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Preparation of $YBa_2Cu_3O_{7-\delta}$ films by MOD method using trifluoroacetate as precursor

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Abstract

The $YBa_2Cu_3O_{7-\delta}$ (YBCO) films have been prepared on $LaAlO_3$(0 0 1) single crystal substrates by metalorganic deposition method using trifluoroacetate as precursor. The processing conditions including pyrolysis and anneal stage were investigated. A rapid pyrolysis schedule has been developed and discussed. The effects of annealing temperature on microstructure, texture and superconducting properties of the YBCO films were also studied. X-ray diffraction analysis showed the YBCO films on (0 0 1) $LaAlO_3$ single crystal substrates have good bi-axial texture. The ac susceptibility and resistivity measurement showed sharp superconducting transition. The critical current density (J_c) of the films deposited on $LaAlO_3$(0 0 1) single crystal substrate was over 1×10^6 A/cm^2 at 77 K and 0 T.

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Keywords: YBCO film; Metalorganic deposition; Texture

1. Introduction

Metalorganic deposition (MOD) process has been extensively investigated for the fabrication of the $YBa_2Cu_3O_{7-\delta}$ (YBCO) coated conductor [1]. Compared with popular physical vapor deposition technology, MOD process has many advantages, such as easy composition control, wide flexibility to coating objects, high deposition rate and low cost of non-vacuum processing equipments. Recently, MOD using trifluroacetates (TFA) has become one of the most promising methods to form YBCO films because this process has high reproducibility to get high critical current density [2–4]. By using TFA salts as precursors, the BaF_2 is formed as an intermediate phase during pyrolysis stage of the metalorganics, instead of $BaCO_3$, which usually forms in F-free chemical solutions in Y–Ba–Cu–O system [5]. Generally a very slow pyrolysis schedule (more than 10 h) was performed for decomposing the metalorganic films using TFA-based solution in order to get a homogeneous, crack-free pyrolyzed film because the drying stress and drastically exothermic decomposition during pyrolysis stage could destroy the integrity of the films [2,3]. The slow pyrolysis schedule,

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however, is not suitable for the fabrication of long length YBCO-coated conductor by continuous reel-to-reel method. In this study, we report a rapid pyrolysis procedure in wet nitrogen with 15% oxygen and results of an effort to optimizing the post-annealing parameters for the TFA process using $LaAlO_3$ as substrate.

2. Experimental

A TFA precursor solution was prepared by decompression distillation method. The acetates of Y, Ba and Cu with 1:2:3 (Y:Ba:Cu) molar ratios were dissolved in de-ionized water with stoichiometric quantity of trifluoroacetic acid. The resulting solution was then put into a decompression distillation device to remove the impurities such as acetic acid and water in the solution. The typical coating solutions with total metallic concentrations of 1.2 mol/l were made by dissolving the residue into methanol. The gel films were coated on 10×10 mm^2 $LaAlO_3$(1 0 0) with a spin rate of 3000 rpm for 120 s.

The gel films were heat-treated in two stages. The first is pyrolysis stage in which the gel film was pyrolyzed to form a uniform fluoride-containing solid film. In this study, the gel films were pyrolyzed in humid nitrogen mixed with different amount of oxygen via a rapid pyrolysis schedule, as shown in Fig. 1. The relationship between pyrolyzed film quality and oxygen content in atmosphere was investigated. The second stage is post-annealing process in which the pyrolyzed films are fired in a controlled atmosphere to form tetragonal YBCO phase and then annealed with dry oxygen at 450 °C for 2 h to form orthorhombic YBCO phase films. In this study we set the firing temperature between 740 and 820 °C. The firing atmosphere was humid (20 °C dewpoint) nitrogen mixed with 500 ppm oxygen. The variation of the microstructure, texture and superconducting properties of the YBCO films with the firing temperatures were investigated.

The microstructures of the YBCO films were characterized by scan electron microscopy (SEM). Crystalline phases in the films and the texture of the film were detected by X-ray diffraction (XRD).

