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Phase and microstructure evolution during the TFA-MOD process of YBCO films

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Abstract-- **We report the phase and microstructure evolutions of metal trifluoroacetate (TFA) precursor films in the TFA-MOD process of YBCO films on the LAO (100) substrates. It was confirmed that the precursor films were decomposed into Y_2O_3, BaF_2, and CuO nanoparticles after the initial heat treatment up to 400°C. After a subsequent heat treatment at higher temperatures ranging from 700 to 850°C for 2 h, these nano-sized phases are converted into YBCO films. High Jc(77K, sf)-YBCO thin films (over 2 MA/cm^2) were successfully fabricated with firing temperatures ranging from 775 to 850oC for 2 h, where films were composed of dense microstructures with large grains.**

1. INTRODUCTION

For the practical application of high temperature superconductors, it is crucial to fabricate the epitaxial YBCO films possessing high J_c (77K, sf) over 1 MA/cm^2 employing a cost-effective process. In this respect, the metal organic deposition using trifluoroacetates (TFA-MOD) process is considered to have a strong advantage compared with other fabrication processes. Since McInytre et al. [1] first reported J_c (77K, sf) values over 1 MA/cm^2 for YBCO films produced by the TFA-MOD method, great efforts have been made for the optimization of this process [2-12], and thus several research groups have recently succeeded in producing a long-length YBCO coated conductor on buffered metallic tapes [13-17]. it is well-known that as-coated film of metal TFA precursors first decomposes into an intermediate film composed of mixed metal oxy-fluorides by a slow heating to 400°C in a humid O_2 atmosphere and then the intermediate film is reacted to produce YBCO films after subsequent firing at the temperature over 700°C in humid/low P(O_2) atmosphere.

As previously mentioned, although the TFA-MOD process is greatly advanced enough to produce a long-length coated conductor, some points are not in agreement. For instance, the phase evolution in the TFA-MOD process is controversial in the literature [3, 18, 19]. Smith et al. [3] reported that the intermediate film after the first heat treatment up to 400 °C was composed of $Y_2Cu_2O_5$, BaF_2 and CuO phases by analyzing the quenched film prior to the introduction of water vapor at the subsequent firing temperature. However, Paranthaman et al. [18] reported that the intermediate film consisted of amorphous Y_2O_3, Cu_2O/CuO, and crystalline BaF_2 phase. On the other hand, Araki et al. [19] reported that the film consisted of CuO nanocrystallites and Y-Ba-O-F amorphous matrix. More recently, Rupich et al. [20] reported that the intermediate film was composed of Y_2O_3, BaF_2, and CuO nanocrystallites.

In this study, to unveil the above contradiction, thermal decomposition reaction and phase evolution of as-coated film during the first heat treatment were carefully analyzed using TG-DTA and XRD. Further, we also investigated the effect of firing temperature on the microstructural and superconducting properties of YBCO films on LAO (100) substrates.

2. EXPERIMENTAL PROCEDURE

Metal-TFA precursor solutions were prepared by dissolving stoichiometric Y, Ba, and Cu acetates with 1:2:3 molar ratio in de-ionized water with a stoichiometric quantity of trifluoroacetic acid at room temperature. The solution was refluxed for 3 h to react with trifluoroacetic acid sufficiently. The solvent was removed at 80°C in a drying oven for 12 h, resulting in a glassy blue residue. The residue was again dissolved in methyl alcohol to make the final solution with the total cation concentration of 1.5 M. The final solution was deposited onto LAO (100) single-crystal substrates by spin coating with the spinning rate of 4000 rpm and duration time of 120s. Two-stage heat treatments were used to covert as-coated films into YBCO films, as shown in Fig. 1. In the second heat treatment, the intermediate films were fired at various temperatures from 725 to 850°C with temperature interval of 25°C.

Microstructures of the samples were observed by a field emission scanning electron microscope (FE-SEM). Thermal decomposition of TFA precursor gels was characterized by a differential thermal analysis (DTA) and thermogravimetry analysis (TGA). Superconducting properties were measured by the standard four-probe method.

