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# Fabrication of YBCO films on metal tapes by the TFA-MOD process

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# TFA-MOD법에 의한 금속기판 위 YBCO 박막 제조

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**Abstract**

YBCO thin films on metal substrates were prepared by the metal-organic deposition using trifluoroacetates (TFA-MOD). To compensate the loss of Ba element from the precursor films due to the reaction with $CeO_2$ cap layer, we have employed Ba-excessive precursor solutions of $YBa_{2+x}Cu_3O_{7-\delta}$ ($0 \leq x \leq 0.1$). The precursor solutions were dip-coated on the metal substrates with $CeO_2$ cap layer, initially heated up to 400℃, and finally fired at the various high temperatures for 2 h in a reduced oxygen atmosphere. With this approach, YBCO films possessing critical temperature over 85 K could be successfully prepared on the metal substrates. The highest $T_{c,zero}$ value of 86 K was obtained from the Ba-excessive YBCO film of x=0.005 in $YBa_{2+x}Cu_3O_{7-\delta}$ fired at 750℃ for 2 h. However, unexpected $T_c$ suppression even in Ba-excessive YBCO samples requires further identification.

*Keywords* : TFA-MOD, YBCO thin films, metal substrate, critical temperature

## I. Introduction

YBCO coated conductors have been fabricated by various vacuum processes, such as pulsed laser deposition, e-beam co-evaporation, sputtering, and metal-organic chemical vapor deposition. However, these vacuum processes are hardly considered cost-effective for real applications. In this respect, non-vacuum processes, including MOD and sol-gel, have drawn great attention as the promising alternatives [1,2]. High-$J_c$ YBCO coated conductors have recently been reported by several research groups using the TFA-MOD process [3~9].

Unlike the single crystal substrates, formation of the $BaCeO_3$ layer between YBCO film and $CeO_2$ cap layer of metal substrates is unavoidable for the films prepared by the TFA-MOD method, leading to a serious degradation in $J_c$ for the YBCO film thickness

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less than ~ 0.2 μm [10,11] while this problem becomes much less serious for thicker films. In this study, we tried to overcome this problem employing a Ba-excessive nominal composition. Thus, various nominal compositions of $YBa_{2+x}Cu_3O_{7-\delta}$ ($0 \leq x \leq 0.1$) were prepared for precursor solutions to compensate the loss of Ba element, and then we tried to find optimum firing conditions on the basis of our recent experimental results on single crystal substrates [12].

## II. Experimental

TFA precursor solutions were prepared by dissolving YBCO powders and TFA salts of Ba corresponding to 0.5 mol%, 2.5 mol%, 5 mol%, 7.5 mol%, and 10 mol% Ba excessive nominal composition into a solvent composed of trifluoroacetic acid mixed with de-ionized water. The solutions were stirred until YBCO powders and TFA salts of Ba were completely dissolved, and dried at 80℃ to form a glassy blue gel. The coating solutions having total metallic concentration of 1.5 M were made by dissolving the gel into appropriate amount of methyl alcohol. Thus prepared coating solutions were dip-coated onto $CeO_2$/IBAD-YSZ/Stainless Steel substrate at a withdrawal speed of 5 mm/sec. Dip-coated gel films were slowly heated up to 400℃ in 4.2% humidified oxygen with a flow rate of 400 ml/min to form the oxy-fluorides films. The films were subsequently fired at 750 ~ 800℃ for 2 h with 4.2% humidified Ar gas mixed with 1000 ppm oxygen gas and finally oxygenated at 450℃ for 1 h in a pure oxygen atmosphere. Ag protect layers of ~1.5 μm thickness were deposited on fired YBCO films using rf-magnetron sputtering.

The phases of YBCO films were analyzed by X-ray diffraction (XRD) using CuKα radiation. The surface morphology and film thickness of samples were observed by field emission scanning electron microscopy (FE-SEM). The critical temperature ($T_c$) of the films was measured by the standard four probe method.

