Partial substitution of rare-earth ions for yttrium through multi-layer precursors in the YBa$_2$Cu$_3$O$_7$ films grown by fluorine-free metal organic deposition

H. Matsui*, M. Sohma, I. Yamaguchi, T. Manabe, T. Kumagai

Abstract

We have studied the effects of partial substitution of rare-earth (RE) ions for yttrium in YBa$_2$Cu$_3$O$_7$ films prepared by fluorine-free metal organic deposition. The substitution was conducted through Y/RE multi-layer precursor films. We found that critical current density ($J_c$) in self field strongly depends on RE elements and increased by up to 44% with respect to an unsubstituted sample. Structural characteristics of the films were investigated using x-ray diffraction and transmission/scanning electron microscope, and we found several characteristic RE-dependences indicative of their close relation to the $J_c$ enhancement.

1. Introduction

Introduction of artificial pinning centres (APC) into superconducting YBa$_2$Cu$_3$O$_7$ (YBCO) films for the purpose of raising critical current density ($J_c$) has been widely studied. However, there are not many examples that succeeded in this approach with chemical means, because of the inherent difficulty in creating nm-size local disorders, which are believed to be the most effective APC, without degrading the superconducting matrix surrounding them. Among the successful examples of APC, substitution of rare-earth (RE) ions for yttrium is a rather popular approach [1-4]. It has been repetitively reported that in-field $J_c$ is enhanced by the RE substitution in YBCO films prepared by pulse-laser deposition (PLD) and the trifluoroacetate(TFA)-based metal-organic deposition (MOD). However, there remain some
questions about the APC induced by the RE substitution, for example, what sort of defect is formed, whether it depends on RE element and on fabrication process, and whether self-field \( J_c \) is enhanced. Therefore, it is required to accumulate further experimental observations of APC induced by a RE substitution in various fabrication processes.

Fluorine-free (FF) MOD is a low-cost and environmentally-compatible fabrication process of YBCO, and has achieved micrometre film thicknesses with assistance of UV-irradiation [5]. We have recently revealed with transmission electron microscope (TEM) that the FF-MOD YBCO films lack natural pinning centres (defects) as thickness exceeds about 400 nm resulting in a rapid decrease of \( J_c \) on film thickening [6]. Therefore, it has a special importance for the FF-MOD YBCO films to develop an effective APC introduction method. In addition, the dense and defect-poor YBCO matrix of thick FF-MOD films provides an ideal platform for studying the formation of APC by a RE substitution.

In this paper, we report the effects of partial substitution of RE ions for Y in the YBCO films grown by FF-MOD. The substitution was conducted through Y/RE multi-layer precursor films, since a simple mixing of RE into Y-Ba-Cu solution resulted in a degradation of the epitaxial growth of YBCO. We observed a noticeable dependence of \( J_c \) on the radius of RE ions, which yields a remarkable increase of self-field \( J_c \) by up to 44 % with respect to an unsubstituted sample. We also argue structural changes induced by the RE substitutions showing x-ray diffraction (XRD), TEM, and scanning electron microscope (SEM) data.

2. Experimental details

The fluorine-free RE-Ba-Cu (RE=Yb, Y, Gd, Nd, La) metalorganic solution was prepared by dissolving acetates of RE, Ba, and Cu in a 1:2:3 cation ratio into the mixture of propionic acid and tripropylamine, and by substituting the solvent by methanol. The solution was applied onto 10x10-mm-sized CeO2-buffered (40 nm) SrTiO3 (STO) substrates using a spin coater. The coated substrates were irradiated with an ultraviolet KrCl excimer lamp (λ = 222 nm) in ambient atmosphere for 15 min, and prefired at 500°C for 30 min. The above process was repeated to adjust film thickness and to form the multi-layer structure schematically drawn in Fig. 1(a). The precursor films were annealed for crystallization at 760°C in a stream of N2 gas mixed with 10-Pa oxygen, and then furnace-cooled to room temperature. The oxygenation of YBCO was done below 550°C during the furnace cooling. A standard x-ray diffractometer (MAC Science MXP3A) with a Cu-Ka radiation source mounted on a horizontal \( \theta \)–\( 2\theta \) goniometer was employed to examine the crystalline quality of films. \( J_c \) values were measured by the inductive method using THEVA Cryoscan. TEM images of the samples prepared by the focused ion beam method were taken with Hitachi HD-2000 at the operating voltage of 200 kV. The surface SEM images were taken with JEOL JSM-5400.