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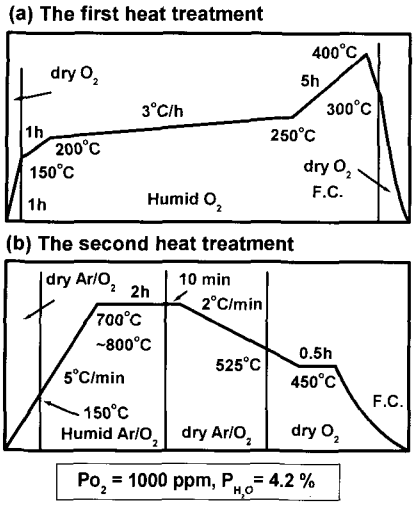

Fig. 1. Heat treatment schedules for (a) the first stage and (b) the second stage.

3. RESULTS AND DISCUSSION

To investigate the phase evolution of the as-coated film during the first heat treatment, XRD analyses were performed on the samples air-quenched at 200°C, 250°C and 400°C. For this experiment, the TFA precursor solution was coated onto an amorphous SiO_2 layered (~0.3 μm) Si (100) substrates. The results are shown in Fig. 2. XRD peaks of the films quenched at 250°C and 400°C belong to Y_2O_3, BaF_2, and CuO phases, while the film quenched at 200°C remains amorphous phases, indicating that metal oxides and fluoride in the intermediate film start to form at the temperature between 200°C and 250°C. In addition, broad diffraction peaks with low intensities imply that the particle sizes of crystallites are very small, which is demonstrated in Fig. 3. The crystallites with several tens of nanometers are observed. This result is in good agreement with that of previous report from Rupich et al. [20].

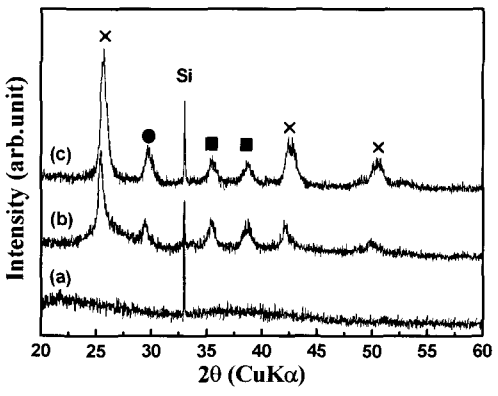

Fig. 2. XRD patterns of the films quenched from (a) 200°C, (b) 250°C, and (c) 400°C in the same condition as the first heat treatment. Where Si : silicon double diffraction peak, ×: BaF_2 ● : Y_2O_3, and ■ : CuO.

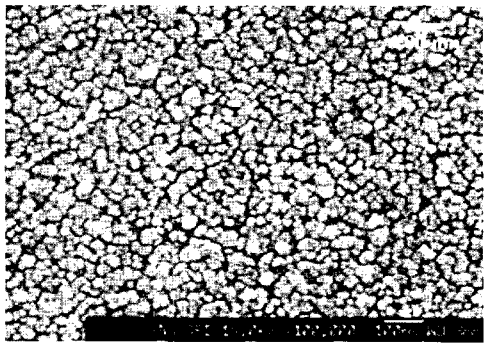

Fig. 3. FE-SEM micrograph of the intermediate film on LAO (100) substrate after the first heat treatment.

Organic components in metal-TFA precursors are thermally decomposed during the first heat treatment. TG-DTA of metal-TFA precursors gel prepared by drying the precursors solution were performed as shown in Fig. 4. There are two major exothermic peaks relevant to a drastic weight loss in the temperature region from 255 to 320°C. Since these exothermic peaks were attributed to the decomposition reactions of each Y-, Ba- and Cu-TFA precursor, we performed TG-DTA for each Y-, Ba-, and Cu-TFA precursor gel prepared by dissolving each Y, Ba, and Cu acetate in trifluoroacetic acid, respectively. The results are shown in Fig. 5. It can be clearly understood that the first exothermic peak in Fig. 4 is due to thermal decomposition of Ba- and Cu-TFA precursors, and the second peak results from that of Y- and Cu-TFA precursors.

