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Fabrication and characterization of (Nd,Eu,Gd)$Ba_2Cu_3O_y$ films by metal-organic deposition using TFA-containing solutions without introduction of water vapor

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Abstract

(Nd,Eu,Gd)$Ba_2Cu_3O_y$ (NEG) films were prepared on $LaAlO_3$ single-crystal substrates by metal organic deposition (MOD) using fluorine-free solutions of metal 2-ethylhexanates (2-EH) or metal naphthenates (MN) with a small amount of trifluoroacetic acids (TFA) added. The addition of TFA to fluorine-free solutions lowered the growth temperatures, promoted crystal growth, and improved the superconducting properties of NEG films. This was similar to the effects observed on the growth of superconducting films by TFA-MOD using metal-trifluoroacetates. We report the successful growth of NEG films with T_c of 92.6 K and J_c of 0.36 MA/cm^2 without introduction of water vapor.

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*Keywords***:** Metal organic deposition; NEG films; TFA

1. Introduction

$REBa_2Cu_3O_y$ (REBCO) superconductors having a high critical current density (J_c) in high magnetic fields have been extensively researched for application as next-generation conductor coatings. Improving J_c-B properties and developing a cost effective process are required for the application of REBCO thin films to electric power or superconducting magnet systems. NEG superconductors have been reported to have a relatively high T_c and high J_c in a high magnetic field [1]. A metal organic deposition (MOD) technique is well known to be suitable for mass production of REBCO-coated conductors because the technique is a non-vacuum, cost-effective process. However, there have been very few reports of NEG films prepared by MOD [2]. Several coating solutions, such as naphthenates [3], 2-ethylhexanates [4], acetylacetonates [5], or trifluoroacetates [6,7] have been researched for preparation of superconducting films by MOD. It has been reported that the superconducting properties and structures of REBCO films strongly depend on the MOD coating solution used. In particular, high-quality REBCO thin films with high J_c have been prepared by the so-called TFA-MOD process using metal-trifluoroacetates [8-10] as coating materials. However,

the TFA-MOD technique is a complicated process compared to MOD using fluorine-free solutions, since the technique requires controlling the partial pressure and flow distribution of water vapor during the heating process, as well as a relatively long-duration heat treatment. In the present study, we prepared NEG films by a MOD technique using fluorine-free solutions (metal 2-EH and MN) with a small quantity of added trifluoroacetic acid (TFA) (not metal-trifluoroacetates), but without any introduction of water vapor. We then investigated the effects of TFA on the crystal growth and superconducting properties of the resulting NEG films.

2. Experimental

The initial coating solutions were prepared by mixing stoichiometric amounts (Nd:Eu:Gd:Ba:Cu = 2/12:5/12:5/12:2:3) of metal 2-ethylhexanates or naphthenates dissolved in a toluene solvent at a concentration of 5 wt%. TFA was then added to the solutions at a volume ratio of 1.0 or 2.4 vol%. The final solutions were applied to 10 × 10 mm^2 $LaAlO_3$ (100) single-crystal substrates by spin coating at 3500 rpm for 30 s. The coated films were dried at 120ºC for 10 min and calcined at 475ºC for 20 min in air. During the calcining process, the dried films were heated and cooled rapidly by taking

them in and out of a heated muffle furnace. The calcined precursor films were fired at a heating rate of 10ºC/min at firing temperatures of 830-850ºC for 60-120 min, then cooled to room temperature in a tube furnace. The firing process was performed in gas mixtures of N_2 and O_2 with an oxygen partial pressure of 0.1 or 2 ppm at a flow rate of 0.1 *l*/min. Finally, the fired NEG films were annealed at 350ºC for 2 h in O_2, then cooled to 200ºC at a cooling rate of 3ºC/min. The phases present in the films were measured by X-ray diffractometry (XRD). The electrical resistivity of the NEG films was measured by a standard four-probe technique to determine T_c values. The J_c values of the samples in a magnetic field were calculated from *B*–*M* curves measured by a superconducting quantum interference device. The surface morphology of the samples was observed by scanning electron microscopy (SEM). The fluorine content of the precursor films was measured by energy dispersive X-ray spectroscopy.

3. Results and discussion

Fig. 1 shows the coating solution dependence of NEG (001) XRD peak intensities from films fired at temperatures ranging from 830 to 850ºC ①under an oxygen partial pressure of 2 ppm. The (001) peak intensities of NEG films prepared from

TFA-containing solutions (TFA-added NEG films) were higher than those of films prepared from fluorine-free solutions (F-free NEG films). No crystallization of NEG phase was observed in NEG films prepared from 2-EH (2-EH NEG films) fired at 830ºC. On the other hand, crystal growth of NEG films from TFA-containing solutions was observed at a firing temperature of 830ºC. This suggests that the addition of TFA into fluorine-free solutions promotes crystal growth and allows a lower firing temperature. ③The (001) peak intensity of the TFA-added NEG films fired at 850ºC was higher than those of films fired at below 840ºC. However, the T_c of the TFA-added NEG films fired at 850ºC could not be measured because of the poor connectivity of the surface grains as discussed below in Fig. 2. In addition, TFA-added NEG films fired at 860ºC showed the decomposition of the 123 phase under an oxygen partial pressure of 2 ppm. These results indicate that the TFA-added NEG films were stable below the firing temperature of 850ºC under an oxygen partial pressure of 2 ppm.