3. Results and discussion

Figures 1(b) and 1(c) show cross-sectional energy dispersive x-ray spectroscopy (EDS) images of the Gd-bilayer precursor and the corresponding crystallized film. In the precursor film, the sharp boundaries between the Y and Gd layers are observed supporting the multilayer structure drawn in Fig. 1(a). In the crystallized film, Gd is diffused and concentrated in the middle layer only in a remnant fashion. This means that the multi-layer structure in the precursor film is “melted” during the crystallization of YBCO, and consequently the RE substitution is occurred in relatively wide thickness region. Here, we stress that in our FF-MOD process, an epitaxial \( Y_{1-x}RE_xBa_2Cu_3O_7 \) film cannot be obtained by using a Y/RE mixed solution with the same element ratio as the multi-layer-precursor derived film shown in Fig. 1(c). We do not have a clear explanation for why the two substitution methods (multilayer precursor and mixed
solution) provide different films, but it is possible that existence of RE ions distinct from Y near the substrate interface disturbs more severely the epitaxial growth of YBCO than their existence in the middle layer. We note that in the previous TFA-MOD study [7], the mixed solution method was employed to grow epitaxial \( \text{Y}_1\text{xRE}_{\text{x}}\text{Ba}_2\text{Cu}_3\text{O}_7 \) (RE=Sm, Gd) films. Therefore, the contrasting results between the two substitution methods can be specific to the present FF-MOD process. Hereafter, we call a crystallized film obtained through a bi(tri)-layer precursor as a bi(tri)-layer film/sample for short.

Fig. 1. (a) A schematic drawing of the bi-layer precursor film; (b) Cross-sectional EDS images of the Gd-bilayer precursor film; (c) Same as (b) for the corresponding crystallized film.

Fig. 2. Dependences of \( J_c \) (filled circles,) and of the intensity of YBCO-007-peak in XRD \( \theta–2\theta \) profile (open circles) on the radius of RE ions for the (a) bi- and (b) tri-layer samples. The insets show the same plots of \( I_c \).

Fig. 3. (a-e) XRD \( \theta–2\theta \) profiles of RE-substituted FF-MOD YBCO films. (b) Magnification of the YBCO 002 peak.
Figure 2 shows the main result of this study, the dependences of $J_c$ (left axis) and of the intensity of YBCO-007-peak in a XRD $\theta$–2$\theta$ profile (right axis) on the radius of RE ions. The film thicknesses were set to about 0.6 mm and 0.8 mm for bi- and tri-layer samples, respectively. In both multi-layer structures, it is found that $J_c$ is increased (decreased) for the RE ions larger (smaller) than Y, excluding the end member La. The largest improvement of $J_c$ is about 44% [critical current ($I_c$) = 150 -> 216 A/cm] observed in the Gd-bilayer film. In contrast to $J_c$ showing a rather systematic variation by RE ions, the YBCO 007 peak does not much depend on RE except for La. This indicates that the observed $J_c$ variation is not simply related to the volume of c-axis aligned phase and requires other explanations. In the case of La, both $J_c$ and the YBCO-007 peak are suppressed suggesting that the superconductivity is simply degraded by the c-axis misalignment.

