Low-temperature fabrication of Nd123 epitaxial films by KOH flux method under ambient pressure

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***Abstract*—This study presents a simple and feasible method for fabricating high-performance $REBa_2Cu_3O_y$ (RE123) films. Nd123 films were established on a single crystalline substrate by the KOH flux method at low temperature and ambient pressure. Above 425°C, the Nd123 in the obtained films demonstrated single-phase and biaxial orientation. The T_c^{onset} of Nd123 film was 67.1 K when fabricated at 525°C but reduced at lower fabrication temperatures, presumably because the Nd became increasingly substituted with Ba. Moreover, the T_c^{onset} of the Nd123 film fabricated at 475°C was enhanced by controlling the Nd/Ba composition ratio in the starting materials.**

***Index Terms*—Critical temperature, KOH flux method, Liquid phase epitaxy, $NdBa_2Cu_3O_y$, Superconducting film**

I. Introduction

As is well known, the anisotropic physical properties of RE–Ba–Cu–O superconducting material arise from its layered crystal structure with alternating two-dimensional CuO_2 planes. Moreover, the critical current density (J_c) of the material is higher along the CuO_2 planes (//*ab*-plane) than along the *c*-axis direction. Furthermore, increasing the misorientation angle between the two grains of $REBa_2Cu_3O_y$ (RE123; where RE denotes a rare earth element) seriously degrades the J_c, even in *c*-axis oriented film [1]. Although many groups have recently developed biaxial RE123 coated conductors (CC) for various applications, RE123-CC fabrication needs a high growth temperature during film deposition and a multilayered buffer structure to restrain diffusion from the metallic tape substrate. Consequently, the production rate of RE123-CC is economically infeasible. Moreover, to achieve a high critical current (I_c), thick RE123 film must be fabricated by a special technique. Therefore, for application in superconducting devices, RE123 films must be fabricated at lower temperature and a higher growth rate than in current methods.

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Yoshida et al. fabricated high-performance Sm123 films at relatively low temperature (740°C) by the LTG technique [2]. However, this technique is based on pulsed laser deposition (PLD), which is a slow-growth process and needs a high temperature for RE123-CC fabrications. High growth rate can be achieved by standard liquid-phase growth processes such as top-seeded solution growth (TSSG) [3] and liquid-phase epitaxy (LPE) [4]. For single crystalline bulk crystals and LPE films of RE123, the growth flux is the BaO–CuO flux (so-called self-flux), which achieves growths above 10 μm/min but demands temperatures of approximately 1000°C [5]. Clearly, an RE123 fabrication method that achieves high growth rate at reduced temperature is required for simple, practical RE123-CC production.

Recently, single crystalline $REBa_2Cu_4O_8$ (RE124) has been fabricated by a low-temperature liquid-phase growth process using molten alkali hydroxide (KOH) in an ambient atmosphere [6]–[8]. By this approach, we synthesized biaxial-oriented RE124 epitaxial films on $NdGaO_3$ (001) single crystalline substrate at ~650°C [9]. Furthermore, by controlling the oxygen partial pressure, we fabricated biaxial-oriented Y123 epitaxial films [10]. The critical temperature (T_c) of Y123 film fabricated at 650°C was ~90 K, comparable to that of conventional Y123 films. In a previous work, we fabricated *L*RE-123 (*L*RE = Gd, Eu, Sm, or Nd) films on $SrTiO_3$ (STO) substrate at 525°C by the KOH flux method under ambient pressure. The *L*RE-123 films exhibited a *c*-axis orientation of RE123 with RE124 phases, and the peak intensity of the RE124 phase decreased with increasing ionic radius of the RE. Consequently, the Nd-123 film purely comprised *c*-axis-oriented, single-phase Nd123 [11]. In general, pure Nd123 superconductor is difficult to synthesize because the composition ratio of the Nd^{3+} to Ba^{2+} sites deviates from the stoichiometry [12]. Therefore, to achieve superconducting properties, many groups have investigated the correlation between the fabrication conditions and the Nd/Ba substitution. Moreover, it appears that the synthesis of high-performance Nd123 superconductor requires both low oxygen partial pressure and high growth temperature [13]–[15]. Correspondingly, the T_c of Nd123 film fabricated at 525°C by the KOH flux method under ambient pressure was drastically lower than that of single-crystalline Nd123 film (T_c ~94 K) fabricated by the tri-phase epitaxy method under self-flux [16]. In this investigation, to increase the T_c and reduce the Nd/Ba substitution in the Nd123 film by a simple and feasible method, we fabricated the Nd123 films on STO substrate by the KOH flux method under ambient pressure, varying the fabrication temperature and the Nd/Ba composition ratio in the starting materials.

