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GROWTH OF $NdBa_2Cu_3O_{7-\delta}$ SUPERCONDUCTING THIN FILMS ON $SrTiO_3(100)$ AND $LaSrGaO_4(100)$ SUBSTRATES

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$NdBa_2Cu_3O_{7-\delta}$ superconducting thin films were grown on $SrTiO_3(100)$ and $LaSrGaO_4(100)$ substrates by off-axis rf sputtering and pulsed laser deposition. The effects of several deposition parameters, e.g. gas pressure, substrate temperature and energy density were studied. Thin films grown by off-axis rf sputtering were highly c-axis oriented, but those by pulsed laser deposition were predominantly a-axis oriented under our deposition conditions. However, the c-axis oriented portion for the films grown by pulsed laser deposition was increased by increasing the temperature above 800°C. $T_{c(\mathrm{zero})}$ was 87 K and 83 K for the c- and a-axis oriented films respectively. The critical current density of c-axis oriented films was 10^6-10^7 A/cm^2 below 60 K.

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1. Introduction

Among the $RBa_2Cu_3O_7$ (RBCO) (R: rare-earth element) superconductors, $NdBa_2Cu_3O_{7-\delta}$ (NBCO) has been expected to be a promising material in the fields of both large and small scale applications of high temperature superconductors, such as superconducting magnets and electronic devices, since Yoo et al. [1] succeeded in the fabrication of NBCO bulk superconductors with high critical temperature (T_c) and current density (J_c) by the melt processing technique. NBCO thin films [2, 3] have high stability in air and atomically flat surfaces compared with $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films. It is believed that NBCO migh produce superconducting electronic devices with low flux noise because it has a large flux pinning force.

High quality c-axis oriented NBCO thin films with $T_{c(\mathrm{zero})}$ above 85 K have been obtained by pulsed laser deposition (PLD) [3, 4] and off-axis rf sputtering [5, 6]. Ishimaru et al. [5] fabricated Joshepson junctions reproducibly, using c-axis oriented NBCO thin films with smooth surface morphology by focused ion beam technique. Thin films [7–12] with a- or b-axis perpendicular to the substrates are also desirable for the fabrication of superconducting devices based on the Josephson junction in view of the highly anisotropic coherence length of high temperature superconductors. Although growth of NBCO thin films with a-axis orientation on $SrTiO_3$ (STO)(100) substrates was reported uniquely by Badaye et al. [13], the superconducting transition temperature was not satisfactory compared with that of a-axis oriented YBCO thin films. Moreover, there was no direct evidence for the a-axis orientation of NBCO thin films such as (h00) peaks in the X-ray diffraction patterns.

In this work, we have deposited not only c-axis, but also a-axis oriented NBCO thin films by off-axis rf sputtering or PLD and investigated the effects of several deposition parameters, e.g. gas pressure, substrate temperature and energy density etc., by measuring resistance, critical current density and X-ray diffraction patterns. Especially, the growth of a-axis oriented NBCO films was clearly confirmed by depositing them on $LaSrGaO_4$ (LSGO)(100) substrates.

2. Experimental procedures

We have grown NBCO thin films on STO(100) substrates by off-axis rf sputtering and on STO(100) and LSGO(100) substrates by PLD. Stoichiometric target of $NdBa_2Cu_3O_{7-\delta}$ ($\phi = 5$ cm) for off-axis rf sputtering and off-stoichiometric target of $Nd_{0.9}Ba_{2.1}Cu_3O_{7-\delta}$ ($\phi = 2.5$ cm) for PLD were prepared by the solid state reaction method. We used an off-stoichiometric target for PLD since Badaye et al. [4] reported that the composition of the films grown using a stoichiometric target by PLD had more or less shifted Nd/Ba ratio to $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ ($0.04 \geq x \geq 0.11$). The sputtering target was fired consecutively at 920°C, 950°C and 1000°C for 36 h each with intermediate grindings, while the PLD target was calcined at 920°C for 20 h and sintered at 980°C for 25 h twice with intermediate grindings. Each target was finally annealed at 450–500°C for 1–2 days in an oxygen environment. $T_{c(\text{zero})}$ of each target was about 91 K and 84 K as shown in Fig. 1. Details of target preparation are described elsewhere [6].