To uncover the origin of $J_c$ variation, we investigated structural properties of the films. Figures 3(a-e) shows the XRD $\theta$–2$\theta$ profiles of the tri-layer films of various RE substitute ions. As we mentioned above, the intensity of YBCO 00l peaks are not significantly varied by RE ions. Instead, the peaks at 12.8° and 52.8° are prominent only in the Gd- and Nd-trilayer film showing a clear RE dependence in the growth of secondary phases. These angles are close to those of the YBa$_2$Cu$_4$O$_8$(Y124)-004 (13.0°) and -016 (52.0°) reflections, respectively. Therefore, it is possible that some Y124-like phase is enhanced in the Gd- and Nd-substituted films. In Fig. 3(f), the normalized intensity of YBCO 002 peak is compared among RE ions. The peaks for Gd and Nd are slightly broaden as compared to the other RE ions, suggesting that the layer stacking along c-axis is slightly disordered in those two samples. The observations of the secondary phase and the c-axis peak broadening in the higher $J_c$ films are counterintuitive, because $J_c$ is generally enhanced as improving crystal quality. We will argue this in the latter part of this article.

To further study the relation between the structural property and $J_c$ in the RE-substituted films, we measured cross-sectional TEM of the Gd- and Yb-bilayer film, which showed an enhancement and suppression of $J_c$, respectively. In the Gd-bilayer film [Fig. 4(a-c)], we observed a noticeable vertical-position dependence of nanostructure. While the normal lattice pattern of YBCO is observed in the image taken near the substrate interface [Fig. 4(c)], we find a strongly disordered lattice with high-density stacking faults in the middle layer [Fig. 4(b)]. The stacking-faults are 5-20 nm in length and are terminated by anti-phase boundaries at ends. In the image taken near the surface [Fig. 4(a)], stacking
faults are less prominent than the middle layer, but the stacking sequence is clearly deviated from the normal one, as clearly seen in the left of the view showing a irregular pattern of dark lines. This observation is reminiscent of the previous TEM study of Y$_2$Ba$_4$Cu$_7$O$_{15}$ (Y247) by Berastegui et al. [8], where they showed a random stacking of the single (Y123) and double Cu-O chain (Y124) blocks. Though we cannot conclude the random pattern near the surface of the Gd-bilayer film is due to the Y123-124 stacking since the double Cu-O chains normally appear as bright rows in a TEM image [8,9], this interpretation is qualitatively consistent with the observation of the Y124-related reflections in the XRD spectra [Fig. 3(c)]. We also show in Fig. 4(d) a TEM image of the Yb-bilayer film measured in the middle layer for comparison. It contains neither stacking faults nor an irregular stacking sequence observed in the Gd-case. The results of the comparative TEM measurements between Gd and Yb qualitatively agree with those of XRD, and strongly suggest a RE-dependent character of nanostructure in the present partially RE-substituted YBCO films.

In Fig. 5, we show the surface morphologies obtained with SEM. We observed again a clear RE-dependence consistent with the $J_c$ variation. While the Yb- and Y-trilayer samples show submicron-size precipitates with relatively high density, the Gd and Nd ones show a flat surface with relatively small number of precipitates. The La-trilayer sample shows a considerably disordered surface in agreement with the XRD result. Our EDS analysis indicated that the observed precipitates are Y-Ba-Cu-O compounds with element-ratio shifted from 1:2:3:7. An explanation based on this analysis for the difference in the density of precipitates between Yb/Y and Gd/Nd is that it originates in the inner film structures. Namely, inclusion of high-density anti-phase boundaries as observed in the middle layer of Gd-bilayer sample but not in that of the Yb one (Fig. 4), can shift the element ratio in the middle layer, and the shift can be compensated in the surface region by the growths of secondary phases and precipitates. However, there are other possible explanations for the different surface morphologies. For example, we set the same annealing temperature for all RE ions, while the crystallization temperature of REBa$_2$Cu$_3$O$_7$ (RE-BCO) depends on RE [10]. The annealing temperature shifted from the optimal values can cause RE-dependent surface morphologies. Here, an improvement of surface quality in a multi-layer YBCO film has been reported in previous studies on PLD films [11-13], but there, the improvements were mainly in reduction of pores and of a-axis grains but not of precipitates.