II. Experimental procedure

The starting materials were neodymium oxide, barium carbonate, and copper oxide powders. The solvent was KOH. The Nd-123 films were prepared in three steps. The first step was heat treatment at 700°C under a 5.0 g KOH flux to remove water. In the second step, the temperature was rapidly reduced to 400°C–525°C for growth, and the STO (100) substrate and mixed starting materials (Nd:Ba:Cu; molar ratio $= 1 + x : 2 - x : 3$ ($x = -0.4, -0.2, 0$), total weight = 2.5 g) were placed into the molten KOH. Finally, the Nd123 film was grown under heat treatment for 12 h. All steps were performed at ambient pressure. After cooling to room temperature, the film and powder samples were extracted from the flux, and the obtained samples were washed by ultrasonic cleaning with distilled water and ethanol to eliminate the KOH and K_2CO_3. Finally, the obtained films were subjected to oxygenation annealing with slow cooling from 400°C (or 450°C) to 300°C.

The grown phase, orientation, and lattice parameters were determined by X-ray diffraction (XRD) with a CuKα source. Surface morphology was obtained by scanning electron microscope (SEM). The amount x of Nd/Ba substitution was determined by energy dispersion spectroscopy (EDS) operated in the SEM system. The T_c was characterized by a standard four-probe method.

III. Results and discussion

A. Lower temperature fabrication of Nd123 films

We first discuss the biaxial orientation, Nd/Ba substitution, and T_c of Nd123 films fabricated at lower temperature (Nd:Ba = 1:2 in the starting materials). Fig. 1 shows the XRD 2θ–θ patterns of Nd-123 films fabricated at six temperatures (400°C–525°C at 25°C-intervals). Above 425°C, pure *c*-axis oriented single-phase Nd123 was formed on the STO (100) substrate. Moreover, XRD $2\theta\chi$–ϕ (ϕ-scan) measurements confirmed the complete in-plane orientation of the Nd123 films fabricated at 425°C–525°C. Therefore, we successfully fabricated biaxial-oriented Nd123 films at low temperature (425°C) by the KOH flux method.

Surface SEM images of Nd123 films fabricated at 525°C and 475°C are shown in Fig. 2 (a) and (b), respectively. At 525°C, the surface morphology reveals Nd123 crystals with a grain size of ~10 μm grown as cube-on-cube structures on the STO substrate (Nd123 [100]//STO [100]). In contrast, film fabricated at 475°C show a very smooth surface. Salluzzo et al. [17]–[18] and Bals et al. [19] reported on the surface morphologies of Nd123 films with a controlled Nd:Ba ratio fabricated by DC magnetron sputtering. They also obtained a smooth-surfaced Nd-rich Nd123 film with surface-roughness of a few nm. Moreover, similar tendencies in PLD-Sm123 films were reported by Sudoh et al. [20]. In Sm123 powder synthesized by the conventional solid state reaction method, the grain size of single Sm123 crystals increases with increasing Sm/Ba substitution [21]. Accordingly, the Nd/Ba substitution in Nd123 films increased as the fabrication temperature was lowered.

