Microstructural observations of epitaxial Y123 films on CeO$_2$-buffered sapphire by metal organic deposition

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Abstract. Epitaxial YBa$_2$Cu$_3$O$_7$ (Y123) films were obtained on CeO$_2$-buffered sapphire substrates by a fluorine-free MOD process. A 170-nm-thick homogeneous film revealed a high critical current density ($J_c$ > 4 MA/cm$^2$) at 77 K, whereas a 320-nm-thick film had a low $J_c$ of 0.7 MA/cm$^2$. Both of the films have neither $a$-axis orientation nor BaCeO$_3$ phase by x-ray diffraction. In this article, the microstructures of these Y123 films were observed by cross-sectional transmission electron microscopy. The epitaxial $c$-axis layers were observed successively from the interface with CeO$_2$ buffer to the surface. Selected area diffraction (SAD) exhibited that the orientation relationship among the Y123, CeO$_2$-buffer and sapphire substrate was: Y123(001)[110] || CeO$_2$(100)[100] || Al$_2$O$_3$(-1012)[1-210]. The impurity phase on the surface was revealed to be a CuYO$_2$ compound by energy dispersive X-ray spectroscopy and SAD. The Y123 grains on the surface of the 320-nm-thick film were somewhat inclined to the epitaxial Y123 layer; this is one of the reasons for degraded $J_c$ in the thicker films.

1. Introduction

YBa$_2$Cu$_3$O$_7$ (Y123) superconducting films on CeO$_2$-buffered R-plane sapphire (CbS) are expected for use in SN-type fault current limiters (SFCL) [1] since sapphire has high thermal conductivity and its single crystals are commercially available on a large scale at relatively low cost. The CeO$_2$ buffer layer prevents the reaction between Y123 and sapphire and relaxes large lattice mismatch between them.

For SFCL application, high critical current ($I_c$) is required. Since the $I_c$ is the product of $J_c$, width, and thickness, it is required to produce a thicker [2] and higher-$J_c$ film. However, there is some limitation in the thickness of the Y123 film, i.e., critical thickness (~300 nm), due to the large difference of thermal expansion coefficients between Y123 and sapphire [3]. A Y123 film on sapphire with a thickness thicker than the critical one often results in cracks and degraded $J_c$.

In this article, epitaxial Y123 films of thicknesses 170 nm and 320 nm were prepared by fluorine-free metal organic deposition (MOD) [4,5], which is applicable to large-area substrates at low cost, and their microstructures were observed by transmission electron microscopy (TEM).

2. Experimental

Commercially available R-plane sapphire (-1012) with evaporated CeO$_2$(100) (THEVA) was used as substrates. The surface roughness, $R_s$, was $<$0.5 nm in the 1 $\mu$m $\times$ 1 $\mu$m range by atomic force microscopy. The fabrication method of Y123 film was similar to that described in the previous papers.
Metal acetylacetonates (Nihon Kagaku Sangyo Co., Ltd.; Y:Ba:Cu = 1:2:3 in molar ratio) were used as starting materials for preparing the coating solution. This solution was spin-coated onto CbS, and prefired at ~500 ºC. Film thickness was adjusted by repeating of spin-coating and prefiring; which resulted in thin (~170 nm) and thick (~320 nm) films estimated by TEM observations. These prefired films were (i) heat-treated at 745 ºC in $pO_2 = 10^{-4}$ atm for 90 min in a tube furnace using a gas flow of an Ar-O$_2$ mixture; (ii) subsequently, cooled to room temperature in the furnace after the flow gas was switched to oxygen.

The crystallinity and grain orientation of the films were analyzed by X-ray diffraction (XRD) $\theta$-2$\theta$ scans (MAC Science MXP$^{3A}$). Superconductive critical current density ($J_c$) was inductively measured by THEVA Cryoscan. Thin foils for TEM were prepared by slicing, grinding, dimpling, and then ion-thinning. JEOL high-resolution electron microscope (JEM-4000EX) was used for the microstructural observations.

3. Results & Discussion

An XRD $\theta$-2$\theta$ profile shown in figure 1 for the thick film exhibits that a highly $c$-axis-oriented Y123 film was obtained with no impurities or the $a$-axis-oriented grains. High intensities of the 00$\ell$ peaks suggest that the film had high crystallinity and preferred orientation. A thinner 170-nm-thick film had a similar XRD profile (not shown here). The $J_c$ value of the thicker film, ~0.7 MA/cm$^2$, was lower than that of the thinner film, ~4 MA/cm$^2$.