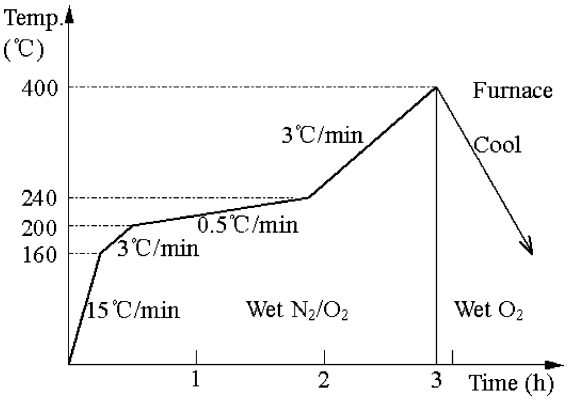

Fig. 1. The heat schedule of pyrolysis process of YBCO TFA precursor.

In-plane texture was quantified by measuring full-width half-maxima (FWHMs) of YBCO(1 0 3) phi-scan and the *c*-axis alignment was determined by measuring the FWHMs of the omega-scan of (0 0 5) peak of YBCO for each sample.

The critical temperature (T_c) of the films was determined by ac susceptibility measurement. The resistivity and transport critical current (J_c) were measured using a standard four-probe technique. I_c values of the films were measured across a 100 μm bridge and determined using a standard at 77 K in self-field with 1 μV/cm criterion. The thickness of the films was determined by both step profilometer and SEM.

3. Results and discussion

Obtaining homogeneous crack-free fluoride-containing solid films through pyrolysis stage is very important for fabricating high quality YBCO films. But the volatilization of water and organic solvent in gel film may cause pores, shrinkage and cracking during pyrolysis process. Our initial experiments revealed that the gel films tend to crack at a temperature range between 200 and 240 °C, and the film quality are greatly influenced by oxygen pressure in pyrolysis stage. Fig. 2 shows the TGA and DTA curves of the TFA gel in nitrogen and oxygen respectively. At temperature lower than 240 °C, organic solvent and water wrapped in gel films runs out, which was revealed from a slow,

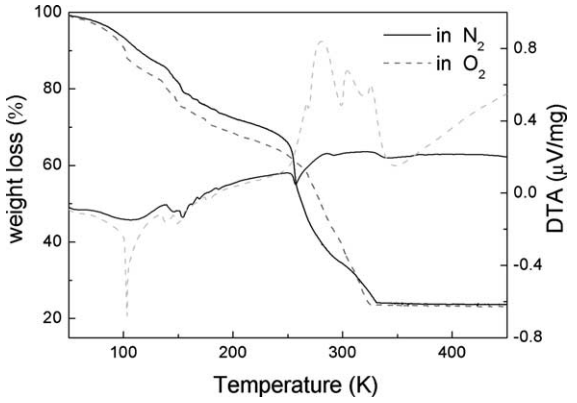

Fig. 2. DTA–TGA plots for precursor gel fired under O_2 and N_2 (5 °C/min).

gently weight loss in TGA curves. However, in this temperature region the weight loss in nitrogen was less and slower than in oxygen, showing a slow drying speed, which helps to relax the drying strain in the film and thus avoid cracking. At temperature between 240 and 340 °C, the TFA salts decompose, which are exothermic reactions. It can be seen that the DTA curve in oxygen has much higher exothermic peaks than in nitrogen, indicating a more drastically exothermic reaction in oxygen, which may increase the cracking tendency of the films. So, a low oxygen atmosphere has potentials to prevent cracking. Our experimental results confirmed that the cracking could be effectively inhibited when the films were pyrolyzed in low-pO_2 atmosphere.

However, the surface of the films became coarser and coarser with the decrease of pO_2 in atmosphere. Fig. 3 shows the surface morphology of films pyrolyzed in humid N_2 mixed with different amount of O_2 via the pyrolysis schedule shown in Fig. 1. There are large amount of particles in the films pyrolyzed in N_2. The EDX analysis showed that the large round particles were Y-riched phase and the little white square particles were Cu-riched phase. Many microcracks were also observed

