Low-temperature liquid-phase epitaxy of $YBa_2Cu_3O_y$ films by the molten KOH method

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We fabricated high-performance $YBa_2Cu_3O_y$ (Y123) films by the liquid-phase epitaxy method using molten KOH flux at low temperatures. The Y123 films fabricated in N_2 atmosphere showed biaxial orientation above 500 °C; moreover, the surface morphology of the Y123 films fabricated above 650 °C suggested spiral growth. The Y123 films fabricated above 650 °C showed a sharp transition with a T_c^{zero} of 90 K.

1. Introduction

$REBa_2Cu_3O_y$-based coated conductors (RE123-CC), where RE stands for rare-earth elements, are used in various fields. RE–Ba–Cu–O superconductors have anisotropic physical properties because of their layered crystal structure, and the critical current density (J_c) along the *ab*-plane (//CuO_2 planes) is superior to that along the *c*-axis direction. Furthermore, in the case of Y123, the increase in the in-plane misorientation angle between two grains seriously degrades J_c even in *c*-axis-oriented films.[1–4] However, it is well known that the fabrication of biaxial Y123 films requires high temperatures (800 °C) that also degrade the superconducting properties owing to the diffusion of impurities from the substrate. Consequently, Y123-CC requires several buffer layers to prevent the diffusion of impurities; thus, the production of Y123-CC is expensive. This calls for a low-temperature and less expensive fabrication method.

Yoshida *et al*. and Miura *et al*. succeeded in fabricating high-performance Sm123 films at 740 °C.[5–8] However, this technique, based on pulsed laser deposition (PLD), still requires temperatures that are too high for RE123-CC. In contrast, the $YBa_2Cu_4O_8$ (Y124) recognized in Y123 thin films along stacking faults [9–11] has a crystalline structure analogous to that of Y123 and is more stable at lower temperatures.[12–13] Additionally, low-temperature preparation methods of single-crystalline RE124 compounds use molten alkali hydroxide (KOH) at an ambient atmosphere.[14–19] We succeeded in firstly synthesizing biaxial Y124 epitaxial films on a $NdGaO_3$ (NGO) single-crystalline substrate by the molten KOH method at ~650 °C.[20] Moreover, we reported the in-field characterization of the Y124 epitaxial film and studied its high critical temperature (T_c)–B properties with respect to the Y123 film.[21] In addition, we tried to fabricate Y123 on other single-crystalline substrates, such as $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) that are commonly used in the deposition of RE123 films. The nucleation of Y124 crystals was not seen on the LAO substrate, and the STO substrate melted above 550 °C because of the KOH flux. Furthermore, the in-field characterization of triaxially oriented Y124 powders prepared by the modulated rotation of magnetic fields was reported by Horii *et al*.[22] Wada *et al*. and Murakami *et al*. reported the *p*–*T* diagram of Y–Ba–Cu–O,[23-25] where the Y123 phase was stable at temperatures higher than that of the Y124 phase at constant oxygen partial pressure [$p(O_2)$]. Moreover, Y123 was stabilized at lower temperatures with decreasing

$p(O_2)$. Recently, we have reported that the *p*–*T* phase diagram of Y123 and Y124 with KOH depended on the growth atmosphere.[26–27] To establish a low-temperature fabrication method of Y123 films, we fabricated Y123 films on an NGO (001) substrate by the molten KOH method in reducing atmosphere and discussed their orientation, growth mode, and superconducting properties.

2. Experimental methods

Yttrium oxide, barium carbonate, and copper oxide powders were used as starting materials, and KOH was used as a solvent. Ten grams of the starting materials were weighed with a molar ratio of Y:Ba:Cu = 1:2:3, mixed and put into an alumina crucible with pure KOH of 100 wt% with the raw materials and the NGO (001) single-crystalline substrate. Then, the mixture was heated in a tube furnace at 500–700 ºC for 12 h in flowing N_2 atmosphere [$p(O_2) < 10^{-4}$ atm]. After cooling to room temperature, the Y123 films were extracted from the flux and washed with distilled water and ethanol in an ultrasonic bath to dispose of KOH and K_2CO_3. Finally, the Y123 films were annealed in oxygen by slowly decreasing the temperature from 450 to 350 °C. X-ray diffraction (XRD) with CuKα radiation was used in the phase identification. Optical microscopy was used to study the surface morphology, and the superconducting properties were measured by the standard four-probe method.