For the off-axis rf sputtering, mixed gas of Ar : O_2 (1 : 1) was used as the sputtering gas. Substrate temperature (T_s), gas pressure (P_{AO}) and rf power (P_{rf})

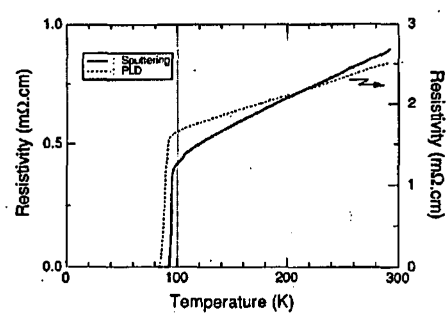

Fig. 1. Temperature dependence of the resistivity of the sputtering target (solid line) and the PLD target (dotted line).

were varied in the range of 740–800°C, 50–300 mTr and 50–70 W respectively. Several *in situ* oxygenation processes for some films were studied, i.e. annealing at 450°C for 3 h, two stage annealing at 650°C and 450°C for 3 h respectively, and rapid cooling under 1 atm oxygen environment.

In the case of PLD, the distance between substrate and target was fixed at 45 mm and every film was deposited using an KrF excimer laser (248 nm) at a repetition rate of 5 Hz for 8 min. The film thickness was about 2800 Å. After the deposition, the chamber was filled with oxygen above 1 atmosphere, then cooled below 100°C in about 50 min. The temperature noted in PLD experiments is that of the substrate holder, but the actual substrate temperature is lower than that by about 30°C in the range of the deposition temperatures. The deposition was carried out in the range of temperature 780–830°C, laser power on the target (P_1), 1.6–1.9 J/cm^2 and oxygen pressure (P_O), 200–450 mTr.

Electrical resistance was measured by the conventional four-probe method. For some films, measurements of electrical resistance were carried out before and after patterning them crosswise. Patterning was carried out by wet or dry etching. Wet etching was performed in 1% phosphoric aqueous solution, while dry etching was by Ar ion milling for 30–35 min. An X-ray diffraction pattern of each film was taken with Cu K_α radiation. The thickness of STO(100) and LSGO(100) substrates was 1 mm and 0.5 mm respectively.

3. Results and discussion

3.1. NBCO films by off-axis rf sputtering

All films grown at our various deposition conditions are highly *c*-axis oriented as shown in Fig. 2. We did not observe any significant impurity phase for any film. The typical *c*-axis lattice parameter of grown NBCO thin films is about 11.77 Å which is nearly the same as that of the target used [6]. The target and the grown films have also nearly the same Nd/Ba ratio of 2.1 : 1, determined by electron-probe microanalysis (EPMA), suggesting that the compositions of the grown thin films are nearly the same as that of the target.

We have deposited NBCO thin films under various conditions of temperature and gas pressure at a fixed value of P_{rf} = 50 W. The superconducting transition

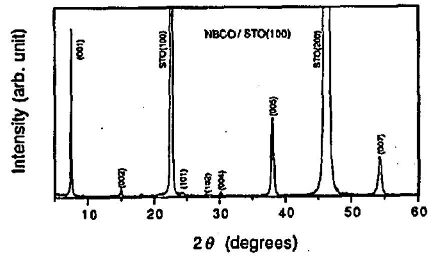

Fig. 2. Typical X-ray diffraction pattern for NBCO thin films grown on STO(100) substrates by off-axis rf sputtering.

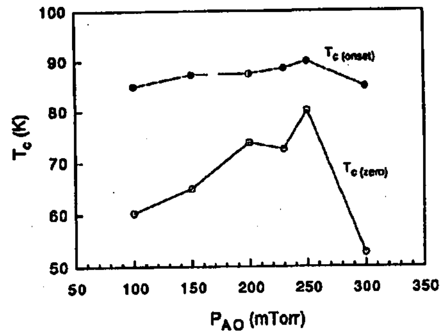

Fig. 3. Effect of gas pressure on the superconducting transition temperatures of NBCO thin films grown on STO(100) substrates by off-axis rf sputtering.

