, showed poor superconductivity due to the formation of $BaCO_3$ intermediate phase. When solutions with F/Ba≥2 were used, the superconductivity of as-prepared YBCO films was related to not only the film thickness, but also the F/Ba ratio in the solution. It was found that, for thick films derived from F/Ba > 2 solutions, the formation of BaF_2/BaOF phase was retarded by the decomposition of $Ba_{1-x}Y_xF_{2+x}$ (BYF) intermediate phase. We also found that extra fluorine in the solution resulted in a large number of impurities and a-axis grains in the thick films, degrading the film superconductivity. F/Ba=2 was the optimal ratio in the solution to fabricate high-J_c YBCO thick films.

1. Introduction

The second generation YBCO coated conductors are of great potential in the application of future power transportation and electrical devices. Although high-quality long-length YBCO tapes have been realized through vacuum deposition routes, the chemical solution deposition (CSD) of YBCO tapes has been paid much attention due to its low-cost and high-efficiency [1–3]. Nowadays, CSD-YBCO films with high current-carrying ability have been realized using trifluoroacetates (TFA) as precursors [4–6].

TFA solution was used to avoid the formation of $BaCO_3$ phase by forming the intermediate phase of BaF_2. It was firstly put forward by Gupta et al. [7]. The TFA solution was initially prepared from yttrium, barium and copper trifluoroacetates (all-TFA solution). The F/Ba mole ratio was as high as 19.5. Furthermore, TFA solutions with reduced fluorine content have been developed so as to improve the film quality and increase the production rate. The fluorine content in the precursor solution was reduced by about 50% and the time needed for the pyrolysis process was greatly shortened as compared to the conventional all-TFA route [8]. Further reduction of the fluorine content in the precursor solution (with F/Ba=4.5 and 2) was realized by Chen and Wu et al. [9,10]. Using these solutions, high-speed pyrolysis process with a heating rate of 10 °C/min was realized and YBCO films with a high J_c of 5MA/cm^2 were obtained. When the F/Ba=2 solution was used, the $BaCO_3$ phase was not detected during the nucleation and growth process of YBCO phase, and the as-prepared YBCO film also showed a high superconductivity. Additionally, further reduction of fluorine content to 0 < F/Ba < 2 in precursor solution has also been investigated. Considering the diverse precursor solutions with different fluorine content, some scientific and technological questions arise: what's the optimal fluorine content in the solution? And how does the fluorine content affect the structure and superconductivity of the as-prepared YBCO films?

Triggered by these viewpoints, a study on the effect of fluorine content on the properties of single coated YBCO films (with thickness less than 300 nm) has been recently conducted by Jin et al. [11]. They concluded that the fluorine content of 15.4–23.1% (F/Ba=3–4.5) in the precursor solution was the optimal window for the production of high-quality YBCO thin films. However, the experimental results from both Wu et al. and our group showed a different result [9,12–14]. Wu et al. reported that the single coated YBCO film derived from F/Ba=2 solution exhibited a J_c of about 5 MA/cm^2, as high as that derived from F/Ba=4.5 solution [9,10]. The different results implied that the underlying role of the fluorine content during the formation process of

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YBCO phase still remained unclear. Additionally, taking into account the practical applications, YBCO coated conductors with critical current (I_c) of several hundred of ampere are required. Thus, the thickness of YBCO films with J_c over $1MA/cm^2$ should be at least more than 1 μm. Therefore, investigations on the effect of the fluorine content on the structure and superconductivity of YBCO thick films are of more significance, which, however, has been seldom systematically investigated up to now.

In this study, a series of low fluorine YBCO precursor solutions with different F/Ba ratios (F/Ba=1–4.5) were synthesized. YBCO films with thickness of 220–230 nm and 1.1–1.2 μm were fabricated. Their structure and superconductivity were comparatively investigated. Our results indicated that the F/Ba=2 in the solution was the optimal ratio for the fabrication of high-quality YBCO thick films. The underlying mechanism was also discussed in the present work.

2. Experimental

The YBCO precursor solution with F/Ba=2 was synthesized by mixing the Y-Ba-Cu solution and Ba-TFA solution. The Y-Ba-Cu-solution was prepared through dissolving yttrium, barium, and copper acetates in a mixture solution of propionic acid and methanol. The Ba-TFA solution was prepared by dissolving the Ba-TFA gel into methanol. In the YBCO precursor solution, the metal ion ratio was controlled at Y:Ba:Cu=1:2:3, and the total metallic ion concentration was controlled at 1.5 mol/L. The detailed synthesis process was similar to that in our previous reports [10,12]. By adjusting the amounts of Y-Ba-Cu solution and the Ba-TFA solution, YBCO precursor solutions with F/Ba=1, 1.5, 1.8, 3 and 4.5, were also synthesized. The YBCO gel films derived from these precursor solutions were produced by the dip-coating method. After the gel films were coated on $LaAlO_3$ substrate, they were pyrolyzed at 400 °C in a humidified oxygen atmosphere. In order to increase film thickness, the coating-pyrolysis process was repeated for several times. Subsequently, the pyrolyzed thick films were annealed at 775 °C and post-annealed at 450 °C under controlled atmosphere, producing the superconducting YBCO films. The details of the heat treatment process can be found elsewhere [12,13].

