MOD-processed YBCO coated conductors
on the CeO$_2$-buffered IBAD-MgO template

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Abstract-- YBCO coated conductors (CC) on the CeO$_2$-buffered IBAD-MgO template were fabricated by metal-organic deposition (MOD) process with Ba-trifluoroacetate and fluorine-free Y and Cu precursor materials. The precursor solution was coated on CeO$_2$-buffered IBAD MgO templates using the multiple dip-coating method, decomposed into inorganic precursors by pyrolysis up to 400 °C within 3 h, and finally fired at 740~800 °C in a reduced oxygen atmosphere. Microstructure, texture, and superconducting properties of YBCO films were found highly sensitive to both the firing temperature and time. The high critical current density (J_C) of 1.15 MA/cm^2 at 77.3K in the self-field could be obtained from 1 µm thick YBCO CC, fired at 740 °C for 3.5 h, implying that high performance YBCO CC is producible on IBAD MgO template. Further enhancement of J_C values is expected by improving the in-plane texture of CeO$_2$-buffer layer and avoiding the metal substrate contamination.

1. INTRODUCTION

YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) CC is very promising for its electrical power applications with the liquid nitrogen refrigeration. Among various processes developed for YBCO CC, the MOD method is regarded as one of the most attractive processes for obtaining high-J_C YBCO CC because it consists of a simple and cost-effective procedure. Up to date, the most extensively studied MOD process is the TFA-MOD process, using metal trifluoroacetates (TFA) as precursor solutions [1, 2].

Although the conventional TFA-MOD process has been successfully used to fabricate high- J_C YBCO films on the single crystal substrates [2, 3] and also on the metal substrates for thin films [3, 4], it has several challenging problems. One is a fatal crack formation which makes it difficult to produce thicker YBCO CC with higher critical currents (I_C). A large amount of HF gas comes out of the TFA precursor film during the pyrolysis process, and therefore, a single-coated TFA precursor film, resulting in YBCO film thicker than ~ 400 nm, easily forms the macroscopic cracks which are unable to be cured at the firing stage. A long processing time for the thermal

decomposition of the TFA precursor film is another problem which retards the production rate of YBCO CC. To overcome these problems, fluorine-free precursor solutions have been tried, and some approaches were reported effective [5, 6]. As such an effort, we also developed a hybrid MOD process employing fluorine-free precursors for Y and Cu but TFA for Ba, and achieved high-J_C over 2 MA/cm^2 at 77.3 K from single-coated YBCO films of 0.8 µm thickness on the LaAlO$_3$ single crystal substrate [7].

Recently, by performing the TFA-MOD process on RABiTS (rolling assisted bi-axially textured substrate) and IBAD (ion beam assisted deposition)-Gd$_2$Zr$_2$O$_7$ (GZO) template, uniform YBCO CCs with I_C > 150 A/cm-width at 77.3 K have been demonstrated over 50-m length [8], [9]. Meanwhile, the IBAD MgO template technology has made great progress, and thus the production rate of the IBAD template could be greatly increased compared with YSZ and GZO template [10]. However, only a few reports are now available for MOD-processed YBCO CCs on the IBAD MgO template [11, 12]. We report a successful fabrication of high performance YBCO CCs on the IBAD MgO template by the MOD process, employing fluorine-free precursors of Y-, Cu-acetylacetonates and Ba-TFA developed in our laboratory [7].

2. EXPERIMENTAL

Bi-axially textured YBCO films were deposited on the IBAD MgO template. Pulsed laser deposition was used for the deposition of CeO$_2$ and LaMnO$_3$ buffer layers on the IBAD MgO templates, resulting in the final architecture of CeO$_2$/LaMnO$_3$/homoepi-MgO/IBAD-MgO/Hastelloy. The precursor solution was prepared mixing fluorine-free Y-, Cu-acetylacetonates with Ba-TFA. Further details on the coating solution preparation are described in our previous report [7]. The coating solution was dip-coated on the CeO$_2$-buffered IBAD-MgO template with the withdrawal speed of 32 m m/min. Dip-coated gel films were decomposed into Y$_2$O$_3$, BaF$_2$ and CuO by the heat treatment up to 500°C with the heating rate of 3°C/min in a humidified oxygen atmosphere. To prepare thicker

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precursor films, we repeated the dip coating and pyrolysis processes. Then the precursor films were fired at the temperature region of 740~800°C for various holding periods in 20.1% humid atmosphere containing 100 ppm oxygen partial pressure in argon, and finally oxygenated at 450°C for 1 h in flowing a pure oxygen gas. All YBCO films had the thickness of 1 μm.