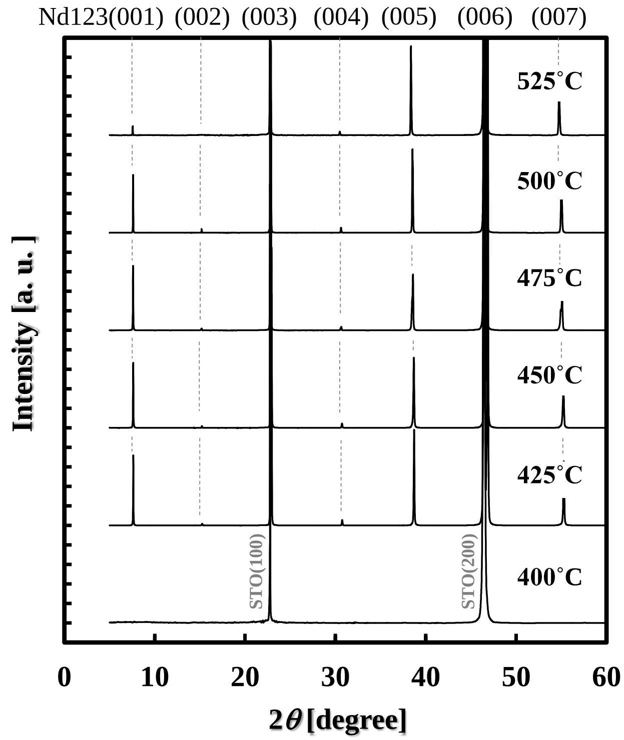

Fig. 1. XRD 2θ–θ patterns of Nd-123 films at different fabrication temperatures. Vertical dashed lines indicate the diffraction angles of the Nd123 (00ℓ) plane.

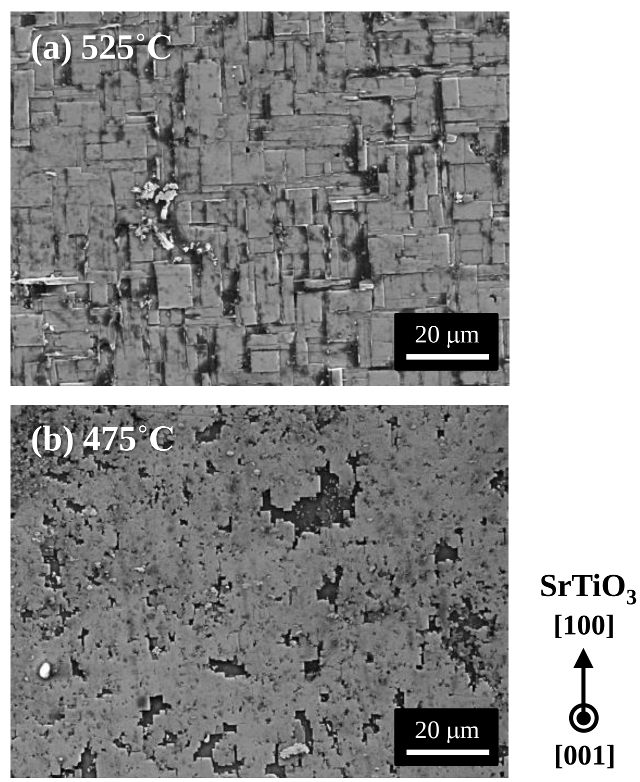

Fig. 2. SEM images of Nd123 films fabricated by (a) 525°C and (b) 475°C. The plane directions of $SrTiO_3$ single crystalline substrate are fixed.

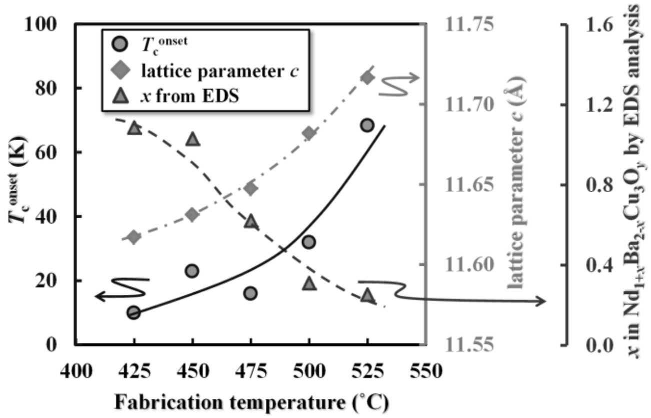

Fig. 3. T_c^{onset}, lattice parameter c, and Nd/Ba substitution x of Nd123 films as functions of fabrication temperature. The amount of Nd/Ba substitution x in $Nd_{1+x}Ba_{2-x}Cu_3O_y$ was determined by EDS analysis.

