Microstructure of coated conductors with La- or Nb-doped SrTiO₃ conductive buffer

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Abstract. A novel configuration for coated conductors (CCs) was proposed to reduce material cost and consisted of YBa₂Cu₃O₇ (YBCO) / conductive buffer(s) / Ni-electroplated {100} <001> textured Cu, and SUS316 lamination tape. Conductive buffers are a key subject to reduce material cost of CCs. In the CC using the conductive buffer of Nb-doped SrTiO₃ (Nb-STO), a high-Jc YBCO (2.5 MA/cm² at 77 K and self-field) was successfully obtained. Moreover, a clean interface between the buffer and the metal tape without oxides was confirmed using TEM analysis. However, the resistivity of the Nb-STO buffer increased to be several Ω cm after the YBCO deposition, which was beyond expectations. Therefore, the La-doped STO (La-STO) conductive buffer was incorporated into CCs as a novel conductive buffer. Two CCs with the different conductive buffers were compared in terms of microstructure analysis using transmission electron microscopy.

1. Introduction

To develop low-cost REBa₂Cu₃O₇ (REBCO, RE: rare earth elements Y, Gd, or Eu) coated-conductors (CCs), novel CC architecture has been proposed [1, 2]. The novel architecture involves the elimination of silver and copper electric stabilizing layers on the superconducting layer by using a conductive buffer and a highly conductive metal tape. By eliminating the expensive silver layer, low-cost REBCO CCs can be realized. A current must pass through the conductive buffer layers and flow through the metal tape after quenching the superconducting layers. Therefore, a key issue for the development of low-cost REBCO CCs is the development of an ideal conductive buffer layer, as the highly conductive metal tape is already available [3], typically as a nickel electroplated cube-textured Cu and stainless-steel laminate. Therefore, the most important issue is the development of conductive buffer layers, which prevent oxygen and metal diffusion, and perform biaxially aligned REBCO crystal growth.

Previous studies have confirmed that YBa₂Cu₃O₇ (YBCO) layers deposited on the Nb-doped SrTiO₃ (Nb-STO) buffered the textured Ni/Cu/SUS316 tapes with a high Jc of 2.5 MA/cm² at 77 K and self-field [1, 2] with the Nb-STO acting as a conductive buffer layer [4]. However, the resistivity of Nb-STO increased form 10⁻³ Ω cm to several Ω cm after deposition of a YBCO superconducting layer. According
to the estimation performed using current–voltage gradients, some of the current flows through the Cu tape, and the remaining current flows through the superconducting layer after the transition to normal conductivity [4]. In anticipation the effects of oxygen introduction to the buffer layers, La-doped SrTiO$_3$ (La-STO) was used as a conductive buffer layer herein. Because La and Nb substitute different sites of SrTiO$_3$, known as the A and B site of Perovskite (ABO$_3$), the resistivity change and oxygen diffusion in La-STO during YBCO deposition are expected to differ from those of Nb-STO. Moreover, La-STO was previously reported as a conductive buffer layer and its properties were characterized [5, 6]. In previous studies, La-STO was fabricated on a STO single substrate, a TiN layer deposited on a Ni-based rolling-assisted biaxially textured substrate (RABiTS) and an Ir layer was deposited on a Cu RABiTS. The YBCO layers were subsequently deposited on the La-STO buffer layers. All YBCO layers showed superconductivity and the lowest $J_C$ was 0.42 MA/cm$^2$ for the YBCO layer on the Ni-based RABiTS. For the Cu RABiTS, although the Ir layer suppressed Cu diffusion, Cu partly diffused though the Ir and YBCO layers, and Cu oxides were formed on the YBCO layers. Herein, the La-STO buffer layer was directly fabricated on textured metal tapes without a template layer, that is, on Ni-electroplated texture Cu tapes. The YBCO layer was subsequently deposited onto the La-STO buffer layer. The crystallinity and the diffusion of oxygen and metals of the YBSO/La-STO and YBCO/Nb-STO were investigated using X-ray diffraction (XRD) and transmission electron microscopy (TEM). These effects of the La-STO and Nb-STO buffer layers were also compared.

2. Experimental procedure

Buffer layers were deposited by a pulsed-laser deposition (PLD) using a Nd-YAG laser ($\lambda$=266 nm) at 800 °C in 97% Ar + 3% H$_2$. The atmosphere pressure was $3 \times 10^{-2}$ Pa for La-STO and $2 \times 10^{-4}$ Pa for

Figure 1 X-ray pole figures. (a) La-STO {110} and (b) Nd-STO {110} pole figures before YBCO deposition; (c) and (d) were YBCO (102) pole figures on La-STO and Nd-STO, respectively.
Nd-STO. The YBCO superconducting layer was deposited by PLD using a KrF excimer laser (\(\lambda=248\) nm) under an O\(_2\) atmosphere of 35 Pa. The YBCO deposition temperature was 765 °C for La-STO and 740 °C for Nd-STO.

The crystallinity and crystal orientation were evaluated using XRD (\(\theta-2\theta\) and pole figure methods). The microstructure was analyzed via TEM with energy dispersive X-ray spectroscopy (EDX). The TEM specimens were prepared by cutting and milling using a focused ion beam, the so-called micro-sampling technique. The current–voltage characteristics of the specimens were measured using a standard 4-probe method and \(J_c\) was defined by an electric field criterion of 1 μV cm\(^{-1}\).