The phase evaluation of the YBCO films was studied by X-ray diffraction (XRD) θ-2θ scans (Mac Science, M18XHF-SRA). In-plane texture was characterized by X-ray phi (φ) scan with four-circle diffractometer (PANalytical, X'pert Pro). Surface morphology and thickness of samples were observed using field emission scanning electron microscope (JEOL, JSM-6330F). Critical temperature (T_C) and critical current I_C were measured with the four-probe method. For this purpose, Ag protect layers of ~1.5 μm thickness were sputtered on YBCO films. I_C values were determined with 1 μV/cm voltage criterion on the I-V curves measured at 77.3 K in a self-field.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD θ-2θ scans of the YBCO films prepared for various holding periods at the given firing temperature. The major peaks correspond to the (00l) reflections of YBCO. We can see that all YBCO films are highly c-axis oriented and a/b-axis oriented peaks at 2θ = 23.27 and 46.73° are undetectable. However, YBCO films fired for relatively short time show BaF$_2$ (111) peak, suggesting that the conversion of the precursor film into YBCO phase is incomplete. As shown in Fig. 1, in the case of our precursor films, leading to 1 μm thick YBCO film, the minimum firing times for complete conversion at the temperatures of 740, 760, 780, and 800°C are 3.5, 2.5, 2, and < 1.5 h, respectively.

All YBCO films show the BaCeO$_3$ (BCO) phase peak at 2θ = 28.69° in Fig. 1. Many studies reported that BCO phase easily formed at the YBCO/CeO$_2$ interface in the case of the MOD process [13] as well as other fabrication techniques, such as PLD [14]. In the case of PLD-processed YBCO film, the reaction between YBCO and CeO$_2$ is reported to yield BCO phase and two more compounds, YCuO$_2$ and CuO at the vicinity of BCO [14]. However, the formation of BCO phase in the MOD-processed YBCO film is significantly different from that of PLD-processed YBCO film. The BCO phase begins to form at the top of CeO$_2$ cap layer during the initial ramping to firing temperature [15], indicating that BCO phase is most probably formed by chemical reaction between Ba element produced by the decomposition of BaF$_2$ and CeO$_2$ cap layer. Further microstructural analysis is, however, required to identify the origin of BCO phase formation in MOD-processed YBCO films on CeO$_2$ layer.

The highly textured epitaxial MgO, CeO$_2$ and YBCO layers were confirmed by φ scans as shown in Fig. 2. The in-plane texture has the full width at half maximum value (Δφ) of 10° for the MgO layer in Fig. 2 (a), whereas the Δφ value of 7° for the CeO$_2$ layer in Fig. 2 (b). Compared with

that of CeO$_2$ cap layer, the in-plane textures of YBCO layers were enhanced to the Δφ values of 3.85~6.4°. The most enhanced in-plane texture of 3.85° was obtained from the sample fired at 740°C for 3.5 h as shown in Fig. 2 (c).
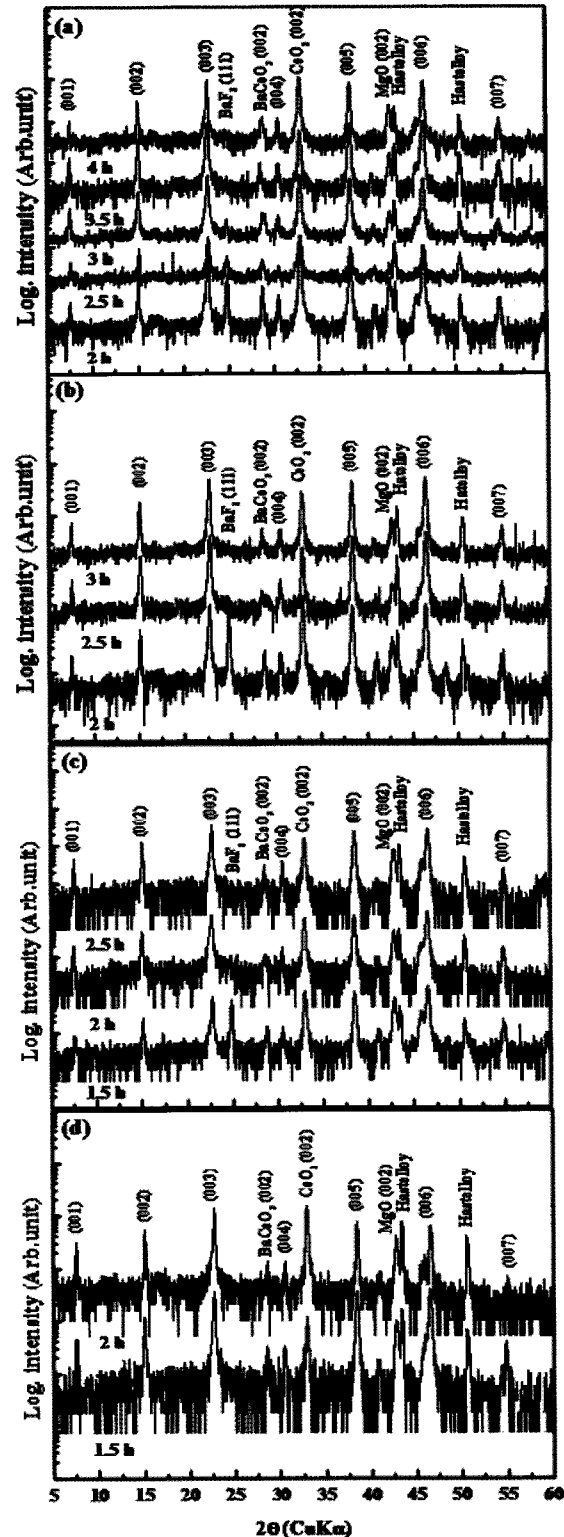