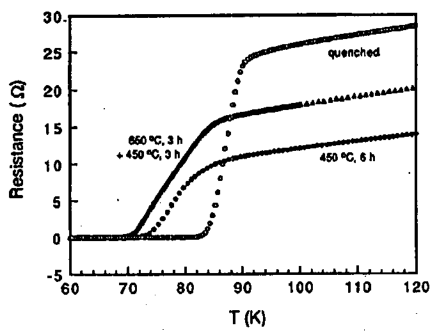

Fig. 4. Effect of *in situ* annealing on the superconducting transitions of NBCO thin films grown on STO(100) substrates by off-axis rf sputtering.

of the films determined by the resistance measurement does not show considerable dependence on the deposition temperature below 780°C, while it has strong dependence on the gas pressure as depicted in Fig. 3. These samples were *in situ* annealed at 450°C for 3 h under 1 atm oxygen. Although the critical temperature was the maximum at 250 mTr, a lot of droplets were observed on that film surface through an optical microscope observation. The critical temperature of the deposited film is lower than that of the target, maybe due to the oxygen deficiency δ in the deposited thin film.

NBCO has a similar δ–T_c relation as YBCO [14] i.e. T_c decreases with increasing oxygen vacancy. Two kinds of *in situ* annealing processes, one at 450°C for 3 h and the other at 650°C and 450°C for 3 h respectively, were carried out for some films. For NBCO thin films deposited under a gas pressure of 150 mTr or 250 mTr, there was no significant change of T_c by the *in situ* annealing. However, quenching gave a higher T_c than the other *in situ* annealing processes for the thin film deposited at $P_{AO} = 200$ mTr as shown in Fig. 4.

The effect of rf power on T_c was studied in the range of $P_{rf} = 50$–90 W at the condition of $T_s = 760$°C, $P_{AO} = 200$ mTr and quenching. The maximum $T_{c(zero)}$

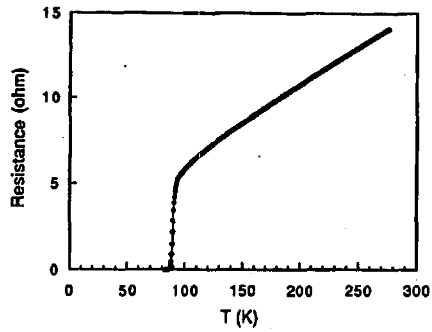

Fig. 5. Temperature dependence of the resistivity of a NBCO thin film grown on STO(100) substrate by off-axis rf sputtering. The film was deposited at $T_s = 760°C$, $P_{rf} = 70$ W and $P_{AO} = 200$ mTr.

of 87 K was achieved for the film deposited at $P_{AO} = 200$ mTr and $P_{rf} = 70$ W as shown in Fig. 5. The critical current density was measured after patterning some films to form a micro-bridge (width = 10 μm, length = 100 μm) by Ar ion milling. In the case of a film deposited at $P_{rf} = 50$ W and $P_{AO} = 200$ mTr, J_c was 5×10^6 A/cm^2 at 10 K, but it decreased very rapidly to below 10^6 A/cm^2 as the temperature increased above 60 K. The resistivity of the bridge was 250 mΩ cm at room temperature. J_c exceeded 10^7 A/cm^2 below 30 K for the film deposited at $P_{rf} = 70$ W and $P_{AO} = 150$ mTr.

3.2. NBCO films by pulsed laser deposition

NBCO thin films were grown on STO(100) and LSGO(100) substrates using an off-stoichiometric target of $Nd_{0.9}Ba_{2.1}Cu_3O_7$ by PLD. Although it is very hard to separate the (h00) peaks of the RBCO phase from those of STO(100) substrates in X-ray diffraction patterns, those of the RBCO phase grown on LSGO(100) substrates can be clearly observed since the (100) peak of LSGO is forbidden [9–12]. Therefore the LSGO(100) substrate is very effective for confirming the growth of a-axis oriented RBCO thin films.

