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Effect of chemically modified precursor solution on MOD-processed YBCO thin films

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***Abstract*-- Effect of chemically modified precursor solution on YBCO coated conductor prepared by MOD-TFA method was investigated. YBCO thin films were deposited on (100)-oriented single crystalline $LaAlO_3$ substrates by conventional MOD-TFA process. The microstructures of YBCO thin films contain maze-like patterns. The origin of this microstructure was delineated by compositional inhomogeneity during the pyrolysis process and it was shown that addition of diethanolamine (DEA) improve the microstructure of grown YBCO films. In addition, it was demonstrated that the chemical modification of precursor solution makes no harmful effect on biaxial texture of YBCO thin films.**

1. INTRODUCTION

YBCO-based coated conductors (CC), produced by deposition of superconductor on biaxially textured flexible substrates are currently promising HTSC wire architecture for power electric application due to their high critical current density at liquid nitrogen temperatures (J_c > 1 MA/cm^2 @ 77K). Many efforts are in progress to develop long HTSC wire with high current carrying capacity by coated conductor architecture. Typical methods for producing YBCO-based coated conductors are PLD, e-beam evaporation, liquid phase epitaxy (LPE), metallorganic deposition (MOD), etc [1-3]. Among them, high vacuum deposition methods are predominant and they produces YBCO thin films with relatively high J_c [1]. However, those high vacuum deposition methods require an expensive vacuum system and other expensive facility such as high power laser.

MOD processing of YBCO thin film has been studied as an alternative method because it is non-vacuum process. MOD is one of chemical solution processing techniques which offer many desirable aspects, such as precise control of metal oxide precursor stoichiometry, ease of forming epitaxial oxides, relatively easy scale-up of the film and low cost [4]. Recently, a 7.5 m-long YBCO CC with I_c of 127 A/cm-w was successfully fabricated by MOD process [5].

However, poor film morphology and YBCO grain misorientation indicate that improvements can be made in MOD processing of YBCO CC. Morphological defects such as cracks, pores, non-superconducting secondary phases are harmful for current transporting capacity. In addition, it was reported that metallic salt of copper precipitates in the MOD processing and it cause compositional inhomogeneity of YBCO thin films [6]. This study focuses on the microstructural improvements by modification of precursor solution for MOD process. In particular, various organic additives are introduced into precursor solution to suppress compositional inhomogeneity and improve microstructures.

2. EXPERIMENTALS

Metal acetates are used as precursor materials for YBCO films. Firstly, acetate salts of Yttrium, Barium and Copper are dissolved in deionized water and TFA. This process was followed by distillation of impurities such as water, excess TFA, etc. and dilution with methanol. Diethanolamine (DEA), Dimethylformamide (DMF) and Polyethylene glycol (PEG) are employed as chemical additives to modify the precursor solution.

Single crystalline $LaAlO_3$ with (100) plane was used as substrates for YBCO deposition. $LaAlO_3$ substrates were pre-treated by isoproanol and acetone, followed by annealing at high temperature.

YBCO Gel films were deposited by dip coating methods and dried on hot plates. Dried gel films were pyrolyzed and crystallized at the optimized temperature and atmospheres. Texture and microstructures of grown YBCO thin films are characterized with XRD, SEM/EDS, etc.

3. RESULTS AND DISCUSSIONS

3.1. MOD-processed YBCO thin films

Firstly, a YBCO thin film was fabricated by conventional MOD-TFA method. Fig.1 shows an X-ray diffractogram of grown YBCO thin film. Peaks indicating (00*l*) reflections of YBCO are predominant over entire range of diffraction angles. The theta rocking curve indicates that the out-of-plane misalignment of YBCO is about 1.49° (Fig. 2). However, the existence of secondary phase such as CuO and (103) reflection of YBCO are indicated.

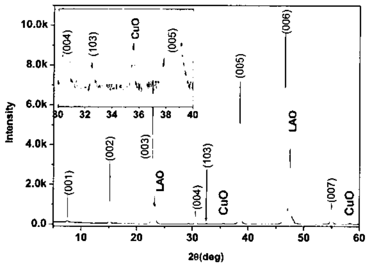

Fig. 1. A 2th-th scan profile of YBCO thin film prepared by MOD-TFA method without additives

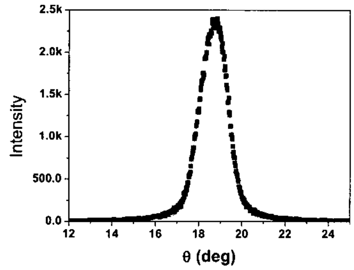

Fig. 2. Theta-scan profile of YBCO thin film.

Fig.1 shows an X-ray diffractogram of grown YBCO thin film. Peaks indicating (00*l*) reflections of YBCO are predominant over entire range of diffraction angles. The theta rocking curve indicates that the out-of-plane misalignment of YBCO is about 1.49° (Fig. 2). However, the existence of secondary phase such as CuO and (103) reflection of YBCO are indicated.

An (103) pole figure of YBCO thin film is presented in Fig. 3. This pole figure shows well-developed contours discretely spaced by 90° in phi angle which indicating in-plane texture of YBCO thin film.