Finally we discuss interplays among the above experimental results and their implications for the origin of the RE-dependence of $J_c$. As we already mentioned, the results from XRD and TEM are well correlated with each other. The appearance of Y124-related reflection and the broadening of the YBCO 002 peak in the θ–2θ profiles for Gd and Nd but not for Y and Yb correspond to the irregular layer pattern near the surface and the high density stacking faults in the middle layer, respectively, observed in the TEM image of Gd but not in that of Yb. The results from SEM also showed the same classification of RE in the density of precipitates, suggesting its relation to the inner structures. We think there are two possible reasons for the RE-dependent structural properties. First, in this study, we fixed the annealing temperature at 760 °C, which is optimal for an unsubstituted film. Since the crystallization temperature of RE-BCO films increases linearly with the radius of RE [10], our Gd, Nd, and La (Yb) substituted films are expected to have been heated at slightly lower (higher) temperature than their own optimal values. In our FF-MOD process, the preferential growth orientation of YBCO is changed from c- to a-axis as annealing temperature is decreased from optimal [14]. Therefore, the difference in structural properties between RE ions larger and smaller than Y can be related to the competition of growth orientation. The second possible explanation for the RE-dependent structural disorder is the coexistence of different RE-ion radii itself. In manganese oxide perovskites, it is recognized that increase of the ion-radius variance at the A-site leads to random displacement of the oxygen ions [15]. In the same mechanism, coexistence of RE ions in epitaxial YBCO films can induce ion displacements and consequent stacking faults. But in this scenario, it requires an additional explanation for why disorders were induced only for the large ions
but not for the small one. In both explanations, the results of La substitution can be attributed to the excessive difference of ionic radius from Y.

At present, we cannot conclude why $J_c$ was increased by the Gd and Nd substitutions. While the inner structure is disordered by stacking faults and secondary phases, the Gd and Nd films are superior in surface smoothness than Y and Yb. A simple argument is that the crystallinity in the vicinity of the surface made a critical influence on $J_c$. In our previous study on the detailed thickness dependence of FF-MOD films, it was strongly suggested that the thickness range extending from about 400 nm above the substrate interface to the surface is the so-called “dead layer”, which does not contribute to $I_c$ [6]. However, it was also suggested in Ref. 6 by the XRD and TEM results that the dead layer is superior in crystallinity compared to the rest part of film, supporting an insufficient-pinning scenario of the current suppression in the upper layer. More plausible explanation for the $J_c$ enhancement by the Gd and Nd substitutions is that the high-density stacking faults observed in Fig. 4(b) improved the vortex-pinning condition. Yamasaki et al. [9] studied the pinning property of thin (<300 nm) YBCO films prepared by FF-MOD with field-angle-dependence of $J_c$ and with TEM. They suggested that the main source of vortex pinning in the pristine samples is dislocations at the edges of stacking faults parallel to the ab-plane. The stacking faults observed in Ref. 9 are very similar to those of Fig. 4(b), but the density is incomparably higher in the Gd-substituted film. It is possible that the substitution of large RE ions for Y has an effect in increasing the number of linear pinning centres already exist in a pristine sample. Further studies including $J_c(\theta)$ measurements will conclude the mechanism of the $J_c$ variation in RE-substituted FF-MOD YBCO films.

4. Conclusion

We have studied the effects of partial substitution of rare-earth ions (Yb, Gd, Nd, La) for Y through multi-layer precursors in the epitaxial YBCO films prepared by FF-MOD. Self-field $J_c$ was enhanced by up to 44% on increasing the radius of RE from Y to Gd and Nd, but decreased as further increasing the radius to La or as decreasing the radius to Yb. XRD and TEM analyses indicated that stacking faults, anti-phase boundaries and irregular layer stacking are enhanced by the Gd and Nd substitutions but not by the Yb one. SEM measurements suggested that surface quality is enhanced by the Gd and Nd substitutions. The present results indicate that substitution of particular RE ions for Y in epitaxial YBCO films grown by fluorine-free MOD induces nanostructural disorders and enhances $J_c$.

References