We observed their microstructures by cross-sectional TEM to clarify the origin of the difference of $J_c$ between them. Figure 2 shows a low-magnification TEM image for the thin but high-$J_c$ film. The stripe-like contrast due to the $c$-plane of Y123 was clearly seen from the interface with CeO$_2$ to the surface. The whole $c$-axis-oriented Y123 layers were very dense in the 170-nm-thick film; no $a$-axis-oriented grains were observed. The interface between CeO$_2$ and Y123 was very smooth and no reaction product phases such as BaCeO$_3$ were observed. The SAD patterns (inset of figure 2) exhibited that the orientation relationship among them is: Al$_2$O$_3$[1-210]//CeO$_2$[100]//Y123[110].

There were a few particles with a ~50 nm diameter on the surface represented by ‘P’ in figure 2, which has been revealed to be a CuYO$_2$ compound by electron dispersive spectroscopy (EDS) and SAD as shown in figure 3. The SAD pattern can be indexed as the delafossite structure (ICDD No. 39-0244) with a twin structure irradiated by the electron beam from the [2-1-10] direction.

High-resolution TEM (HRTEM) images are shown in figure 4. The rows of white spots that appeared to be the Cu-O planes are successively spread in the upper, middle, and lower layers. The intervals of these planes are ~1.17 nm apart from each other, which correspond to the $c$-axis parameter of Y123, although the planes were wavy in some parts due to the inserted extra Cu-O planes, or stacking faults, indicated by black triangle pairs [6]. In the surface region, figure 4(a), the Cu-O planes
were wavy in some places owing to many short stacking faults, which led to a scale-like pattern in the low-magnification TEM image (figure 2). In the middle part, figure 4(b), alternate long stacking faults are seen, the intervals of two adjacent stacking faults were ~2.52 nm, which corresponds to $c/2$ of the Y247 phase. These were observed as a long white line in the low-magnification TEM image (figure 2). Anyway, it was found that very dense Y123 films from the interface with CeO$_2$ buffer to the surface were obtained by TEM observations in figure 2 and figure 4.

A typical low-magnification TEM image for the thick low-$J_c$ film is shown in figure 5. The stripe due to $c$-axis orientation of Y123 was seen from the interface with CeO$_2$ to the surface. However, in the region thicker than ~250 nm, the contrast was different from that of the thinner part and some grain boundaries indicated by small circles were observed. Close examination showed that the $c$-axis of the upper left grain was somewhat inclined. Another grain or a pore denoted by ‘P*’ in the right-hand and lower region. The composition, crystallinity, and preferred orientation of these grains and the Y123 layer were estimated by SAD and EDS. Figures 6(a)-(c) show SAD patterns of the lower, middle, and upper regions of the Y123 layer using an electron irradiation from the Al$_2$O$_3$[1-210] direction, so that the orientation relationship be the same as that in the thin high-$J_c$ film. The number of diffraction spots became less and the reflection grew streaky as the upper position was measured. These may be related to the degraded crystallinity and increasing stacking faults. There were many white lines ascribed to the stacking faults in the upper part in figure 5. It was also found from the SAD pattern, figure 6(d), that the region near the surface denoted by ‘4’ in figure 5 had an orientation slightly different from that of the lower Y123 layer. Their EDS spectra (not shown) were almost the same. The precipitate denoted by ‘P*’ was considered to be the CuYO$_2$ compound because its EDS spectrum was similar to that in figure 3 although a small amount of Ba peaks were seen. It is interesting that the $c$-axis-oriented

Figure 3. EDS spectrum and SAD patterns of the precipitate ‘P’ in Fig. 2.

Figure 4. HRTEM images of (a) upper, (b) middle, and (c) lower parts of Y123 layer for the thin film.
Y123 phase grew over such precipitates. The fact that grain boundaries were clearly seen and different orientation occurred at the region ~250 nm from the interface might be related to the critical thickness of ~300 nm. Occurrence of these grains might have caused degradation of \( J_c \) in the thick film.

4. Summary

Epitaxial Y123 films were obtained on CeO\(_2\)-buffered sapphire substrates by the fluorine-free MOD process. Cross sectional TEM observations revealed that the c-axis-oriented epitaxial Y123 layers grew up to ~200 nm thickness. No distinct grain boundaries were observed in the 170-nm-thick film; thus, it exhibited high \( J_c \) of 4 MA/cm\(^2\), although some impurity phase was found. In contrast, there were Y123 grains on the surface of the 320-nm-thick film, of which the orientation was slightly different from that of the epitaxial Y123 layer; this is one of the reasons for degraded \( J_c \) ~0.7 MA/cm\(^2\), in the thicker films. The origin of these misoriented grains has not been clarified; whether it be caused by the difference of thermal expansion coefficient between Y123 and sapphire or not. In order to prepare thicker epitaxial Y123 film with high \( I_c \), further investigation that relates preparation conditions with microstructures such as crack or grain formation is required.

Figure 5. Low magnification cross-sectional TEM image for the thick film.

Figure 6. SAD patterns from the areas denoted by (a) ‘1’, (b) ‘2’, (c) ‘3’ and (d) ‘4’ in Fig. 5.

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