3. Results and discussion

3.1 Phase identification and orientation

Figure 1(a) shows the XRD 2θ–θ patterns of films fabricated at 500–700 °C. It is seen that a *c*-axis-oriented Y123 phase grew on the NGO (001) substrate. Some precipitation of Y211 and Cu_2O phases occurred above 700 °C, whereas a Ba–Cu–O phase in the residual flux solvent was detected in all samples. As suggested by the peak intensity of Y123 (00ℓ), the Y123 films comprise high-quality crystals that are also obtained by conventional PLD and liquid-phase growth. Figure 1(b) shows the in-plane orientation of the Y123 phase with respect to the NGO substrate. We see that the Y123 phase fabricated at 500–700 °C showed in-plane alignment with the NGO substrate, e.g., Y123 [110]//NGO [100] and high orientation above 550 °C. Furthermore, the *c*-axis length of the oxygen-annealed Y123 phase was 11.692 Å. This result suggests that the oxygen content of the annealed Y123 phase is 6.9.[28)] Thus, we succeeded in fabricating biaxial and oxygenated Y123 films by the molten KOH flux method at 500 °C.

3.2 Growth mode and superconducting properties

Figure 2 shows the surface morphology of the Y123 film fabricated at 650 °C. Similar spiral growth morphologies with broad terraces are seen in the high-T_c samples obtained by the liquid-phase growth process.[29)] Spiral growth in all Y123 crystals was observed above 650 °C. However, the Y123 films fabricated at 500–700 °C have a bulk thickness of ~20 μm and several deep cracks (indicated by arrows in Fig. 2) because the thermal expansion coefficient of the Y123 phase is larger than that of the NGO substrate. Consequently, we evaluated the T_c and not J_c, because the cracks caused the strong degradation of J_c.

The ρ–T curve of the Y123 film fabricated at 650 °C is shown in Fig. 3. The Y123 films fabricated above 650 °C showed linear temperature dependence of resistivity within the 100–300 K range and a sharp transition near 90 K. In addition, the Y123 films fabricated below 650 °C showed linear temperature dependence of resistivity. Figure 4 shows the T_c of the Y123 films as a function of fabrication temperature. We see that the T_c^{zero} of the Y123 film fabricated at 650 °C reached up to 90.4 K, whereas that of the film fabricated below 650 °C decreased.

The results suggest that we succeeded in fabricating high-T_c^{zero} (~90 K) Y123 epitaxial films at the low temperature of 650–700 °C by the molten KOH method in reducing atmosphere. The J_c measurements were made possible with crack-free Y123 films prepared by controlling the film thickness via the top-seeded solution growth (TSSG) technique[30)] or by changing the substrate to another with a larger thermal expansion coefficient than that of the Y123 phase. Finally, we expect lower fabrication temperatures by using the KOH–NaOH eutectic flux instead of the KOH flux.

4. Conclusions

We fabricated Y123 films on NGO substrates by the molten KOH method in reducing atmosphere. We identified the phases and discussed the orientation, growth mode, and superconducting properties of the Y123 films. The Y123 films showed biaxial orientation above 500 °C on NGO (001) with a 45° rotation in the direction of the *ab*-plane. Moreover, via optical microscopy, we confirmed the spiral growth mode in Y123 films above 650 °C. The Y123 films fabricated above 650 °C showed a sharp transition with T_c^{zero} of 90 K. The molten KOH method is suitable for the low-temperature production of Y123 films with high crystallinity and sharp superconducting properties.

Acknowledgment

This research was partially supported by a Grant-in-Aid for Scientific Research (26870382) from the Japan Society for the Promotion of Science.

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Figure Captions

Fig. 1. (a) XRD 2θ–θ patterns of Y123 films and NGO (001) substrate as a function of fabrication temperature. The white triangles denote diffraction angles from the Y123 (00ℓ) plane. (b) XRD $2\theta\chi$–ϕ patterns (ϕ-scan) of Y123 films and NGO (001) substrate. The diffracting planes of Y123 and NGO are (103) and (204), respectively.

Fig. 2. Surface morphology of Y123 film fabricated at 650 °C. The arrows indicate the crack.