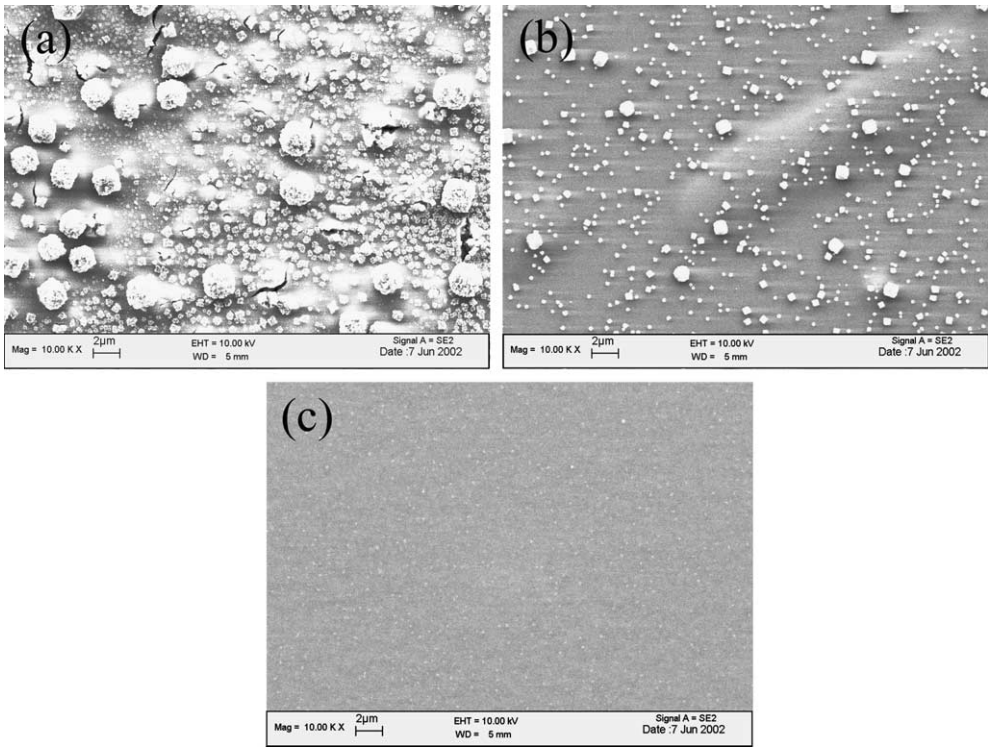

Fig. 3. SEM micrographs of the films pyrolyzed under different atmospheres. (a) N_2, (b) N_2/2%O_2 and (c) N_2/15%O_2.

around the large precipitates. In the films pyrolyzed in $N_2/2\%O_2$, little white particles were observed and these particles were identified to be Cu-riched phase. The formation mechanism of these particles is not clear at present. A possible explanation is that the decomposition rate and temperature region of these three TFA salts are strongly influenced by the oxygen content in atmosphere, which may lead to uneven precipitation [6].

According to the results above, nitrogen mixed with 15% oxygen was adopted to pyrolyze the film. Homogeneous, crack-free films were obtained and the surface of the films were smooth and almost no precipitates can be seen in SEM micrograph (Fig. 3c), indicating good quality of the pyrolyzed films.

Using the films pyrolyzed via the process above, the annealing process was investigated. Fig. 4 shows a typical θ–2θ XRD pattern of YBCO films fired between 740 and 820 °C in humid N_2 with 500 ppm O_2. Only $(00l)$ diffraction peaks of YBCO can be seen, indicating these films were highly *c*-axis oriented. In-plane texture and *c*-axis alignment of the YBCO films were determined from the FWHMs of X-ray phi- and-omega scans. All samples showed strong fourfold symmetry in their phi-scans. The average FWHM of the phi-scan of the sample fired at 780 °C was approximate

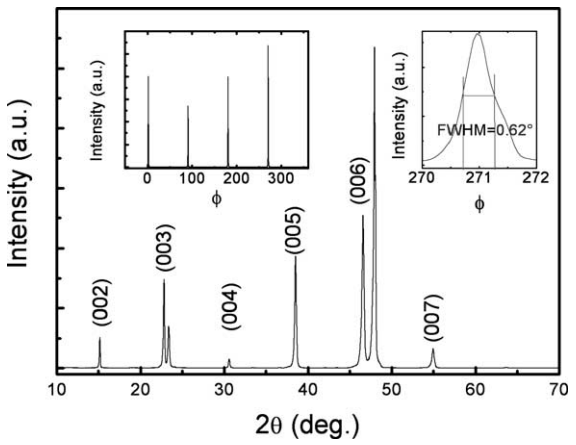

Fig. 4. XRD pattern of the film fired at 780 °C for 80 min. The inset on left is phi-scan of this film and the inset on right is magnification of the fourth peak in phi-scan.