Fig. 2 shows TFA-added 2-EH and MN NEG film surfaces fired at 850ºC under an oxygen partial pressure of 2 ppm. Fine square crystals were observed in the TFA-added 2-EH NEG film. On the other hand, large square plate-like crystals with flat surfaces were observed in TFA-added MN-NEG films. Similar grain growth was reported for films prepared by the TFA-MOD technique using metal-trifluoroacetates [11-13]. From

the SEM and XRD results, we hypothesize that the NEG phase grew from a quasi-liquid phase resulting from TFA addition, as occurs in the case of crystal growth by TFA-MOD [10].

Fig. 3(a) shows XRD patterns of NEG films prepared from 2.4 vol% TFA-containing solutions④, fired at 840℃ under an oxygen partial pressure of 2 ppm. The diffraction peaks of the NEG, BaF_2, and fluorine-containing impurity phase were observed in TFA-added 2-EH and MN NEG films. The presence of the BaF_2 and impurity phase indicates that the fired films still contained fluorine. T_c (onset) and T_c (zero) of TFA-added 2-EH and MN NEG films is illustrated in Fig. 3(b). For comparison, the T_c of F-free 2-EH and MN NEG films is also shown in Fig. 3(b). T_c and ΔT_c of TFA-added 2-EH and MN NEG films were 84.2 K and 6.6 K, and 78.9 K and 10.5 K, respectively. On the other hand, T_c and ΔT_c of 2-EH and MN NEG films were 84.0 K and 6.2 K, and 85.4 K and 3.9 K, respectively. The lower T_c values and broad superconducting transition observed for TFA-added NEG films may have been caused by the formation of BaF_2 and impurity phase in the film. In order to improve T_c and ΔT_c of TFA-added NEG films, we attempted to remove residual fluorine from the films by long-duration heat treatment.

Fig. 4 shows the heat treatment time dependence of XRD patterns for TFA 1.0

vol% added (a) 2-EH and (b) MN NEG films, ⑥fired at 840℃ under an oxygen partial pressure of 2 ppm. Diffraction peaks of BaF_2 and impurity phase were observed from TFA-added 2-EH NEG films, even after long-duration heat treatment. However, the residual fluorine content of the TFA-added 2-EH NEG films was decreased by heat treatment. The atomic ratio of fluorine to barium in the TFA-added 2-EH NEG films fired for 60, 90, and 120 min were 0.32, 0.03, and 0.01, respectively. On the other hand, no BaF_2 or impurity phase was observed for TFA-added MN films fired for 90, 120 min, and fluorine was not detected after firing for 90 min. This indicates that fluorine was more easily removed from TFA-added MN NEG films than from TFA-added 2-EH NEG films. Assuming that fluorine left the films as the NEG phase grew from the quasi-liquid phase [10], more fluorine should have left the 2-EH NEG films than the MN NEG films at the same firing temperature, since the crystal growth temperature of 2-EH NEG film is higher than that of MN NEG film, as shown in Fig. 1. T_c and ΔT_c of 2-EH and MN NEG films fired for 90 min were 86.8 K and 4.9 K, and 86.9 K and 6.7 K, respectively. Moreover, T_c and ΔT_c of TFA-added MN NEG film fired for 120 min were 85.2 K, 4.9 K. On the other hand, T_c and ΔT_c of TFA-added 2-EH NEG film fired for 120 min were improved to 92.6 K and 2.2 K, respectively.

Table.1 shows the superconducting properties of ⑨TFA 1.0vol% added NEG

films fired for 120 min. ⑧TFA-added NEG films fired at 840ºC under an oxygen partial pressure of 0.1 ppm showed the decomposition of the 123 phase under an oxygen partial pressure of 0.1 ppm. Therefore, we carried the firing the TFA-added films at 830 ºC for an oxygen partial pressure of 0.1 ppm. By decreasing the oxygen partial pressure during the firing process, fluorine could be removed from the films without introducing water vapor. TFA-added MN film fired at 0.1 ppm oxygen partial pressure showed improved T_c and ΔT_c with J_c of 0.21 MA/cm^2. J_c of the 2-EH film increased to 0.36 MA/cm^2 from ⑪0.15 MA/cm^2 after firing at 0.1 ppm of oxygen. Residual fluorine was not detected in the TFA-added 2-EH films fired at an oxygen partial pressure of 0.1 ppm, probably because desorption of fluorine from the film was promoted at lower oxygen partial pressures due to a decrease in the formation temperature of the quasi-liquid phase during the growth of NEG films. It is apparent that fluorine is easier to remove from TFA-added NEG films than from films prepared by TFA-MOD.