Fig. 1. XRD patterns of YBCO films for various holding periods at the given firing temperatures: (a) 740°C, (b) 760°C, (c) 780°C, and (d) 800°C. The holding periods are represented in the figure.
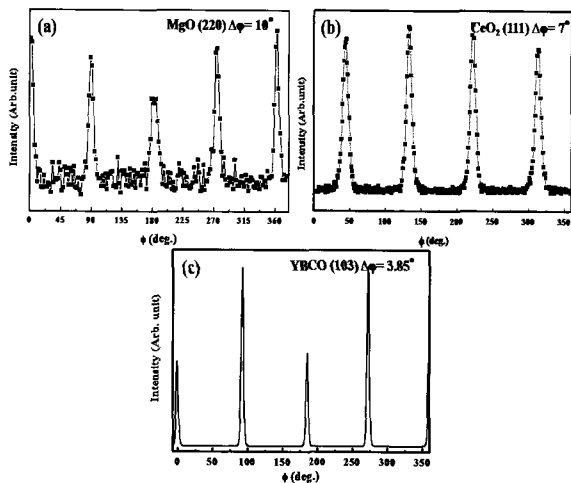
Fig. 2. XRD φ scans of MgO (a), CeO₂ (b), and YBCO film fired at 740°C for 3.5 h (c). FWHM values of (103) φ scan in YBCO films fired at 740°C~800°C for various holding periods.

Surface morphologies of YBCO films are represented in Fig. 3. One can see that surface morphologies of YBCO films are significantly different from each other. The films fired at 740°C for short holding periods show long elongated phases which are regarded as the second phase including unreacted BaF₂ since these are reduced with increasing holding time, and finally unobservable in the film fired for 3.5 h. It is in good agreement with XRD results shown in Fig. 1 (a). The a/b-axis oriented YBCO grains of a rod shape [16] are hardly found in all YBCO films, which is also in accordance with Fig. 1. In addition, the YBCO grain size is increased with increasing both

firing temperature and holding period. However, with increasing the firing temperature at a given holding period or increasing the holding period at a given firing temperature, the porosity of films is also increased.

The misoriented YBCO grains are randomly observed for the films fired at 780 and 800°C. Typical morphology of misoriented grains is represented in Fig .4. It is suggested that the formation of misoriented grains is attributed to the liquid phase formation of Ba-O-F which can float the YBCO grains at the firing temperature [17]. M. Yoshizumi *et al.* [18] reported that a Ba-O-F phase formed a melt at temperature region of 500 ~ 600°C when F/Ba ratio is larger than 2. The floating effect of the Ba-O-F liquid phase for YBCO grains would be larger at higher firing temperatures, and thus misoriented grains could be found only for the films fired over 780°C.

