Fabrication of YBa$_2$Cu$_3$O$_y$ coated conductor by Vapor-Liquid-Solid growth technique using a Reel-to-Reel system

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Abstract. To optimize the production cost of REBCO-coated conductors, the deposition rate needs to be increased. The vapour-liquid-solid (VLS) growth technique is a suitable method for fabricating a film with a high deposition rate and good crystal orientation. This technique enables growth through a liquid phase. There have been studies conducted on the fabrication of REBCO films using the VLS growth technique. However, very few studies have been performed on a system for depositing REBCO-coated conductors with VLS growth techniques while moving the substrate. In this study, we evaluate the reel-to-reel pulsed laser deposition system, pure YBCO-coated conductors, and the BHO 3 vol% doped YBCO-coated conductors, which were fabricated using the VLS growth technique under high-speed deposition conditions with an average deposition rate of 17 nm/s, achieved $J_c > 2.0$ MA/cm$^2$, $J_c > 1.0$ MA/cm$^2$ at 77 K and self-field, respectively. In addition, the $J_c$ in the magnetic fields of the BaHfO$_3$-doped YBCO coated conductors could be improved by introducing discontinuous BHO nanorods.

1. Introduction
To reduce the production cost of REBa$_2$Cu$_3$O$_y$ (REBCO, RE: rare earth) superconducting coated conductors, it is necessary to increase the deposition rate. The pulsed laser deposition (PLD) method is a widely used technique for the fabrication of REBCO-coated conductors. However, in the PLD method, $a$-axis grains that inhibit superconducting current grow as the deposition rate increases [1]. Therefore, the problem with the PLD method is a tradeoff relationship between the deposition rate and the $a$-axis grain ratio.

Recently, many methods for the fabrication of REBCO films through the liquid phase have been developed [2-4]. One such method is the liquid phase epitaxy (LPE) method, which can produce samples with excellent crystallinity. Using the LPE method, it is possible to fabricate the film at a growth speed that is 10 to 100 times more than that of the vapour-phase method. Thus, it has been reported that NdBa$_2$Cu$_3$O$_y$ films using the LPE method can be fabricated at a very high growth rate of 10 μm/min [4].
However, when a REBCO-coated conductor is fabricated using the LPE method, the substrate temperature needs to be as high as the peritectic temperature of REBCO (1000–1100°C). At that temperature, the metal elements diffuse from the metal tape and fuse with the REBCO, which can reduce its superconducting property.

In the vapour-liquid-solid (VLS) growth technique, the raw materials are supplied from the gas phase and crystals grow at the solid-liquid interface [5–7]. Figure 1 shows a schematic diagram of the VLS growth technique. As shown in the figure, the VLS growth method consists of a three-layer lamination of a solid layer, liquid layer, and vapour layer. The growth procedure is as follows:

(i) The solid layer is fabricated as a seed crystal on a substrate using a conventional vapour-phase method.

(ii) Materials constituting the liquid layer were deposited on the solid layer. In this deposition, meltback occurs, due to which the solid layer continues to dissolve in the liquid phase until the liquid phase reaches an equilibrium state.

(iii) Raw materials constituting the REBCO are supplied from the vapour phase to the liquid layer. The raw materials condense in the liquid layer.

(iv) When the raw materials in the liquid layer become supersaturated, the crystal growth of the REBCO starts at the solid-liquid interface.

The VLS growth technique is a liquid-phase growth method using the PLD method, and REBCO-coated conductor is fabricated in a reduced pressure atmosphere. Therefore, it is possible to fabricate a film with fewer defects and better crystallinity than those in the vapour phase deposition method, and the substrate temperature is lower than that of the LPE method [5],[6]. It has been reported that a NdBCO film fabricated on a single crystal substrate using the VLS growth technique has excellent crystallinity, similar to a single crystal, at a relatively low substrate temperature.

We have reported high-speed deposition [8] and the introduction of artificial pinning centres (APCs) to SmBa$_2$Cu$_3$O$_y$ thin films [9] fabricated by the VLS growth technique (VLS-SmBCO). However, the aforementioned results are for a static system in which the substrate is always fixed under the heater. There are few reports on the VLS growth technique for film fabrication while taking up the substrate with a reel (reel-to-reel system, RtR system). Here, there is a problem in that the liquid layer does not liquefy due to the RtR system. In the case of a static system, the substrate temperature is maintained at a constant value during the deposition because the substrate is always kept under the heater. On the contrary, the RtR system is used, since the film is fabricated while moving the substrate, the substrate is separated from the heater after the liquid material deposition and the liquid layer is solidified once. After that, the sample approaches the heater again and the solidified liquid layer in the sample is liquefied before the raw material is supplied. Therefore because the liquid layer is solidified once, there is a possibility that the composition of the liquid layer is changed and the liquid layer is not liquefied.