4. Conclusion

We prepared NEG films by MOD using MN or 2-EH coating solutions with a small amount of TFA added. The addition of TFA to the fluorine-free solutions lowered

growth temperatures, promoted crystal growth, and improved the superconducting properties of the resulting NEG films. NEG films with T_c of 92.6 K and J_c of 0.36 MA/cm^2 were successfully grown from TFA-containing 2-EH solution. Firing under a low oxygen partial pressure of 0.1 ppm promoted crystal growth in TFA-added 2-EH and MN NEG films, and resulted in decreased impurities in the films. Fluorine was removed from NEG films prepared from TFA-containing solutions without the introduction of water vapor by long-duration (120 min) heat treatment. Promotion of crystal growth and a decrease in impurities were observed for TFA-added 2-EH and MN NEG films fired at the low oxygen partial pressure of 0.1 ppm.

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Table.1
Superconducting properties of TFA 1.0 vol% added NEG films fired for 120min

Coating solution	T_c[K]	ΔT_c[K]	J_c[MA/cm^2]	Firing temperature[℃]	O_2 partial pressure[ppm]	F/Ba atomic ratio
2-EH+TFA	92.6	2.2	0.15	840	2	0.01
2-EH+TFA	89.4	2.0	0.36	830	0.1	0
MN+TFA	85.2	4.9	–	840	2	0
MN+TFA	91.5	2.6	0.21	830	0.1	0

Table.1 WTP-19 / ISS2008

Figure captions

Fig. 1 Coating solution dependence of NEG (001) XRD peak intensities of the films fired at temperatures ranging from 830 to 850ºC ②under an oxygen partial pressure of 2ppm.

Fig. 2 SEM images of NEG film surfaces prepared from (a) 2-EH and (b) MN solutions with addition of TFA at a volume ratio of 2.4 vol%, fired at 850ºC under an oxygen partial pressure of 2 ppm.

Fig. 3 (a) XRD patterns and (b) coating solution dependence of T_c for NEG films prepared from 2.4 vol% TFA-containing solutions ⑤, fired at 840℃ under an oxygen partial pressure of 2 ppm.

Fig. 4 Heat treatment duration dependence of XRD patterns for TFA-added (a) 2-EH and (b) MN NEG films⑦, fired at 840℃ under an oxygen partial pressure of 2 ppm.