As a preliminary experiment, we grew NBCO thin films on STO(100) substrates under various oxygen pressures and could obtain relatively good quality films in the range of $P_O = 250$–350 mTr. Therefore growth of NBCO thin films was carried out at the fixed oxygen pressure of 250 mTr. Figure 6 shows X-ray diffraction patterns of NBCO thin films grown on STO(100) substrates at various temperatures. The (h00) peaks of the STO(100) substrate are clearly visible, while (00l) peaks of NBCO phase are very weak for the films grown below 800°C. However, (00l) peaks of the NBCO phase also become evident as the temperature is increased to 820°C. Although the (h00) peaks of the NBCO phase were not observed, Fig. 6 is considered to suggest that highly a-axis oriented films were grown below 800°C and c-axis oriented films were also deposited at the elevated temperature of 820°C, i.e. a- and c-axis oriented films coexist at 820°C. The film orientation will be discussed again in the context of growth of NBCO films on

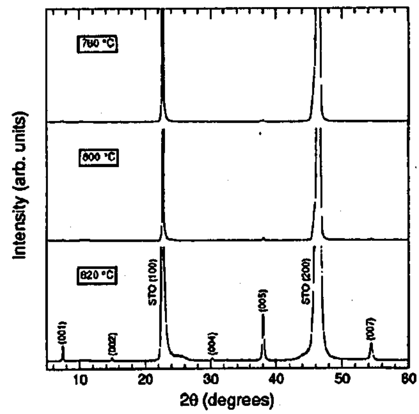

Fig. 6. X-ray diffraction patterns of NBCO thin films grown on STO(100) substrates by pulsed laser deposition. The film was deposited at $P_{\mathrm{l}} = 1.7\ \mathrm{J/cm^2}$, $P_{\mathrm{O}} = 250$ mTr.

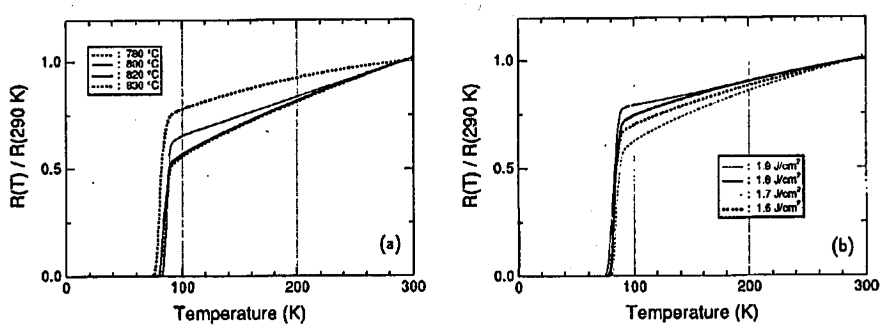

Fig. 7. Temperature dependence of relative resistances of NBCO thin films grown on STO(100) substrates by pulsed laser deposition. Deposition conditions are (a) $P_{\mathrm{l}} = 1.7\ \mathrm{J/cm^2}$, $P_{\mathrm{O}} = 250$ mTr and T_s is varied, (b) $T_s = 800°\mathrm{C}$, $P_{\mathrm{O}} = 250$ mTr and P_{l} is varied.

LSGO(100) substrates later. X-ray diffraction patterns did not change noticeably by varying the laser power in the range of our deposition condition.

Figure 7 is the temperature dependence of the relative resistance for the thin films explained in Fig. 6. $T_{c(\mathrm{onset})}$ is about 90 K for all films, however, $T_{c(\mathrm{zero})}$ is lower than that of the c-axis oriented NBCO films. At the optimum condition ($T_s = 800°\mathrm{C}$, $P_l = 1.7\ \mathrm{J/cm^2}$ and $P_{\mathrm{O}} = 250$ mTr), ΔT_c of 7 K and $T_{c(\mathrm{zero})}$ of 83 K are comparable to those of a-axis oriented YBCO films [10] grown on STO(100) or LSGO(100) substrates. Films show metallic resistivity behavior in the normal state, but have a rather gentle slope compared with the c-axis oriented NBCO film shown in Fig. 5. The slope of the R–T curve between 100 K and 270 K ($\Delta R/R(270\ \mathrm{K})$) for the a-axis oriented film grown at 800°C is about 0.32 while that of the c-axis oriented film shown in Fig. 5 is about 0.58. As the deposition temperature increases, the slope of the R–T curve in the normal state increases as a whole. This tendency suggests that the fraction of c-axis oriented film increases with increasing temperature which is consistent with the results of X-ray diffraction measurement.