Fig. 3. ρ–T curve of Y123 film fabricated at 650 °C. The dip near 273 K denotes the noise.

Fig. 4. T_c of Y123 films as a function of fabrication temperature.

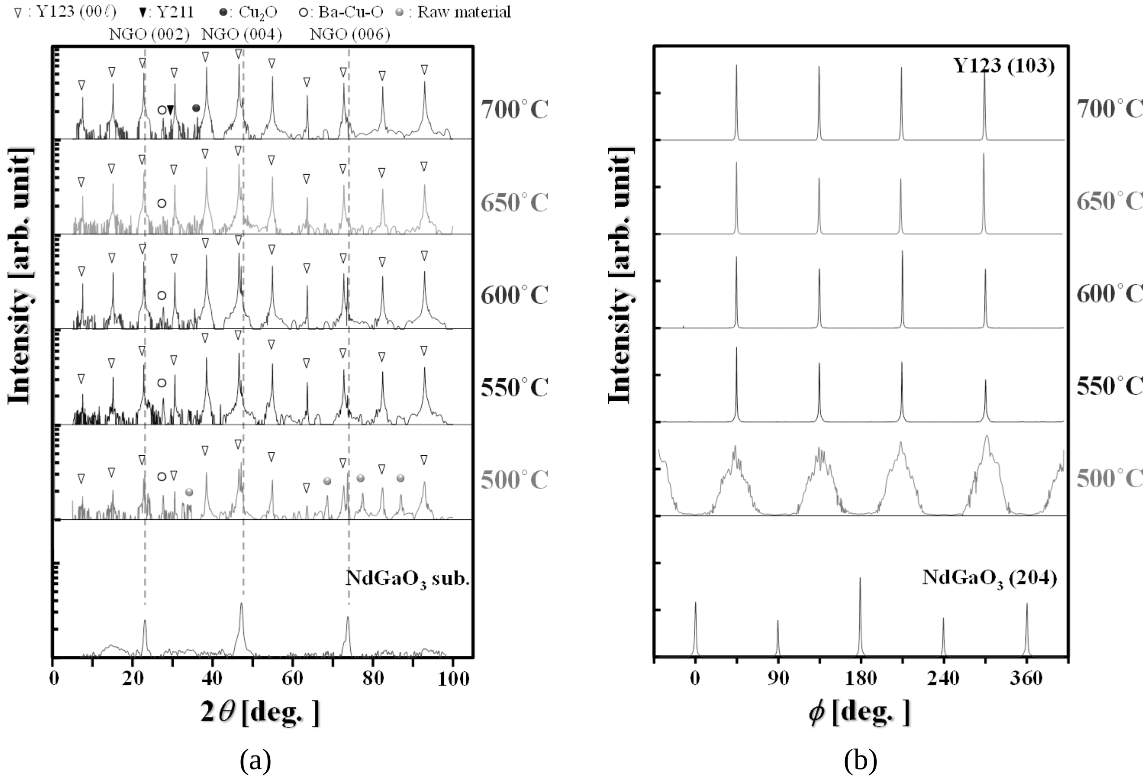

▽ : Y123 (00ℓ) ▼: Y211 ●: Cu2O ○: Ba-Cu-O ●: Raw material
NGO (002) NGO (004) NGO (006)
700°C
650°C
600°C
550°C
500°C
NdGaO3 sub.
Intensity [arb. unit]
2θ [deg.]
(a)
Y123 (103)
NdGaO3 (204)
ϕ [deg.]
(b)

Fig. 1.