In consideration of the above, in this study, VLS-YBCO films were fabricated using the RtR system for high-speed deposition using the VLS growth method even when the film was fabricated while moving the substrate.
2. Experimental method

The VLS-YBCO films were fabricated by PLD on a 5 mm wide CeO$_2$/LaMnO$_3$/IBAD-MgO/Y$_2$O$_3$/Gd$_2$Zr$_2$O$_7$/Hatelloy C-276 substrate [10]. Table 1 shows the fabrication conditions for VLS-YBCO films, and Table 2 shows the fabrication conditions for each layer of the VLS growth technique. First, as a solid layer on the CeO$_2$ intermediate layer, pure YBCO or 3 vol% BHO-doped YBCO thin films were fabricated at a substrate temperature ($T_s$) of 860°C, oxygen partial pressure ($P_{O_2}$) of 53 Pa, laser energy density ($E$) of 2.6 J/cm$^2$, and substrate moving speed ($v_s$) of 3.6 m/hr. Subsequently, using a Ba$_3$Cu$_7$O$_{10}$ target with Ag10wt% as a liquid layer on the solid layer, the liquid layer was fabricated at a $P_{O_2}$ of 200 Pa, $T_s$ of 860°C, $E$ of 3.3 J/cm$^2$, and $v_s$ of 7.2 m/hr. Finally, pure YBCO or 3 vol% BHO-doped YBCO raw materials were supplied to the liquid layer at a $P_{O_2}$ of 200 Pa, $T_s$ of 910°C, $E$ of 3.3 J/cm$^2$, and $v_s$ of 1.8 m/hr. In addition, as a comparative sample to confirm the effect of the liquid phase, a sample without a liquid layer was fabricated by excluding the liquid layer deposition from the condition of the BHO-doped VLS-YBCO sample.

The surfaces of the VLS-YBCO films were observed using a scanning electron microscope (SEM). The crystalline orientation of the films was evaluated by X-ray diffraction (XRD) analysis. The evaluation method for the $a$-axis grain mixture ratio was obtained by dividing the peak intensity of the YBCO (200) plane by the peak intensity of the YBCO (005) plane, expressed as a percentage. The $c$-axis orientation was evaluated by measuring the full width at half maximum of the rocking curve peak intensity on the YBCO (005) ($\Delta \omega_o$). In-plane orientation was evaluated by measuring the full width at half maximum of the in-plane peak intensity on the YBCO (103) ($\Delta \phi$). The superconducting property is measured by the four-probe method using a physical properties measurement system (PPMS). The superconducting state was defined with an electric field criterion of 1 $\mu$V/cm.

### Table 1. Fabrication parameters of VLS-YBCO films.

| Parameters                  | Conditions                  |
|-----------------------------|-----------------------------|
| Method                      | PLD method                  |
| Laser source (wavelength)   | KrF raser ($\lambda = 248$ nm) |
| Substrate                   | CeO$_2$ buffered IBAD-MgO   |
| Energy density              | 2.6, 3.3 J/cm$^2$           |
| Distance between target substrates | 55 mm                      |
| Substrate temperature       | 870, 910, 930°C             |

### Table 2. Parameters for fabricating each layer of VLS-YBCO films.

| Solid | Liquid | Vapour |
|-------|--------|--------|
| YBa$_2$Cu$_3$O$_y$ pure or BaHfO$_3$(3vol%) | Ba$_3$Cu$_7$O$_{10}$ +Ag10wt% | YBa$_2$Cu$_3$O$_y$ pure or BaHfO$_3$(3vol%) |
| Oxygen partial pressure       | 53 Pa       | 200 Pa  |
| Substrate temperature         | 860°C       | 860°C   | 910°C   |
| Thickness                     | 200 nm      | 75 nm   | 1.4 $\mu$m |
| Deposition rate                | 7 nm/s      | 8 nm/s  | 26 nm/s |
| Substrate moving speed         | 3.6 m/hr    | 7.2 m/hr| 1.8 m/hr |
3. Results

Figure 2 shows the surface SEM images of the YBCO films. In figure 2, (a) shows a VLS-YBCO fabricated in the static system, (b) shows a sample without a liquid layer fabricated by the RtR system, (c) shows a pure VLS-YBCO fabricated by the RtR system, and (d) shows a BHO-doped VLS-YBCO fabricated by the RtR system. As shown in figure 2(a), a large number of grains are scattered on the surface. These grains are composed of the condensation and solidification of the liquid layer. In the case of figure 2(b), grains like figure 2(a) were not observed, and the surface was rough. In the case of figure 2(c) and (d), there is a possibility that the films have grown through the liquid phase even with the RtR system because grains such as those shown in figure 2(a) were observed.