## III. Results and discussion

Fig. 1 shows XRD $\theta$-$2\theta$ results for the YBCO film with fired at various temperatures. Sharp peaks of YBCO (00*l*) reflections represent that YBCO grains in all films are highly *c*-axis oriented. Minor $BaCeO_3$ phase peaks, most probably formed between YBCO and $CeO_2$ cap layer as previously reported by many researchers [3],[4],[6],[9],[10],[11] are also detected in all samples. The $BaCeO_3$ peak intensities are increased with increasing firing temperature, suggesting that larger amount of $BaCeO_3$ phase is formed at higher firing temperature. In addition, YBCO film fired at 725℃ for 2 h has a small amount of unreacted $BaF_2$ phase, indicating that the YBCO formation reaction was uncompleted at this low temperature.

XRD patterns of YBCO films fired at 750℃ for 2h are shown in Fig. 2. It is observed that Ba-excessive YBCO films are also highly *c*-axis oriented, and minor $BaCeO_3$ phase peaks are commonly observed.

Surface morphologies of YBCO films are represented in Fig. 3. The *a*-axis oriented grains are hardly observed in all samples. Grain size increased with increasing firing temperature. However, YBCO films fired at 775 and 800℃ have porous surface

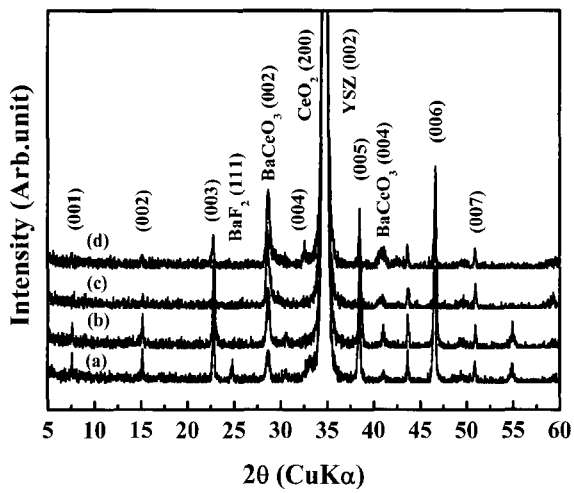


Fig. 1. XRD-patterns of YBCO films on $CeO_2$/IBAD-YSZ/ Stainless Steel substrates with firing temperature: (a) 725℃, (b) 750℃, (c) 775℃ and (d) 800℃ for 2 h.

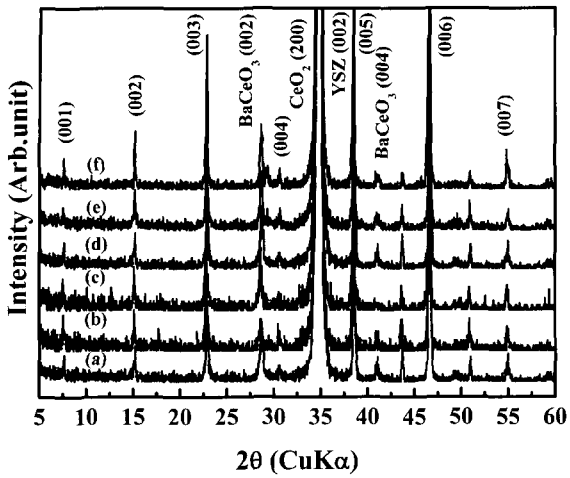


Fig. 2. XRD patterns of YBCO film and Ba-excessive YBCO films: (a) x=0, (b) x=0.005, (c) x=0.025, (d) x=0.05, (e) x=0.075 and (f) x=0.1 in $YBa_{2+x}Cu_3O_{7-\delta}$.