The effect of laser power on the resistance of the NBCO films grown on STO(100) substrates is also shown in Fig. 7. All films show metallic resistivity behavior. The superconducting transition temperature was not changed after patterning for most films and there was no explicit anisotropy in the resistivity for the two perpendicular directions on STO(100) substrates. In some cases, however, the superconducting transition temperature was decreased by 5–10 K after patterning.

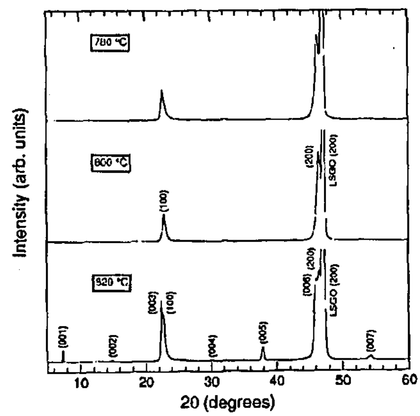

Fig. 8. X-ray diffraction patterns of NBCO thin films grown on LSGO(100) substrates by pulsed laser deposition. Films were deposited at $P_l = 1.7$ J/cm^2, $P_O = 250$ mTr.

Figure 8 shows the X-ray diffraction patterns of NBCO thin films grown on LSGO(100) substrates at various temperatures. For the films grown on LSGO(100) substrates, (h00) peaks of, not only the substrate, but also NBCO phase are clearly visible. However, we could not separate the (h00) peaks of the NBCO phase from those of the substrate, for the films grown on STO(100) substrates although it was suspected that films with a-axis orientation were also grown on them. Both (h00) and (00l) peaks of NBCO phase coexist as the deposition temperature is increased to 820°C, especially, the (003) and (006) peaks of NBCO phase are also observed as separate peaks from the (100) and (200) peaks of the NBCO phase. Figure 8 explicity shows that mostly a-axis oriented films were grown on LSGO(100) substrates below 800°C, but a c-axis oriented part was also deposited at the elevated temperature of 820°C. From the results for films on LSGO(100) substrates, we consider that highly a-axis oriented thin films were also grown on STO(100) substrates below 800°C, although we could observe no direct evidence for the a-axis orientation of the NBCO phase on the STO(100) substrate. X-ray diffraction patterns did not change noticeably by varying the laser power in the range of our deposition conditions.

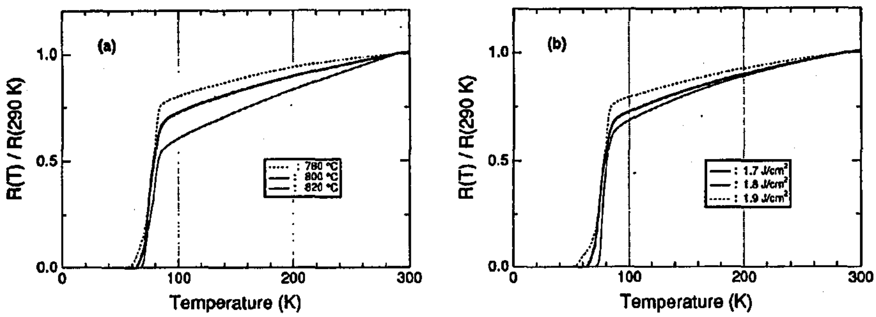

Fig. 9. Temperature dependence of relative resistances of NBCO thin films grown on LSGO(100) substrates by pulsed laser deposition. Deposition conditions are (a) $P_1 = 1.7\ \mathrm{J/cm^2}$, $P_O = 250$ mTr and T_s is varied, (b) $T_s = 800°\mathrm{C}$, $P_O = 250$ mTr and P_1 is varied.

The effects of temperature and laser power on the superconducting transitions of NBCO thin films grown on LSGO(100) substrates are depicted in Fig. 9. Films show metallic resistivity behaviour in the normal state. The slope of the R–T curves shows the same trend as that of the NBCO films on STO(100) substrates. It becomes more steep with increasing deposition temperature due to the increment of the fraction of c-axis oriented part as shown in the X-ray diffraction patterns. $T_{c(\mathrm{onset})}$ is about 85 K and the resistance falls to zero between 52–71 K. The maximum $T_{c(\mathrm{zero})}$ of 71 K was achieved for the film grown at $T_s = 800°\mathrm{C}$, $P_1 = 1.8\ \mathrm{J/cm^2}$ and $P_O = 250$ mTr. In the case of a-axis oriented YBCO thin films [10] grown by the off-axis rf sputtering, the superconducting transition temperatures of the films on STO(100) and LSGO(100) were nearly the same. In this work, however, $T_{c(\mathrm{zero})}$ of a-axis oriented NBCO films on LSGO(100) is lower than that of a-axis oriented NBCO films on STO(100) which is considered to suggest that the deposition condition for the LSGO(100) substrates is not optimized yet.