3. Results and discussion

3.1. Crystal orientation of the buffer and YBCO superconducting layers using XRD pole-figures

Figure 1 shows the XRD pole-figures of the buffer layers obtained before YBCO deposition because the peaks from the buffer layers and the YBCO overlapped. The XRD pole-figures of the YBCO (102) on of La-STO and Nd-STO buffer layers are also shown in figures 1 (c) and (d). The all pole-figures showed a good biaxial alignment, indicating that the average crystallographic orientation of both YBCO and La-STO or Nd-STO buffer layers were nearly the same and did not differ greatly.

3.2. Cross-sectional microstructural analysis

Cross-sectional STEM images of the YBCO CCs prepared using La-STO and Nb-STO buffer layers are shown in figures 2 (a) and (b), respectively. The bright thin contrast regions were partially observed at the interface between the buffer layer and metal tape in Figure 2 (a). These regions were composed of Ni oxides according to the associated EDX analysis. The EDX mappings of each element of the YBCO CC with the La-STO buffer layer is shown in figure 3 (a). Oxygen penetrated the nickel surface, indicating that it diffused through the La-STO buffer layer. The presence of Ni oxides at the interface was confirmed by electron diffraction, as shown in figure 4 (c). Three spots corresponding to La-STO, Ni oxide, and Ni were observed in the regions surrounded by the circle in figure 4 (c), which was enlarged in figure 4 (h). By contrast, the YBCO CC prepared using Nb-STO showed a bright region or a slightly bright thin layer at the interface between the Nb-STO buffer layer and metal tape, but the interface was very clear in the EDX mapping and two spots in the electron diffraction in the region.
surrounded by the circle (figure 5 (c)). An enlarged image of the circle in figure 5 (c) is provided in figure 5 (h), indicating that Ni oxides were not formed at the interface. Herein, although Ni oxides were not observed at the interface of the YBCO CC prepared using the Nb-STO buffer layer, Ni oxides were previously observed at the interface before modifying the preparation conditions including buffer layer thickness, temperature, and doping level. Therefore, the oxygen diffusion was likely prevented in the La-STO sample by adjusting the relevant preparation conditions.

Nickel was not detected in all buffer and YBCO layers, as shown in figures 3 (a) and (b). Therefore, it was concluded that the La-STO and Nb-STO buffer layers prevented Ni diffusion, but their effects on the Cu diffusion remained unclear because no copper was detected at the nickel surface. However, Cu was rarely detected at the Ni surface as shown in reference [7], where metal tapes were annealed at 900 °C for 20 min to clean up the surface without oxides. Consequently, Ni and Cu mutually diffused and Cu was detected in small quantities at the Ni surface, where the Cu-rich phase was formed in the YBCO layer. Metal tapes are always annealed under a flow of 3% H₂ and 97% Ar to obtain a clean surface without oxides, but the required annealing conditions (temperature and annealing time) depend on type of metal tapes. The metal tapes used for the La-STO and Nb-STO depositions were annealed at 865 °C for 20 min and at 700 °C for 30 min under a 3% H₂ and 97% Ar mixture, respectively. No Cu was observed at the Ni surface in either sample. Therefore, although the effect of the La-STO on Cu diffusion was not clear, it was concluded that the ideal annealing conditions of the metal tapes during surface cleaning was < 865 °C for 20 min through analysis of data obtained herein and from previous examinations.

Furthermore, the grain boundaries in the YBCO layer, which appeared as bright lines across the YBCO layer, were observed in figure 2 (a) which showed the STEM image of the YBCO CC prepared

![Figure 3. STEM image and EDX mappings of Y, Ba, Cu, O, Ni, Sr, Ti, and La or Nb in the YBCO CCs prepared using La-STO (a) and Nb-STO (b), respectively.](image-url)
using the La-STO buffer layer. Figure 3 (a) also included one of these grain boundaries. According to figure 3 (a), an Y-rich phase was present at the starting point of the grain boundary, and the YBCO grew irregularly on the Y-rich phase, adopted a crevasse-like morphology. It is likely that the Y-rich phase formation occurred owing to the unoptimized preparation conditions of the YBCO layer on the La-STO buffer layer.

Figures 4 and 5 show the STEM images and selected area electron diffractions (SAEDs) corresponding to each circle in the STEM images for the YBCO CCs prepared using the La-STO and Nb-STO buffer layers, respectively. The La-STO and Nb-STO buffer layers and the YBCO deposited
on the both buffer layers exhibited epitaxial growth, consistent with the X-ray pole figure measurements. The SAEDs shown in figures 4 (f) and (g) were slightly misaligned, but the misalignment angle was < 1°, which did not affect the biaxial alignment.

4. Conclusions
YBCO CCs were prepared using two types of conductive buffer layers (La- and Nb-doped SrTiO$_3$) to develop the low-cost CCs. The conductive buffer layers were prepared by partially substituting large valence ions at the A and B sites of SrTiO$_3$ as known ABO$_3$ of Perovskite. One was the La-doped SrTiO$_3$ and the other was the Nb-doped SrTiO$_3$. According to the microstructural analysis of both buffer layers using TEM, although the effect of both buffer layers on Ni diffusion was similar, the effect on the oxygen penetration differed. Ni did not diffuse into both buffer layers, but Nb-STO prevented oxygen penetration towards the metal tape, while La-STO did not. However, the oxygen penetration may be prevented in La-STO sample after adjusting the layer thickness and the doping level similar to that of the previous Nb-STO examination. In addition, the preparation conditions of the YBCO layers on the La-STO buffer layer were not optimized. In the future, the superconducting properties such as $T_c$ and $J_c$ will be compared for the YBCO samples fabricated on La-STO and Nb-STO, after adjusting the preparation conditions of the La-STO buffer layers and subsequently deposited YBCO layers.

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