Experimental study in the development of HTS NMR probe

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Abstract. We investigated the effect of introducing artificial pinning centers (APCs) into YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) thin films to improve the critical current density ($J_c$) and reduce the microwave surface resistance ($R_s$) in a high dc magnetic field. Introduction of the APC was realized by dispersing BaHfO$_3$ (BHO) particulates in the YBCO thin films. Four types of sintered YBCO ceramics with x wt % (x = 0.5, 1.0, 2.0) BHO were used as laser targets in order to fabricate YBCO thin films with various amounts of BHO and investigate the influence of the BHO doping concentration. $J_c$ was measured by a four probe method. We measured $J_c$ in a magnetic field which was applied parallel to the c-axis ($J_c(p)$), and $J_c$ in a magnetic field which was applied perpendicular to the c-axis ($J_c(n)$). The $R_s$ was calculated using a correlating equation of $J_c$ and $R_s$. The $J_c(p)$ at 5 T and 20 K of 1.5 wt% BHO doped YBCO thin film was the largest at 3.4 MA/cm$^2$. The $J_c(n)$ of 1.5 wt% BHO doped YBCO thin film was 2.5 MA/cm$^2$, which is comparable to non-doped. The $R_s(n)$ and $R_s(p)$ of all YBCO thin films was less than 25 $\mu\Omega$ at 500 MHz. Therefore, we clarified the possibility that the most effective way to fabricate thin film for NMR coil application is by doping YBCO with BHO 1.5 wt%.

1. Introduction

High resolution nuclear magnetic resonance (NMR) spectroscopy is an important technique for determining molecular structure and physical properties of liquid samples [1]. A major drawback is its low signal-to-noise ratio (S/N) compared with other spectroscopic methods. (S/N) can be improved by raising the magnetic field strength, lowering the temperature of the sample, or improving the performance of the radio frequency (RF) probe and electronics [2]. RF probes can be improved in three general ways: First, reducing the volume of the detection coil, the signal per nuclear spin can be increased [3]. Second, by cooling the coils and preamplifiers, the noise can be reduced by up to a factor of four [4]. Finally, coils built from low-loss materials such as superconductors can improve the sensitivity [5]. In particular, the $R_s$ of high temperature superconductivity (HTS) thin film is smaller than that of the conducting metals usually used in the microwave frequency region [6], and improvement of sensitivity in nuclear magnetic resonance (NMR) analysis can be expected from the characteristics of the low $R_s$ under a high magnetic field. However, when NMR pick-up coils are applied to high magnetic fields, such as 11.7 T in the case of a 500 MHz NMR, the $J_c$ of HTS films reduce rapidly according to the applied magnetic fields. Furthermore, the pick-up coils are necessary to generate a radio frequency during the excitation phase of a pulsed NMR experiment. Due to these factors, superconducting of NMR pick-up coils are not yet wide spread.

In particular, because the magnetic field is applied perpendicular to the c-axis, it is necessary to improve the $J_c$ and $R_s$ for NMR detection coil applications. It has been reported that to improve the $J_c$ at high magnetic fields, high temperature superconductivity (HTS) thin film doped with BaMo$_3$ (M = Metal, Zr,
Sn) as APCs are effective [7]-[8]. Recently, H. Tobita et al reported that GdBCO coated conductors doped with BHO exhibit superior properties as APC material [9]. Additionally, Y. Ichino et al reported that a $J_c$ of 2 MA/cm$^2$ at 20 K, 10 T was obtained by doping a 3.7 vol% of BHO to SmBCO films. In this study, we will clarify the doping amount of BHO suitable for NMR pick-up coils by evaluating the $J_c$ of YBCO films doped with BHO at a low temperature and high magnetic field, targeting an increase in $J_c$ and a decrease in $R_s$ for YBCO thin films [10].

2. Experiment

Non-doped and BHO doped YBCO thin films with a thickness of 200 nm were deposited by using a pulsed-laser-deposition (PLD) method which used a KrF excimer laser ($\lambda = 248$ nm) on MgO (100) single crystalline substrates. The laser energy and repetition rate were 180 mJ and 1 Hz, respectively. We used commercial 1.5, 2.0 and 3.0 wt% BHO doped YBCO targets to fabricate BHO doped YBCO thin films. For comparison, we also used a non-doped YBCO target. The holder was heated by a SiC heater, and a substrate was attached directly to the holder and was heated by heat conduction. The holder was rotated to form homogeneous films. In this study, all films were deposited at approximately 720 °C with an oxygen pressure of 250 mTorr. The deposited thin films were then annealed at 430 °C with an oxygen pressure of 2000 Pa for 1 hour. For the analysis of the transport properties, UV photolithography and dry etching were used in order to obtain 2 mm long and 100 μm wide strip patterns. Au was deposited in order to reduce contact resistance to the electrode. The patterned samples were then lodged on a sample holder and mounted in cryostat endowed with a 5 T superconducting magnet. The standard 1 μV/cm criterion was used to evaluate critical current values from the characteristics collected in the four probe configuration. In this study, since we could not use the 1 μV/cm standard due to influence of noise from the characteristics of $I-V$.

We defined the critical current values by using the standard 1 μV/cm after averaging the data from 10 experiments. The $R_s$ values were calculated using a correlation equation with $J_c$ and $R_s$ [11-12].

$$R_s [\text{m} \Omega] = 1.8 \times J_c^{-1} [\text{MA/cm}^2] \text{ at 21.8 GHz} \quad (1)$$

The crystalline of the films was evaluated by X-ray diffraction (XRD) to obtain the $\theta/2\theta$ value and $\phi$-scans. The $\delta\omega$ was the full-width half-maximum (FWHM) of the rocking curve of the (005) peak of the films, and the $\delta\phi$ was the FWHM of the $\phi$-scan of the (102) plane of the thin films.