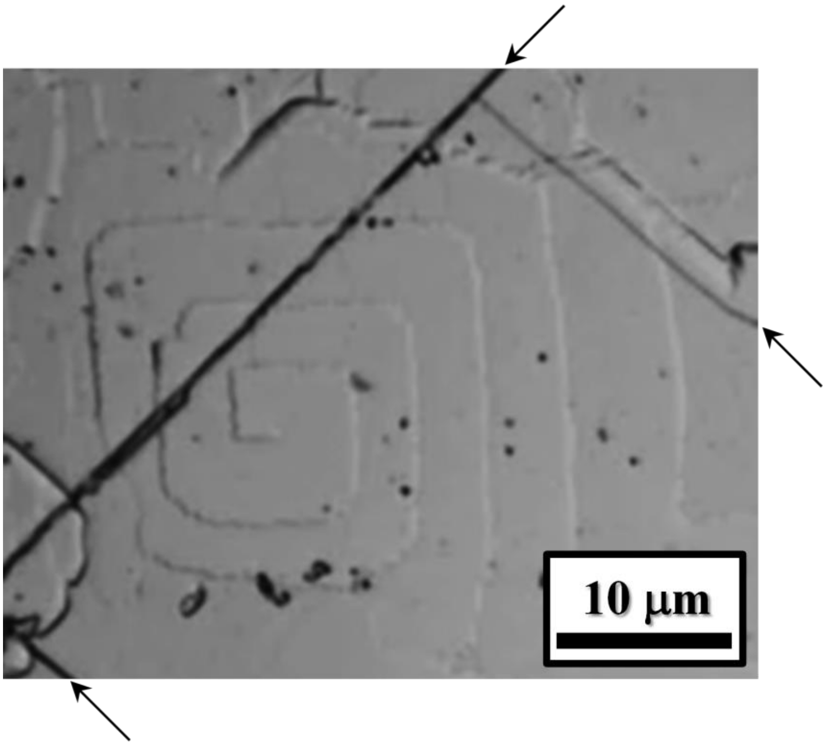
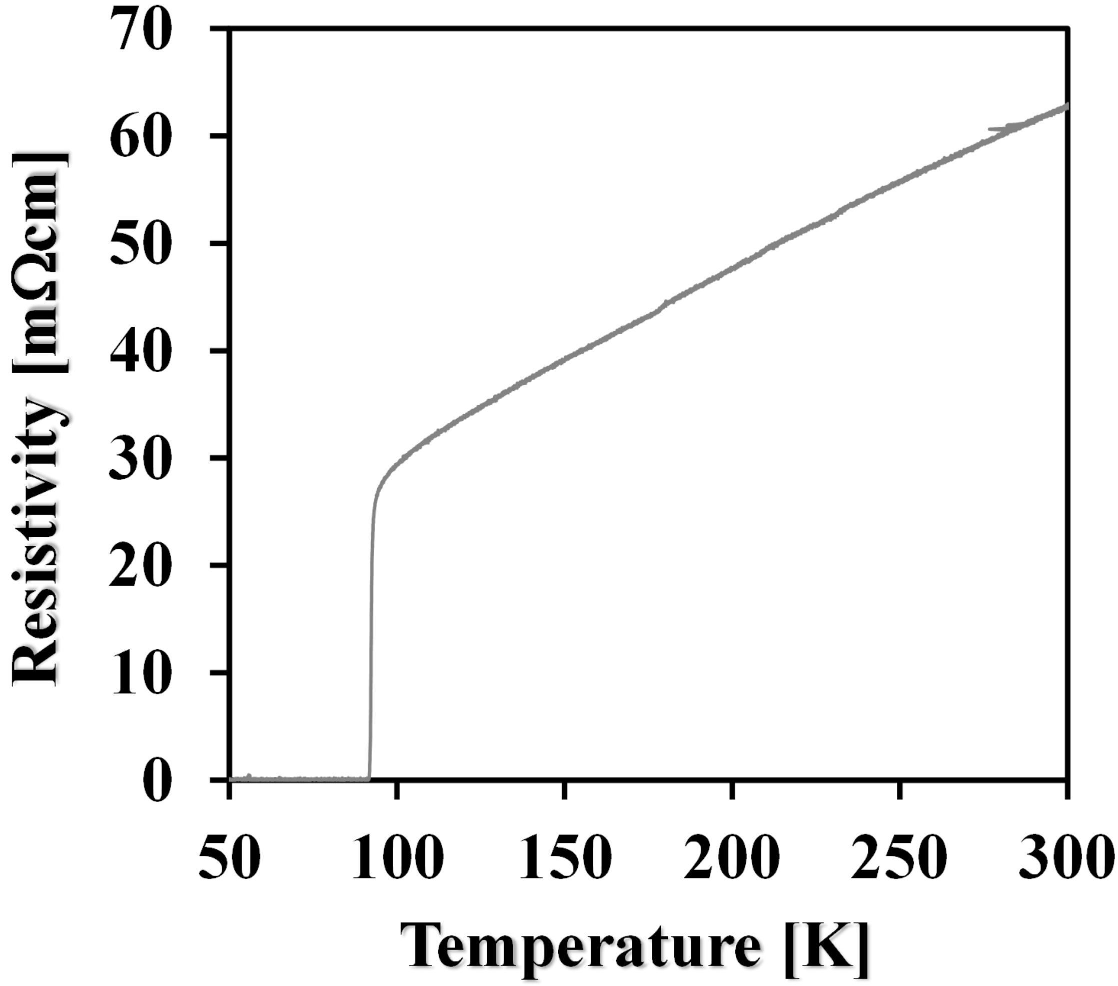


Fig. 2.