Fig. 5 shows $T_{C,\text{zero}}$ values of YBCO films as a function of firing temperature and holding period. For instance, with increasing the holding period at 740°C, $T_{C,\text{zero}}$ values are improved from 70 to 90 K due to the conversion of unreacted BaF₂ phase into YBCO. If unreacted phases including BaF₂ cover YBCO grains, the oxygenation of YBCO grains during the oxygen annealing would be hindered, resulting in depressed $T_{C,\text{zero}}$ values. Therefore, high performance YBCO films could be obtained from fully reacted YBCO films for relatively long holding period at the given firing temperature. The highest $T_{C,\text{zero}}$ value of 90 K was achieved from the YBCO film fired at 740°C for 3.5 h. However, $T_{C,\text{zero}}$ value decreased with increasing the firing temperature for each optimum holding period, which is probably caused by the contamination from the metal substrates through the Ba-O-F liquid phase. The Ba-O-F liquid phase would rapidly wet the IBAD template surface
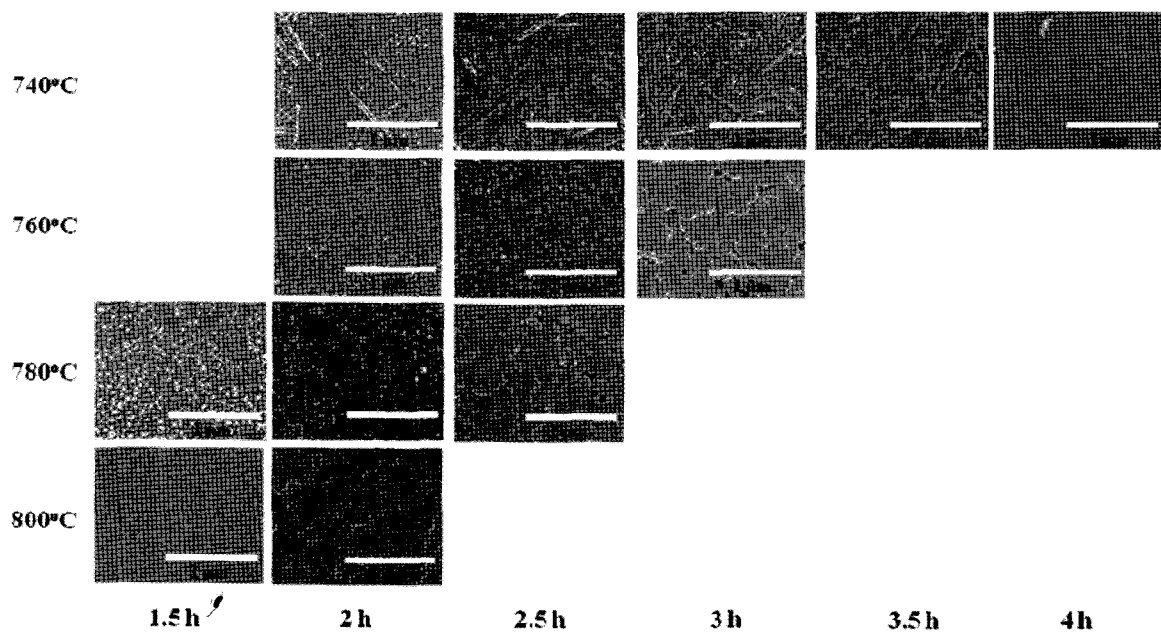

Fig. 3. SEM micrographs of YBCO films fired at 740-800°C for various holding periods.

Fig. 4. The misoriented YBCO grain in film fired at 780°C for 2 h.

because it has very low surface tension. Thus, degraded $T_{C,zero}$ value are related to the contamination from the metal substrate because the dip-coating method normally deposits the precursor film on the flank and back side of the metal substrate. Even though a small amount of Ni, Cr and Mo elements included in Hastelloy substrate diffuse into the YBCO film through the Ba-O-F liquid phase, $T_{C,zero}$ values can be degraded. At higher temperature, diffusion rate of those metal elements in Hastelloy into YBCO will be faster and consequently $T_{C,zero}$ values can be decreased with increasing firing temperature. In addition, YBCO films fired over optimum holing period at a given firing temperature show degraded $T_{C,zero}$ values, which may also be caused by the contamination from the metal substrate.