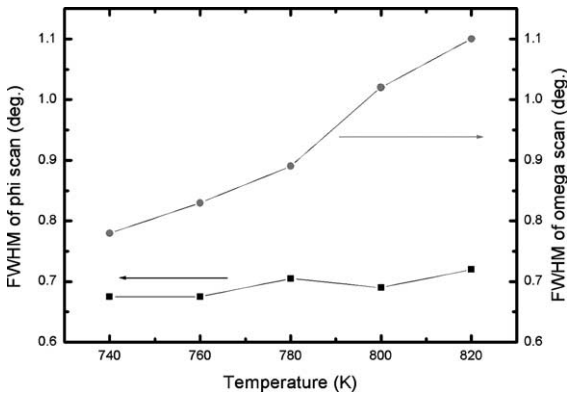

Fig. 5. Plots of the FWHMs of the (1 0 3) phi-scan and (0 0 5) omega-scans for the YBCO reflections as a function of heat treatment.

0.70°, just as seen in Fig. 4, which indicates a high degree of grain-to-grain alignment. The variation of the phi-scan FWHMs correlated to heat-treatment temperature are shown in Fig. 5. The FWHM values ranged from 0.62° to 0.72° over the temperature range of this study and showed little correlation with firing temperature. A plot of the FWHMs of the omega-scans for the YBCO (0 0 5) reflections as a function of heat treatment was also shown in Fig. 5. The FWHM value increased from 0.78° to 1.1° with the firing temperature increase, implying the *c*-axis alignment of the films was degraded at high firing temperatures.

Fig. 6 shows the top surface microstructures for the samples prepared at five different temperatures. YBCO grain size, secondary phase particles and pores on the surface of each sample were different. The average size of the YBCO grains of samples fired at temperatures higher than 800 °C were larger than 1 μm and the film seems to be dense. Needle-shaped grains, which appear to be *a*-axis-oriented grain, were observed. Some large particles, which were analyzed by EDS to be Ba and Cu rich phase, were also observed in these films. These particles are usually thought to be $BaCuO_2$ phase and originated from the decomposition process of YBCO at high temperature [7]. In the films with the firing temperature lower than 780 °C, the grain size of YBCO became small and the films seemed to have large amount of pores. However, there were