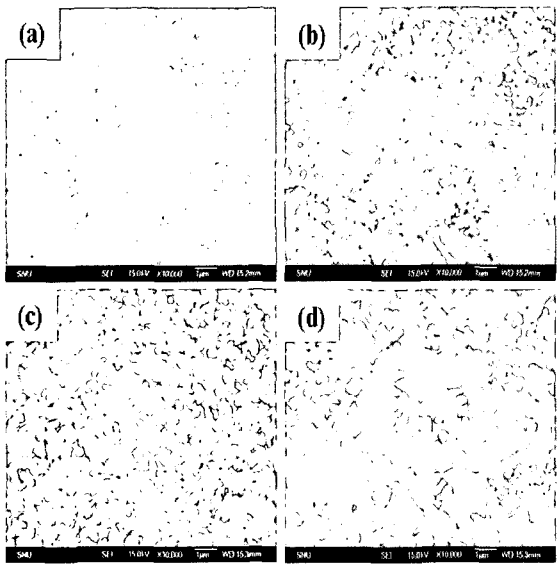


Fig. 3. Surface morphologies of YBCO films on $CeO_2$/IBAD-YSZ/Stainless steel substrates fired at (a) 725℃, (b) 750℃, (c) 775℃ and (d) 800℃.

morphology and poor grain connectivity. Fig. 4 shows characteristic microstructures of YBCO films having five different nominal compositions. With increasing x (i.e., excessive Ba content) up to 0.025, porosity of samples are almost unaltered while average grain size is apparently reduced for x = 0.025. With further increasing x up to 0.1, YBCO films become very porous.

$T_{c,zero}$ and $T_{c,onset}$ values of YBCO films measured by the standard four probe method are shown in Fig. 5. The YBCO films had $T_{c,zero}$ values of 57-85 K. All YBCO films exhibited a broad transition width ($\Delta T_c$) except the film ($\Delta T_c$ = 1.8 K) fired at 750℃. Depressed $T_{c,zero}$ with a broad superconducting transition of YBCO film of x=0 fired at 725℃ is surely caused by the existence of unreacted phases including $BaF_2$ phase. The YBCO films fired at 775 and 800℃ show a broad superconducting transition, which might be originated from a serious Ba loss of precursor films to form large amount of $BaCeO_3$ phase through the reaction with $CeO_2$ cap layer. Since an excessive loss of Ba element from the stoichiometric cation ratio Y:Ba:Cu = 1:2:3 would result in a reduced YBCO phase formation with

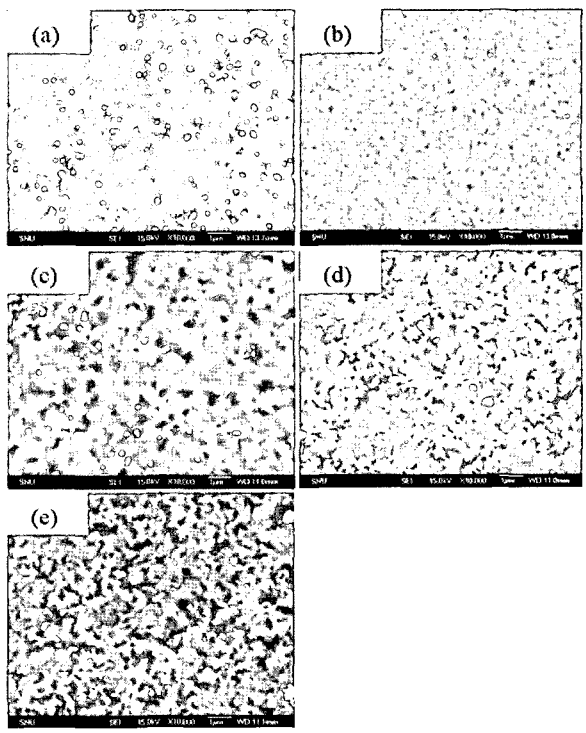


Fig. 4. Surface morphologies of Ba-excessive YBCO films on $CeO_2$/IBAD-YSZ/Stainless steel substrates fired at 750℃ for 2 h : (a) x=0.005, (b) x=0.025, (c) x=0.05, (d) x=0.075, and (e) x=0.1.