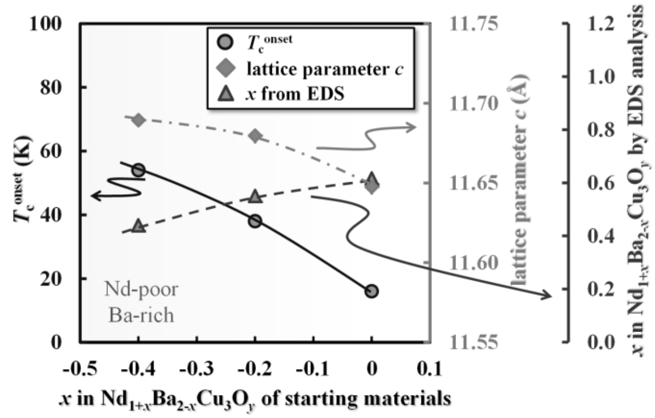

Fig. 4. T_c^{onset}, lattice parameter c, and Nd/Ba substitution x of Nd123 films versus the amount x in the $Nd_{1+x}Ba_{2-x}Cu_3O_y$ starting materials.

From standard four-probe measurements, the T_c^{onset} and T_c^{zero} of Nd123 film fabricated at 525°C was 67.1 and 33.0 K respectively, much lower than in well-known single crystalline Nd123 film [16]. Conversely, Nd123 films fabricated below 500°C showed no transition above 10 K. Takita et al. reported that in single crystalline bulk Nd123 prepared by the conventional solid state reaction, the T_c reduces and the lattice parameter c shrinks with increasing amount of Nd/Ba substitution [22]. Fig. 3 plots the T_c^{onset}, lattice parameter c, and Nd/Ba substitution x of the Nd123 films as functions of fabrication temperature. Here the amount x of Nd/Ba substitution in $Nd_{1+x}Ba_{2-x}Cu_3O_y$ was determined by EDS analysis. As the fabrication temperature decreased, the T_c^{onset} lowered and the lattice parameter c shrunk. Furthermore, the x of the obtained films qualitatively increased with decreasing fabrication temperature. The T_c reduction in Nd123 films fabricated at lower temperature is most likely caused by the increased Nd/Ba substitution.

B. Controlling the Nd/Ba composition ratio in Nd123 films.

As is well known, the RE/Ba substitution x in Nd123 single crystals prepared by the TSSG method and in La123 films grown by the vapor–liquid–solid process can be suppressed by increasing the Ba ratio in the self-flux [23]–[25]. Moreover, the T_c of vapor-phase-grown Nd123 film can be increased by a Ba-rich target [26]–[27]. Inspired by these studies, we endeavored to fabricate Nd123 films from Ba-rich starting materials. Fig. 4 plots the T_c^{onset}, lattice parameter c, and Nd/Ba substitution x of Nd123 films fabricated at 475°C versus x in the starting materials. As the Ba composition ratio increased in the starting materials, the T_c^{onset} increased, the lattice parameter c elongated, and the amount x of Nd/Ba substitution decreased. These results suggest that supressing the Nd/Ba substitution by selecting the proper flux composition ratio and applying an oxygen-controlled melt growth (OCMG) process [12] increases the T_c of Nd123 films fabricated at lower temperature.

IV. Conclusion

By applying the KOH flux method under ambient pressure, we fabricated Nd123 films on STO (100) substrate at comparatively low temperatures and investigated their orientation and superconducting properties. The films fabricated at 425°C–525°C showed a biaxial orientation of single-phase Nd123. Although the low-temperature fabrication drastically lowered the T_c of the Nd123 film compared to single crystalline Nd123, we successfully boosted the T_c^{onset} by increasing the Ba composition ratio in the starting materials. The Nd/Ba substitution in the Nd123 films was thought to be sufficiently suppressed by predetermining the flux composition ratio and adopting the OCMG process. We conclude that the KOH method is suitable for producing low-temperature RE123 film with high crystalline perfection and good superconducting properties.

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