It is well known that the a-axis oriented YBCO films on LSGO(100) substrates have in-plane orientation due to the anisotropic in-plane structure of the substrate, i.e. b- and c-axis of the grown YBCO films preferentially align along the [010] and [001] directions on the LSGO(100) substrate [7–10]. Therefore a-axis oriented YBCO films on LSGO(100) have a resistivity anisotropy ratio of about 10 at room temperature. We measured the anisotropy of the resistance of the a-axis oriented NBCO films after patterning them crosswise by wet etching or Ar ion milling. The resistance falls to zero at the same temperature for both directions. On the contrary to the a-axis oriented YBCO films, however, the resistance of a-axis oriented NBCO films along the two perpendicular directions of the substrate does not have significant anisotropic behavior for both STO(100) and LSGO(100) substrates as Fig. 10 shows. The superconducting transition temperature was not changed after patterning for the most films although it decreased by 5–10 K after patterning for some cases.

The inset in Fig. 10 shows the ϕ-scanned diffraction pattern at the (102) peak of a-axis oriented film on LSGO(100) substrate. Sharp peaks are observed

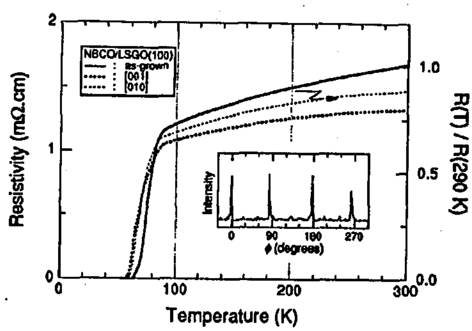

Fig. 10. Temperature dependence of the resistance of an a-axis oriented NBCO thin film grown on LSGO(100) substrates before (solid line) and after wet etching (dotted lines). The inset represents the ϕ-scanned diffraction pattern of the film at the (102) peak. The film was deposited at $T_s = 800°C$, $P_l = 1.7$ J/cm^2, $P_O = 250$ mTr.

with an interval of $\pi/2$ indicating that the film has a fourfold symmetry, i.e. it does not have a unique in-plane orientation which is consistent with the results of resistance measurement.

In summary, we grew NBCO thin films on STO(100) substrates using a stoichiometric $NdBa_2Cu_3O_7$ target by off-axis rf sputtering under various conditions. All films grown by off-axis rf sputtering are highly c-axis oriented and a maximum $T_{c(zero)}$ of 87 K was achieved for the film grown at the deposition condition of $T_s = 760°C$, $P_{AO} = 200$ mTr and $P_{rf} = 70$ W followed by quenching. Films deposited at $T_s = 760°C$, $P_{rf} = 70$ W and $P_{AO} = 150$ mTr have $J_c \geq 10^7$ A/cm^2 below 30 K. We have also grown NBCO thin films on STO(100) and LSGO(100) substrates using an off-stoichiometric target of $Nd_{0.9}Ba_{2.1}Cu_3O_7$ by pulsed laser deposition. a-axis oriented thin films were predominantly grown on both substrates below 800°C, however, the fraction of the c-axis oriented part increased by increasing the temperature above 800°C. The slope in the R–T curve of a-axis oriented films was less steep than that of c-axis oriented films. Maximum $T_{c(zero)}$ of 83 K was attained for the a-axis oriented NBCO film grown on STO(100) substrate at the deposition condition of $T_s = 800°C$, $P_l = 1.7$ J/cm^2 and $P_O = 250$ mTr. However, there is no indication of in-plane orientation of a-axis oriented NBCO films on LSGO(100) substrates which is contrary to the case of a-axis oriented YBCO films on LSGO(100) substrates.

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