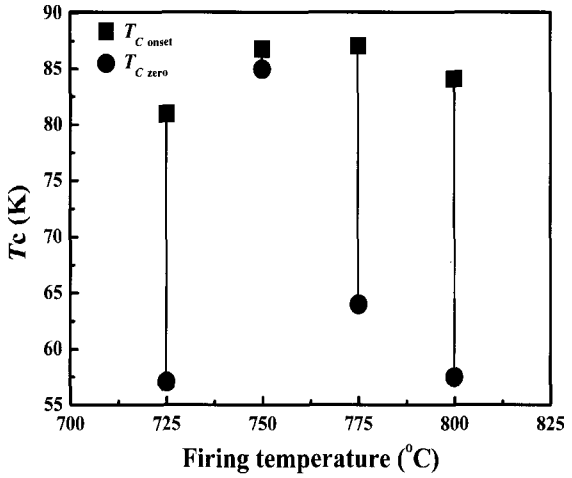


Fig. 5. $T_c$ values of YBCO films fired at temperature range of 725℃~800℃.

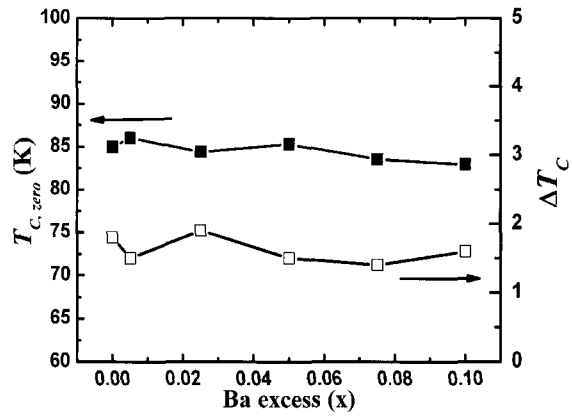


Fig. 6. $T_{c,zero}$ and values of YBCO film and Ba-excessive YBCO films fired at 750℃ for 2 h.

increased second phases such as CuO and $Y_2BaCuO_5$. Detailed microstructure analysis with transmission electron microscopy will clarify this point.

Fig. 6 shows $T_{c,zero}$ and $\Delta T_c$ values of YBCO films of Ba-excessive YBCO films fired at 750℃ for 2 h. The firing temperature of 750℃ was selected on the basis of the data in Fig. 5. Those of YBCO film with x=0 is also presented for a comparison. These samples exhibited $T_{c,zero}$ values of 82.9~86 K and transition width, $\Delta T_c$ values of 1.4~1.9 K. The highest $T_{c,zero}$ value of 86 K was obtained from the Ba-excessive YBCO film (x=0.005) fired at 750℃ for 2 h, and $T_{c,zero}$ values are slightly decreased with increasing x.

In the present experiments, it was impossible to achieve YBCO films with $T_{c,zero}$ above 90 K while YBCO films on single crystal substrates were routinely obtained using the TFA-MOD process with the same experimental apparatus [12]. The origin for this $T_c$, suppression on metal tapes is unclear at the moment. Especially, different from our expectation, $T_c$ suppression occurred even in Ba- compensated YBCO samples. Since thicker YBCO films on metal tapes, prepared by TFA-MOD, were reported to have $T_c$ above 90 K [3], lowered $T_c$ values by ~ 5 K in our thin films (~ 0.25 μm thickness) may be related to the film thickness and/or a potential contamination from metal substrates, which requires further investigation.

## IV. Summary

YBCO and Ba-excessive YBCO thin films on metal substrates were fabricated by the TFA-MOD process using YBCO powder and Ba trifluoroacetates as precursor materials. Microstructure and superconducting properties of YBCO films on metal substrates were highly sensitive to the firing temperature and nominal composition of precursor solution. The highest $T_{c,zero}$ value of 86 K was obtained from the Ba-excessive YBCO film of x=0.005 in $YBa_{2+x}Cu_3O_{7-\delta}$ fired at 750℃ for 2 h. The YBCO films fired at higher 775℃ exhibited a broad superconducting transition, which is related to the formation of large amount of $BaCeO_3$ phase. The origin for suppressed $T_c$ values even for Ba-excessive YBCO samples is unclear at the moemnt, and thus further study is necessary for its identification.

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