Table 3 shows the crystal orientation of each sample. It can be seen that a sample without a liquid layer has a low crystal orientation because many $a$-axis grains are formed and the $\Delta \omega$ and $\Delta \phi$ values are high due to high-speed deposition in the vapour-phase growth mode. On the contrary, the samples prepared by the VLS growth technique have no $a$-axis grains and the $\Delta \omega$ and $\Delta \phi$ values are lower than that of the sample without a liquid phase. Since the REBCO crystal grew in the liquid phase growth mode instead of the vapour-phase growth mode, it is thought that a sample with high crystal orientation could be produced.

We discuss the superconducting properties of the samples shown above. In the pure VLS-YBCO and the BHO-doped VLS-YBCO using the RtR system, $J_c$ at 77 K under a self-magnetic field were calculated as 2.08 MA/cm$^2$ and 1.06 MA/cm$^2$, respectively. On the contrary, the $J_c$ of the without-

| Sample Type                  | $a$-axis grain percentage | $\Delta \omega$ (°) | $\Delta \phi$ (°) |
|------------------------------|---------------------------|----------------------|-------------------|
| without-liquid layer         | 50%                       | 1.29°                | 2.09°             |
| VLS-YBCO pure                | 0%                        | 0.80°                | 1.83°             |
| VLS-YBCO+ BHO                | 0%                        | 1.04°                | 1.63°             |

Figure 2. Surface SEM images of the YBCO films. (a) VLS-YBCO sample fabricated in the static system (b) sample without liquid layer fabricated by the RtR system (c) pure VLS-YBCO sample fabricated by the RtR system (d) BHO-doped VLS-YBCO sample fabricated by the RtR system.
liquid layer sample is 0.19 MA/cm² at 77 K under a self-magnetic field. It is considered that the reason why $J_c$ was improved is that the crystal growth mode is changed depending on the presence or absence of the liquid layer and the crystal orientation is improved.

Figure 3 shows the $J_c$-$B$ curves of the VLS-YBCO films using the RtR system. It can be seen that the BHO-doped VLS-YBCO resulted in an improvement in $J_c$ in high magnetic fields at both 65 K and 77 K as compared to pure VLS-YBCO. This indicates that BHO acts as an APC.

Figure 4 shows the applied field angular dependence of $J_c$ of the BHO-doped VLS-YBCO. Figures 4 (a) and (b) show the measurement results under (a) 77 K and 1 T, and (b) 65 K and 3 T, respectively. In the case of figure 4(a), the $J_c$ peak value at $B//c$ is low. This is because the pinning force of the $c$-axis-correlated pinning is weak. On the contrary, in the case of figure 4(b), the $J_c$ peak of $B//c$ is sharp. This is because narrow nanorods with a radius close to the coherence length at 65 K act as APCs.

Figure 5 shows cross-sectional TEM images of the BHO-doped VLS-YBCO and EDX mapping of Hf. As shown in the low-magnification cross-sectional TEM image in Figure 5(a), the BHO-doped VLS-YBCO sample is composed of a substrate, solid layer, and vapour layer. In addition, the vapour layer, which is a layer grown through the liquid phase, has a structure in which a thin layer without BHO and a thin layer with BHO are mixed. As shown in the high-magnification cross-sectional TEM image in Figure 5(b), it was confirmed that discontinuous BHO was introduced. The average diameters of the BHO nanorods in the solid and vapour layers were 4.3 and 5.8 nm, respectively.

There are two main reasons why the nanorod diameter differs in the two layers. The first is that the substrate temperatures of the solid and vapour layers are 860 °C and 910 °C, respectively. When the substrate temperature is high, the surface diffusion distance of adatoms becomes longer, and the Hf raw material is easily taken into the nucleus. Therefore, the vapour layer has a wider nanorod diameter than the solid layer. The second reason is the growth mode, due to which the surface diffusion distance between the adatoms became longer
References

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4. Summary

In the fabrication process of REBCO superconducting coated conductors, it is necessary to increase the deposition rate to reduce the production cost. Using the VLS growth technique, which is a growth technique initiated from a liquid phase, it is possible to produce a thin film with good crystal orientation at a high growth rate. In the pure YBCO and BHO, 3 vol% doped YBCO prepared by the VLS growth technique, $J_c$ was found to be 2.0 MA/cm$^2$ and 1.0 MA/cm$^2$ at 77 K under a self-magnetic field, respectively. This technique uses the reel-to-reel system for lengthening the REBCO-coated conductors. In addition, the introduction of BHO improved $J_c$ in magnetic fields. To further improve the $J_c$ in magnetic fields, it is necessary to conduct further study to calculate the optimum amount of BHO.

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