3. Result & Discussion

Figure 1 (a) shows the $\theta/2\theta$ results of the XRD measurement of the YBCO superconducting thin films. Both the non-doped and BHO doped samples showed strong YBCO (00l) peaks. Thus, the observations of the YBCO phase suggest that the YBCO films grew with $c$-axis orientation on the MgO substrate. Figure 1(b) shows X-ray $\phi$-scan diffraction patterns of the (102) face of the YBCO. Each of the YBCO (102) peaks was clearly detected at 90˚ intervals, indicating that thin films have a four-fold symmetry on the MgO substrate. Thus, all thin films were revealed to be epitaxially grown cube-on-cube biaxially oriented thin films. Table 1 shows the $\delta\omega$, $\delta\phi$ and $T_c$ of the non-doped YBCO and BHO doped YBCO thin films. For all BHO doped YBCO thin films other than 3 wt% doped thin film, the value of $\delta\omega$ was less than 1.6 and the value of $\delta\phi$ was less than 1.8. Therefore, no effect on the crystallinity in 2.0 wt% or less for BHO doped YBCO was observed.
Figure 1. (a): X-ray θ-2θ pattern collected on the non-dope and BHO1.5, BHO2.0 and BHO3.0. (b): ϕ-scan of the non-dope and BHO1.5, BHO2.0 and BHO3.0.

Table 1. APC material and composition of the thin film. $T_c$, $\delta \omega$ and $\delta \phi$ of the each thin films.

| Sample name | Super conductor | APC material | Additive amount [wt%] | $\delta \omega$ | $\delta \phi$ | $T_c$ [K] |
|-------------|----------------|--------------|------------------------|----------------|--------------|-----------|
| non-doped   | YBa$_2$Cu$_3$O$_{7-\delta}$ | – | – | 1.62 | 1.79 | 86.9 |
| BHO1.5     | YBa$_2$Cu$_3$O$_{7-\delta}$ | BaHfO$_3$ | 1.5 | 1.34 | 1.79 | 82.3 |
| BHO2.0     | YBa$_2$Cu$_3$O$_{7-\delta}$ | BaHfO$_3$ | 2.0 | 1.54 | 1.71 | 81 |
| BHO3.0     | YBa$_2$Cu$_3$O$_{7-\delta}$ | BaHfO$_3$ | 3.0 | 2.23 | 2.57 | 83 |

Figure 2 (a) shows the $J_c(n)$ and $J_c(p)$ measured at 20 K. The dotted lines represent the $J_c$ fitting data calculated though formulas (1), (2) and (3). These fitting data could be explained by using the two-fluid model for high frequency and low magnetic field limits [13]. The $R_s$ is given as (1) in a low magnetic field and (2) in a high magnetic field [14]. Where $\lambda_c$ is the London penetration depth, $B$ is the dc magnetic field, $\Phi_0$ is the flux quantum, and $\mu$ is the dynamic mobility. The $\eta$ is the viscous drag coefficient which is related to the motion of the magnetic flux.

$$ R_s(B) = R_s(0T) \frac{\Phi_0}{2\lambda_c \eta_{\text{low}}(B,T,d)} $$

Non-doped typically showed $J_c = 6.75$ MA/cm$^2$ in zero magnetic field. The $J_c$ of the YBCO thin films doped with BHO were comparable $J_c$ of non-doped in zero magnetic field. However, the YBCO doped with BHO 1.5 wt% was 7.4 % greater than the non-doped YBCO. Improvement of the $J_c$ and $R_s$ by APCs under a zero magnetic field was reported by Matsumoto et al. and Mukaida et al [1-2]. In particular, the $J_c(p)$ of BHO1.5 was 4.0 MA/cm$^2$ in 5 T, 41 % greater than that of the non-doped. It was possible to improve the $J_c(p)$ by doping the BHO. The $J_c(n)$ of BHO1.5 was 3.4 MA/cm$^2$, and was almost the same for the non-doped.

In addition, it is necessary to generate a magnetic field of B1 = 3.69x10$^3$ T for the 500 MHz NMR pick-up coil. It is assumed that for the application of NMR to a one-turn coil 1mm in width and 1 µm thick, 18.3 A of current will flow through the coil in order to product B1. $J_c(p)$ 2 MA/cm$^2$ critical current density is required at 11.7 T. Thus, it was revealed from the fitting data that the $J_c(p)$ at 10 T of BHO1.5 was 2.0 MA/cm$^2$, and 1.5wt% BHO doped YBCO is the most effective in the application of NMR . Figure 2.(b) shows the $R_s(n)$ and $R_s(p)$ calculated from a correlating equation of $J_c$. The dotted line is the fitting data of $R_s$ under a weak magnetic field calculated by using equation (1) and under a strong magnetic field calculated by using equation (2). The $R_s(p)$ and $R_s(n)$ of BHO1.5 was two orders of magnitude lower than the $R_s$ of copper, and is thus effective for NMR pick-up coils.
4. Conclusion

We measured the $J_c$ of 0, 1.5, 2.0 and 3.0 wt% BHO doped YBCO thin films. In addition, we have calculated the correlating equation of $J_c$. The $J_{c}(p)$ of BHO1.5 was 7.4 % bigger than non-doped in a zero magnetic field. The $J_{c}(p)$ of BHO1.5 in 5 T was 41 % bigger than non-doped. $J_{c}(n)$ was also comparable to the non-doped. The $R_{c}(n)$ and $R_{c}(p)$ of BHO1.5 of 10 T were smaller by approximately two orders of magnitude than the $R_c$ of copper. Therefore, we clarified the possibility that the most effective way to fabricate thin film for NMR coil application is by doping YBCO with BHO 1.5 wt%.

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