I_C and J_C values for YBCO films, determined by measuring I-V curves, are shown in Fig. 6 (a). The J_C and I_C values of all films studied are plotted in Fig. 6 (b) as a function of the holding period at various firing temperatures. The degradation of J_C with increasing the
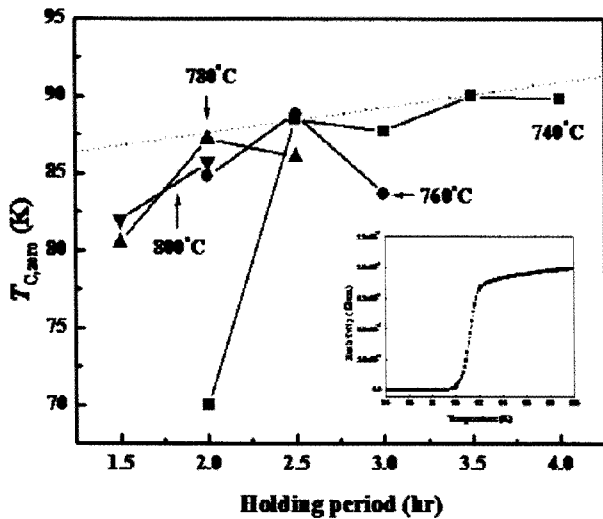
firing temperature for each optimum holding period is strongly correlated with the $T_{C,zero}$ suppression with increasing the firing temperature. Then, J_C values of the films fired over 780°C are very low, which are originated from the degraded T_C value and the existence of misoriented grains (see Fig. 4). Although the films fired at 740°C for 3 h and 760°C for 2.5 h have similar $\Delta\varphi$ and $T_{C,zero}$ values, the film fired at lower firing temperature exhibits degraded J_C value due to the existence of unreacted BaF_2 phase which blocks the supercurrent flow. The YBCO film fired at 740°C for 3.5 h exhibits high I_C values over 100 A/cm-width, corresponding to J_C value of 1.15 MA/cm^2 at 77.3 K in a self-field, which are attributable to the high critical temperature, excellent in-plane textures and dense microstructures with good grain connectivity as shown in Fig. 3. Since our CeO_2 buffer layer has not been fully optimized yet, its in-plane texture is relatively high. Further enhancement of J_C values may be possible by using more highly textured CeO_2 cap layer in addition to avoiding the metal substrate contamination.

Fig. 5. $T_{C,zero}$ values vs holding period for the YBCO films fired at temperature range of 740°C~850°C. The inset shows the ρ-T curve of the film fired at 740°C for 3.5 h.
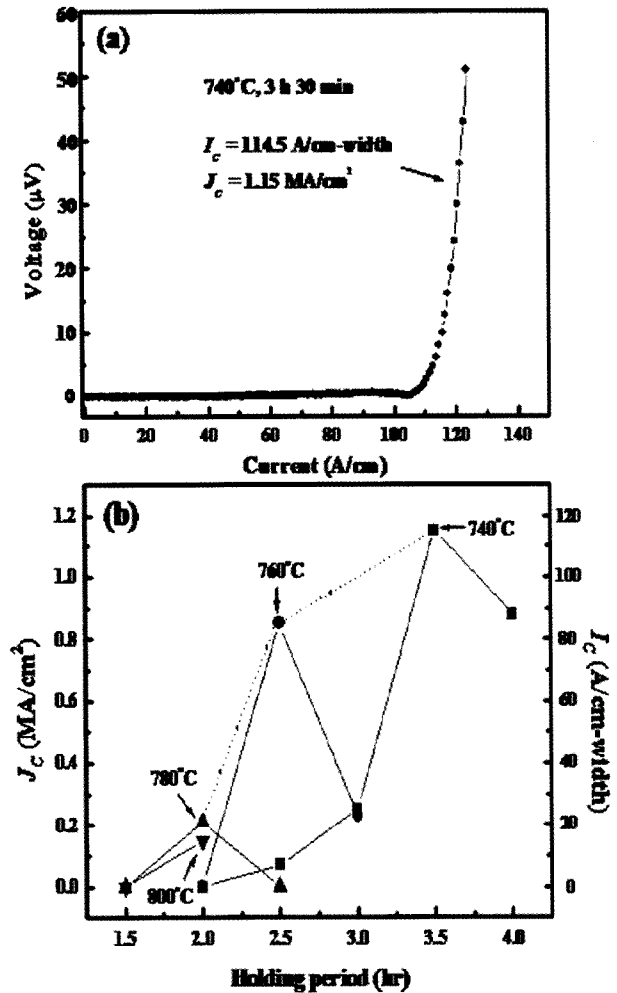
Fig. 6. (a) I-V curve of YBCO film fired at 740°C for 3.5 h, (b) J_C and I_C values at 77.3 K for YBCO films as a function of the holding period at various firing temperatures.

4. SUMMARY

We have successfully fabricated high-I_C YBCO films on the CeO$_2$ capped IBAD-MgO template by the MOD process employing fluorine-free Y, Cu precursors and Ba-TFA. Microstructure, texture, and superconducting properties of YBCO films were found highly sensitive to both the firing temperature and the holding period. Opimization of the MOD-YBCO process resulted in the achievement of 1 μm thick YBCO film with I_C value of 114.5 A/cm-width at 77.3 K in a self-field, corresponding to J_C value of 1.15 MA/cm^2. Present results clearly show that high-I_C YBCO coated conductors are achievable on the IBAD MgO template. Further enhancement of J_C values may be possible by improving the in-plane texture of CeO$_2$-buffer layer and avoiding the metal substrate contamination.

ACKNOWLEDGMENT

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