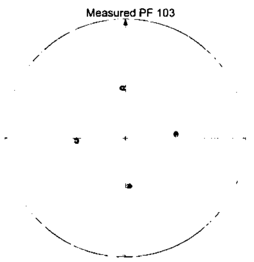

Fig. 3. An (103) pole figure of a YBCO thin film

The phi-scan profile is presented in Fig. 4 and FWHM of peaks characterizing in-plane texture is estimated to be about 3.14°.

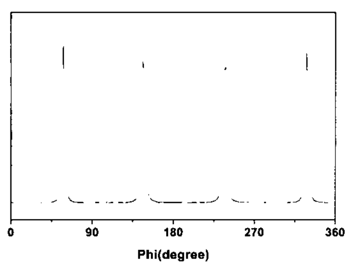

Fig. 4. A phi-scan profile of YBCO thin film.

Thus, XRD finds good biaxial texture of YBCO thin films and existence of non-superconducting phase and off-axis grains of YBCO.

3.2. Effect of chemical additives

The microstructure of YBCO thin films processed with MOD-TFA method are presented in Fig. 5.

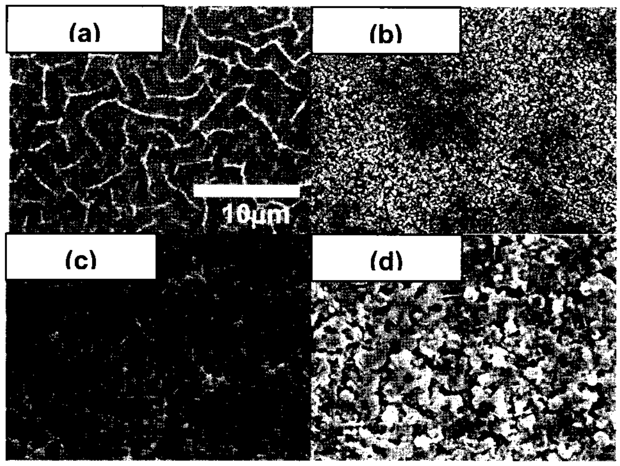

Fig. 5. Surface morphology of grown YBCO films prepared with various additives. (a) none, (b) DEA, (c) DMF, and (d) PEG

The surface of YBCO film processed with conventional precursor solution without chemical modification shows a maze-like microstructure and needle-like grains indicating a/b-axis oriented YBCO grains. The maze-like microstructures were characterized to be Cu-rich phase by SEM/EDS. The existence of Cu-rich phase and a/b-axis grains are consistent with XRD profile in Fig. 1 which indicates CuO and (103) reflections of YBCO. J. T. Dawley *et al.* analyzed the maze-like microstructure in MOD-processed YBCO film and delineated that the Cu-rich phase was originated by precipitation of Cu-rich phase during the pyrolysis process [6].

Fig. 5(b) shows microstructures of YBCO thin films prepared by chemically modified precursor solution with addition of small amount of DEA. Contrary to Fig. 5(a) demonstrating the microstructure of YBCO thin films prepared with conventional precursor solution, microstructure presented in Fig. 5(b) do not show maze-like microstructure and a/b-axis oriented YBCO grains. Since DEA contains amine group (-NH_2) in the molecular structure and acts as a chelating agent for metallic ions, suppression of maze-like microstructure can be attributed to chelation of precursor by addition of DEA. Thus the microstructure of YBCO thin film was improved by addition of chemical additives such as DEA.

However, microstructures of YBCO thin films was not improved by addition of DMF or PEG into precursor solution for MOD process (Fig.5(c-d)). While those microstructures shows no maze-like secondary phases, the surface is very rough and contains needle-like a/b-axis oriented YBCO grains. While DMF and PEG are popularly

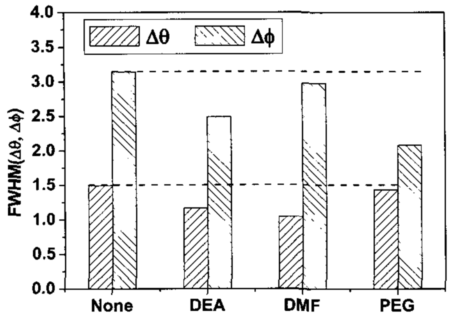

Fig. 6. Biaxial textures of YBCO thin films prepared with or without organic additives.

applied to improve chemical solution process, they lack chelation effect. It could be inferred that the addition of these chemicals into the precursor solution cannot improve microstructures of final YBCO thin films by lack of *chelation effect.*

One of most important performance parameters in superconductor is critical current density (J_c). It is well-known that the J_c is heavily dependent on in-plane or out-of-plane alignment of superconducting grains [7]. In order to characterize the effect of chemically modified precursor solution on the biaxial texture of YBCO thin films, degrees of biaxial texture($\Delta\theta$, $\Delta\phi$) were evaluated by X-ray diffraction method.

4. SUMMARY

In summary, the effects of organic additives of precursor solution on MOD-processed YBCO thin films have been investigated. It was shown that the addition of DEA into precursor solution improves microstructures of YBCO films by removing a/b-axis oriented YBCO grains and maze-like microstructure caused by precipitation of Cu-rich phase. However, the addition of PEG and DMF make harmful effects on microstructures of YBCO thin films. In addition, it was demonstrated that the chemical modification of precursor solution by organic additives causes no harmful effect on biaxial texture of YBCO thin films. In particular, YBCO film prepared with DEA-modified precursor solution shows slightly improved biaxial texture ($\Delta\theta$=1.17° and $\Delta\phi$=2.49°)

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