70
60
50
40
30
20
10
0
Resistivity [mΩcm]
50
100
150
200
250
300
Temperature [K]

Fig. 3.

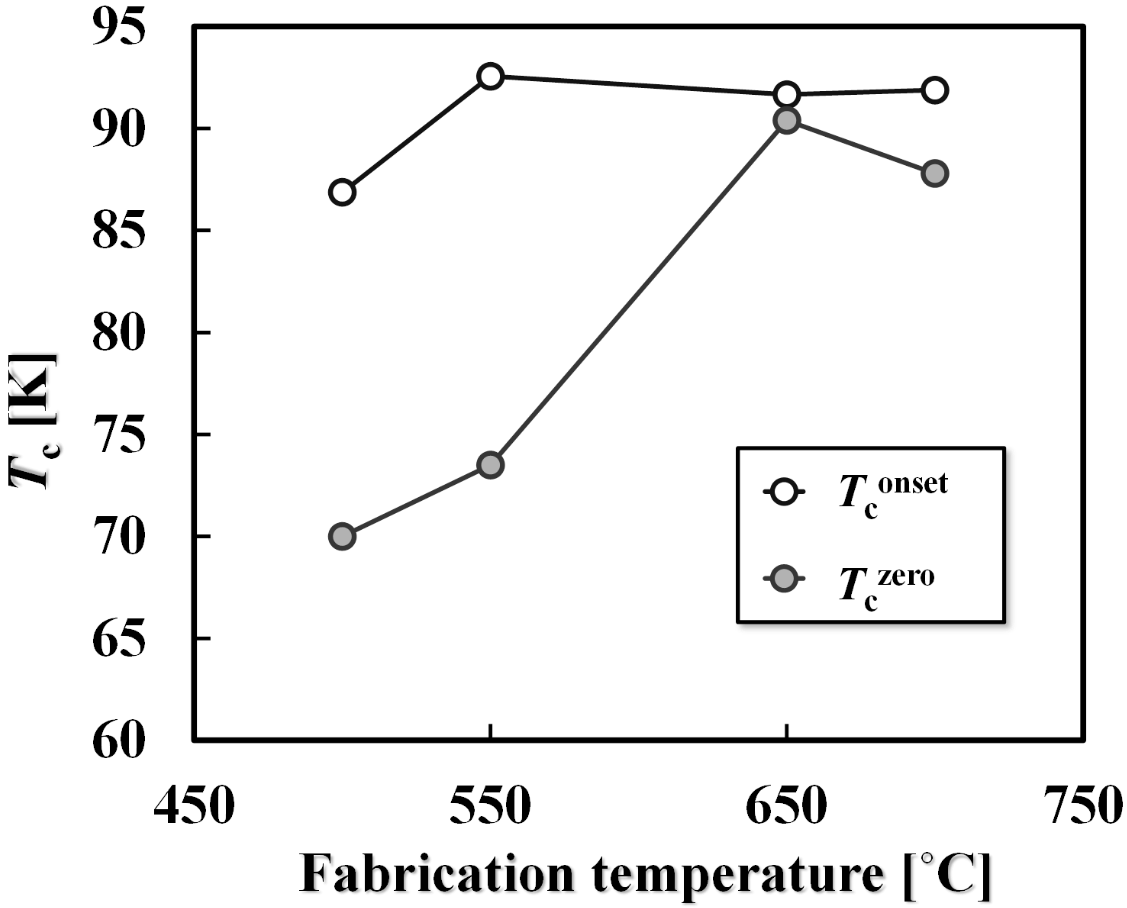

95
90
85
80
75
70
65
60
T_c [K]
450
550
650
750
Fabrication temperature [°C]
T_c^{onset}
T_c^{zero}

Fig. 4.