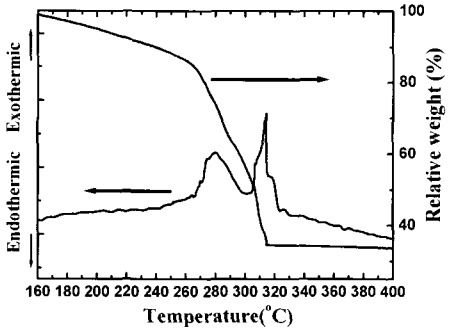

Fig. 4. DTA-TGA curve of metal-TFA precursor gel.

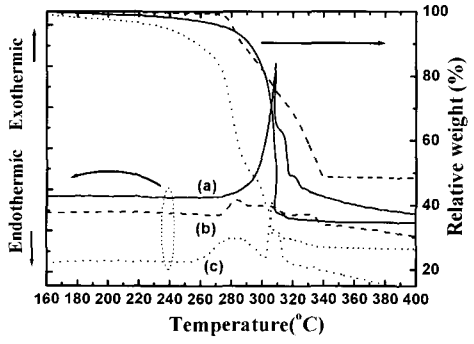

Fig. 5. DTA-TGA curves of (a) Y-, (b) Ba-, and (d) Cu-TFA precursor gels.

As shown in Fig. 4, however, thermal decomposition of metal-TFA precursors begins at the temperature of 255°C. This result seems to be contradictory to the XRD analysis result in Fig. 2 because the crystalline phases in the intermediate film must be formed after thermal decomposition of metal-TFA precursors. This contradiction might be caused by a difference in the thermal decomposition kinetics of metal-TFA precursors since the XRD patterns in Fig. 2 were obtained from the film quenched at 250°C after slowly heating to this temperature with the heating rate of 3°C/h, while TG-DTA were performed with the heating rate of 5°C/min. To clarify this point, we performed TGA for metal-TFA precursors with different heating rates. The results are shown in Fig. 6. When heating rate decreased from 5 to 0.5°C/min, the onset temperatures at which weight losses occurred rapidly decrease from 265°C to 225°C, and the decomposition reactions are completed at much lower temperature, indicating that the heating rate affects the thermal decomposition reaction kinetics of metal-TFA precursor.

All fired samples have thickness of 250 nm, which are observed by cross-sectional FE-SEM, regardless of the firing temperature. Fig. 7 shows the θ-2θ XRD patterns of YBCO films fired at various temperatures for fixed holding time of 2 h. One can see that pure YBCO phase with strong *c*-axis orientation is obtained from the films fired at the temperature higher than 750°C, but a small quantity of BaF_2 phase remains in the film fired at 725°C due to insufficient reaction at this firing temperature.

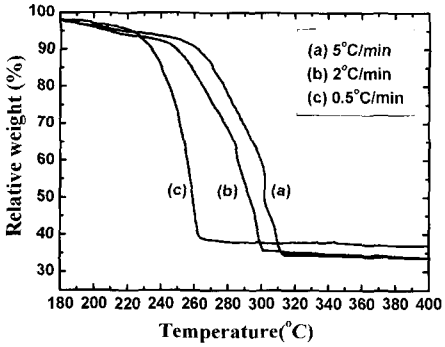

Fig. 6. TGA curves of YBCO-TFA precursor gels as a function of heating rate.