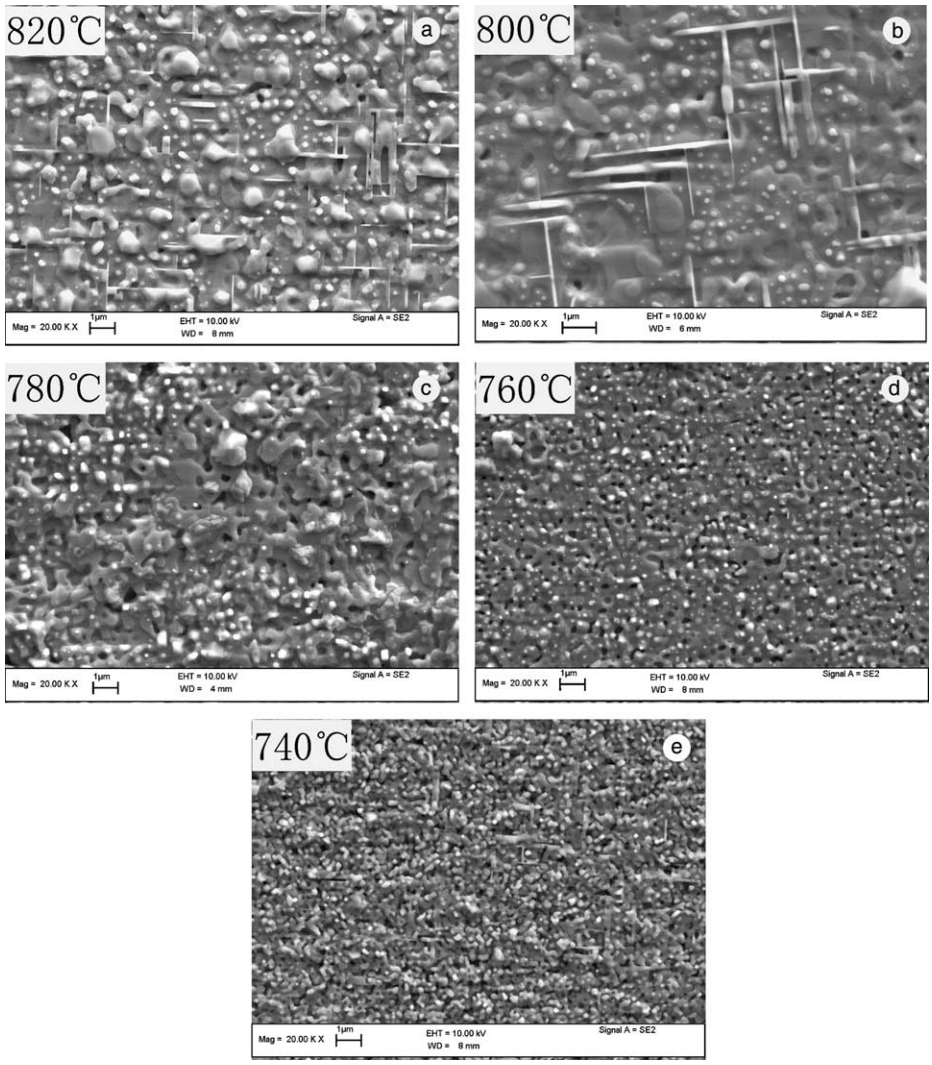

Fig. 6. The top surface microstructures for the samples prepared at five different temperatures.

fewer *a*-axis-oriented grains in the films, indicating that the *c*-axis alignment of the YBCO grains was improved at low temperatures. This observation was well accordant with the result of omega-scan measurement: the film fired at low temperature had better *c*-axis alignment. Smith et al. have observed the similar experimental results in their study and considered that the *a*-axis grain nucleation is influenced by reaction rate in TFA-derived YBCO films, which strongly depends on the firing temperature and partial water pressure [8]. Lowering the firing temperature does have an appreciate effect on film quality, though there is no convincing theoretic explanation at present.

Fig. 7 shows ac susceptibility as a function of temperature for five samples. The T_c of these films is near 90 K. The samples prepared at 740 and 820 °C have a broad transition. Their unfavorable microstructures may be responsible for their broad transition. The samples fired at 780 °C has the sharpest transition, which is consistent with the results of resistance measurement (shown in Fig. 7). The J_c measurement also showed the samples

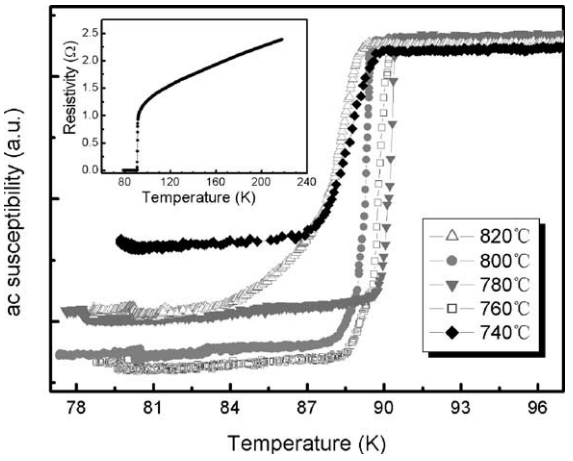

Fig. 7. AC susceptibility as a function of temperature for five samples. Inset shows the dependence of the resistance of a film fired at 780 °C for 80 min on temperature.

fired at 780 °C have the highest J_c values about 1.2 MA/cm^2 compared with the other samples, indicating the optimal firing time in 500 ppm O_2 atmosphere is 780 °C.

4. Conclusion

The pyrolysis and anneal processing conditions for preparing the YBCO films on $LaAlO_3$ substrate by MOD method using TFA as precursors have been investigated. The influence of oxygen content in atmosphere on the quality of pyrolyzed films was studied. A rapid pyrolysis schedule has been developed. Highly bi-axial textured YBCO films have been successfully deposited on (0 0 1) $LaAlO_3$ single crystal substrates. The study shows that low firing temperature will benefit the *c*-axis grain alignment, however low firing temperature also results in small YBCO grain size and high density of pores in the films, which leads to degradation of superconducting properties. The optimal firing temperature in wet N_2 mixed with 500 ppm O_2 may be 780 °C.

Acknowledgement

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