JEM-6700F scanning electron microscopy (SEM) was employed to observe the surface morphologies and cross-sectional morphologies of the films. The film thickness was determined by cross-sectional SEM images. The orientation and phase structure of the films were detected by 7000S-type X-ray diffractometer (XRD) and a high-resolution X-ray diffractometer (Rigaku Smartlab). Magnetization behaviors were investigated by the Multi-function Vibrating Sample Magnetometer (VersaLab-VSM, Quantum Design), and the size of the samples were controlled at 2.0–2.5 mm×2.0–2.5 mm. The J_c values related to the magnetic strength (H) of the films were calculated from the M-H curves according to the Bean Model. The films were also analyzed by Thermo Fisher X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

A series of single-layer YBCO films with thickness of 220–230 nm were fabricated using solutions with different F/Ba ratios. Their surface morphologies and XRD patterns were shown in Figs. 1 and 2, respectively. As can be seen, although the surface of the films derived from F/Ba=1 and 1.5 solutions was smooth, YBCO grains were not well observed, indicating that these films were not well crystallized. For the film derived from solution with F/Ba=1.8, a large number of inter-perpendicular a-axis oriented grains were observed on the surface. The film derived from solutions with F/Ba=2 showed totally different morphologies. No randomly-oriented or a-axis grains were observed on the film surface, indicating that the film was of high c-axis texture. However, when the F/Ba ratio increased from 2 to 4.5, the amount of a-axis grains increased gradually. Fig. 2(A) and (B) displays the XRD patterns of all the films. For the films fabricated using F/Ba=1 and 1.5 solutions, the intensity of (00 *l*) peaks was weak, indicating that these films were of poor crystallinity, consistent to the results revealed by SEM. When the F/Ba ratio increased to 1.8, the intensity of diffraction peaks corresponding to YBCO (00*l*) planes increased greatly. However, (200) peaks corresponding to a-axis grains were still of high intensity. For the films derived from solutions with F/Ba=2–4.5, YBCO (00*l*) peaks with high intensity were observed, which was beneficial to obtain high-J_c YBCO films. Fig. 2(C) presents the J_c values (at 77 K, 0 T) of all the single layer films. As can be seen, YBCO thin films prepared from F/Ba < 2 solutions had low J_c values, which was resulted from their poor crystallinity and texture, as confirmed by the XRD and SEM. The underlying reason, as will be discussed later, is related to the formation of $BaCO_3$ intermediate phase. In contrast, for the YBCO thin films prepared from F/Ba≥2 solutions, they all showed a J_c value of about 5 MA/cm^2 (77 K, 0 T). This is consistent with the results in previous reports [9,10].

Subsequently, these low-fluorine solutions (F/Ba=1–4.5) were used again to fabricate a series of thick films (hereafter denoted as YBCO-x, x=1–4.5) with thickness of 1.1–1.2 μm. To prepare thick films, the coating-pyrolysis process was repeated for five times. After that, the films were annealed at 775 °C for several hours. Surface morphologies of these five-layer films are shown in Fig. 3. The surface of YBCO-1–1.5 samples was covered by many randomly-oriented grains. For YBCO-1.8 film, lots of a-axis grains together with some second phases were observed on its surface. However, for the YBCO-2 sample, almost no second phases were observed. And its surface was mainly covered by c-oriented grains, although some needlelike a-axis grains were observed. Further increase of F/Ba ratio from 2 to 4.5 led to the increase of the amount of a-axis grains.

Theta-2theta XRD was employed to further reveal the information of texture and orientation of these YBCO thick films. The XRD patterns of YBCO-1–1.8 samples are displayed in Fig. 4 (A). In addition to (00*l*) peaks, high-intensity (200) and (103) peaks of YBCO phase were clearly observed, indicating the existence of a large number of a-axis grains and randomly-oriented grains, as confirmed by the SEM results in Fig. 3. In contrast, for the YBCO thick films derived from F/Ba≥2 solutions, the (103) peaks were relatively weak and the (00*l*) peaks were prominent, as shown in Fig. 4 (B), indicating that these films were of better c-orientation. In addition, as compared to YBCO-2 film, two another peaks located at 28.8° and 34° were observed inside the YBCO-3 and YBCO-4.5 samples, corresponding to the second or residual phases. The peak located at 28.8° was assigned to the residual (002)-oriented BaF_2 phase. However, for the peak located at 34°, it remained unclear.

We defined $\alpha = I_{(103)}/I_{(006)}$ and $\beta = I_{(200)}/I_{(006)}$ to determine the relative amount of (103) and (200)-oriented grains in these thick films, where $I_{(103)}$, $I_{(006)}$ and $I_{(200)}$ are the intensities of corresponding diffraction peaks, respectively. The relationship between the F/Ba ratio and α or β is shown in Fig. 5 (A). It was found that when F/Ba < 2, α or β decreased sharply with the increase of F/Ba ratio, indicating that the amount of (200) and (103)-oriented grains decreased with F/Ba ratio. However, when F/Ba≥2, α and β, although increased slowly, kept at the approximate values. Clearly, the YBCO-2 film had the best crystallinity with the lowest amount of residual or second phases. Fig. 5(B) presents the J_c values of these YBCO thick films derived from solutions with different F/Ba ratios. Since the phase structure of YBCO-2 film was superior to other films, its J_c value was the highest, reaching about 3.8 MA/cm^2 (at 77 K, 0 T). Other films, however, had a low current-carrying ability as compared to YBCO-2 film.

From the results acquired above, we can conclude that films derived from F/Ba < 2 solutions show relatively low J_c values, regardless of whether they are thin or thick. For the single-coated YBCO film (with thickness of 220–230 nm), the F/Ba ratio in the range of 2–4.5 has almost no effect on the film superconductivity. However, for the YBCO film with thickness over 1 μm, the F/Ba ratio in the range of 2–4.5 shows great influence on the film structure and superconductivity. To