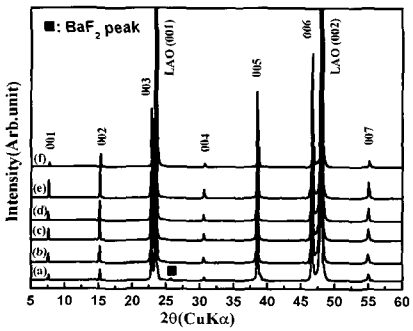

Fig. 7. The θ-2θ XRD patterns of YBCO films fired at (a) 725°C, (b) 750°C, (c) 775°C, (d) 800°C, (e) 825°C, (f) 850°C for 2 h.

Fig. 8 represents FE-SEM micrographs of YBCO films. It is clearly observed that the film fired at 725°C consists of very small YBCO grains with many small pores. The films fired at 750 and 775°C exhibit denser microstructures than the film fired at 725°C which is still composed of small grains. The films fired at the temperature range from 800 to 850°C are composed of larger grains with denser microstructures, compared to other films.

Transport T_c's and J_c's of YBCO films fired at various firing temperatures are represented in Fig. 9. The samples fired at the temperature range from 750 to 850°C exhibit high T_c's over 90 K but the sample fired at 725°C shows a depressed T_c of 72 K due to unreacted phase of BaF_2 which can play a role in hindering YBCO phase from oxidizing [21]. High J_c's (77K, sf) higher than 2 MA/cm^2 are obtained from YBCO films fired at the temperature range from 775 to 850°C, which results from their high T_c's over 90 K, strong *c*-axis orientation, and dense microstructures with large grains.

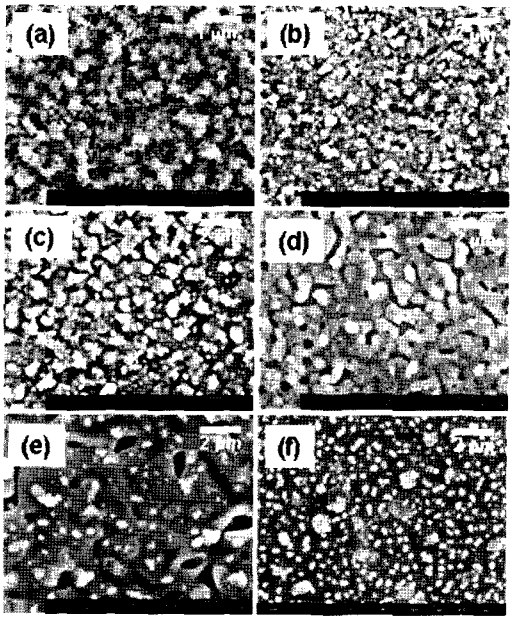

Fig. 8. FE-SEM micrographs of YBCO films fired at (a) 725°C, (b) 750°C, (c) 775°C, (d) 800°C, (e) 825°C and (f) 850°C for 2 h.

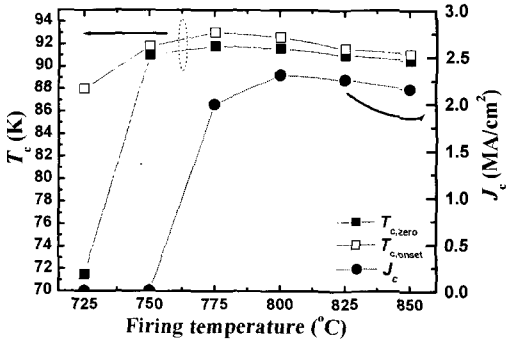

Fig. 9. T_c and J_c values of YBCO films as a function of firing temperature.

4. SUMMARY

It was confirmed that Y, Ba, and Cu-TFA precursors in the as-coated films was converted into the Y_2O_3, BaF_2, and CuO crystallites with several tens of nanometers after the first heat treatment. It was also figured out that the heating rate during the conversion process affected thermal decomposition reaction kinetics of metal TFA precursors. In addition, high J_c(77K, sf)-YBCO thin films (over 2 MA/cm^2) were successfully fabricated on LAO (100) substrates when the samples were fired the temperature from 775 to 850°C for 2 h, where films were composed of dense microstructures with large grains.

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