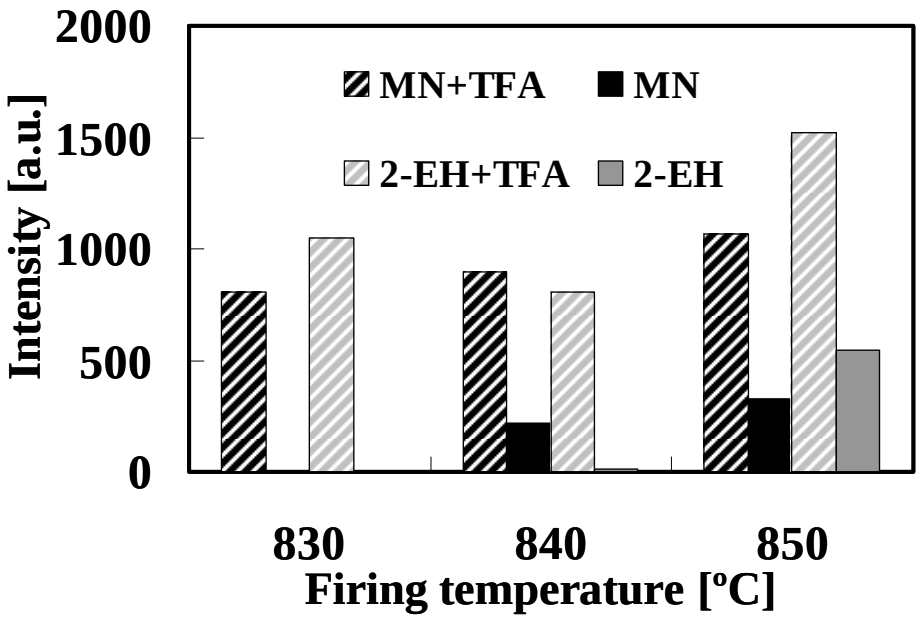

Fig.1 WTP-19 / ISS2008

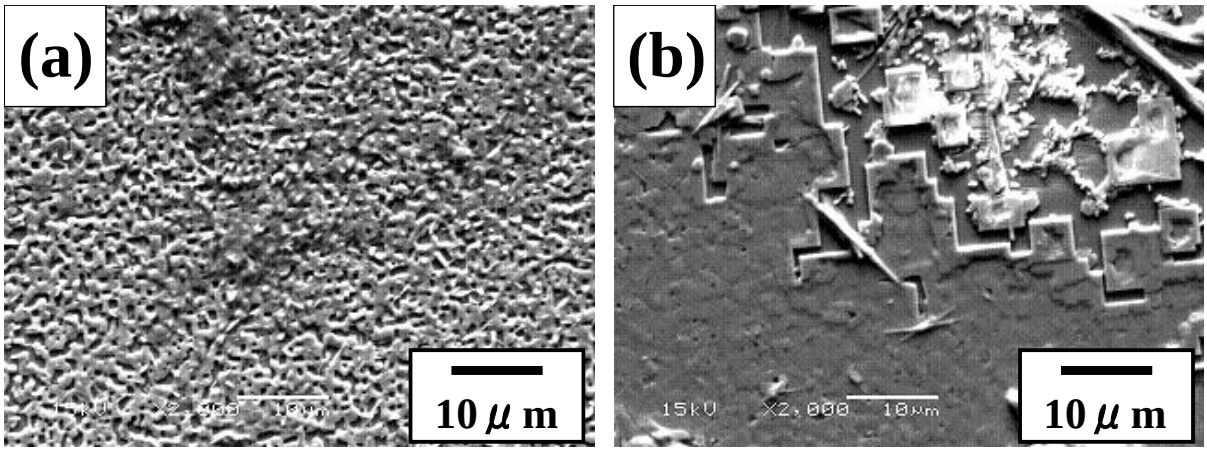

Fig.2 WTP-19 / ISS2008

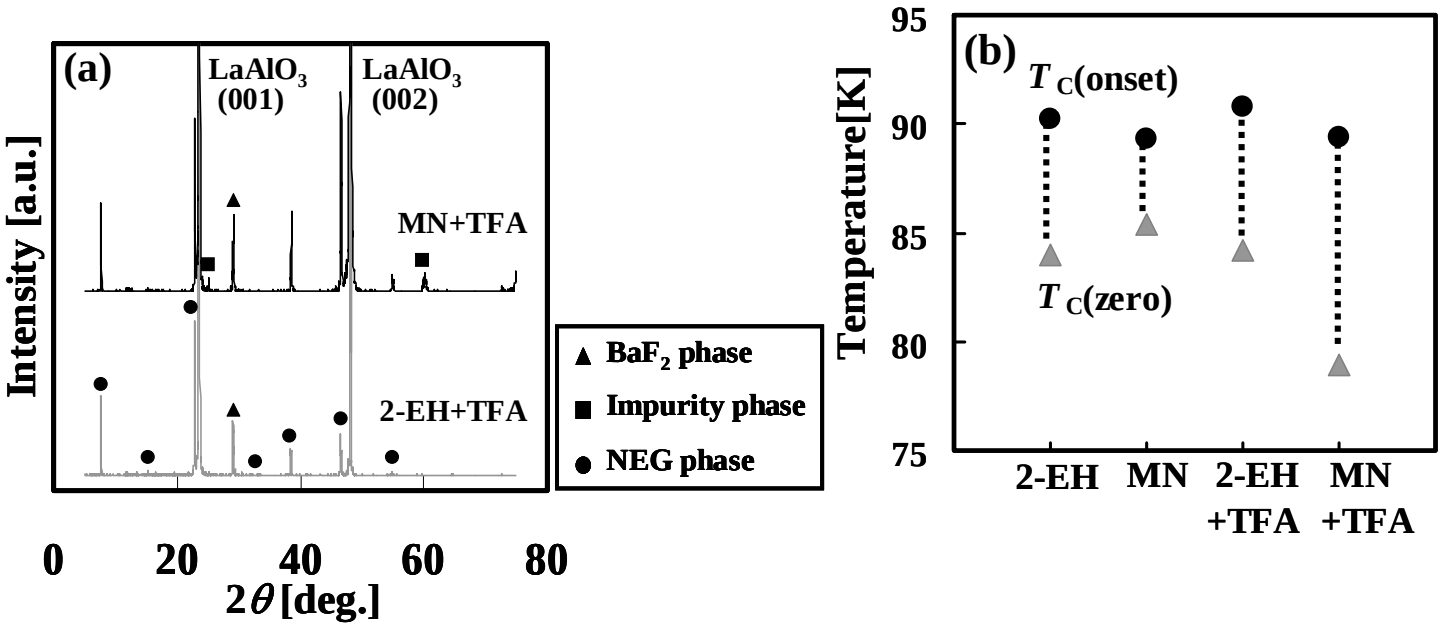

Fig.3 WTP-19 / ISS2008

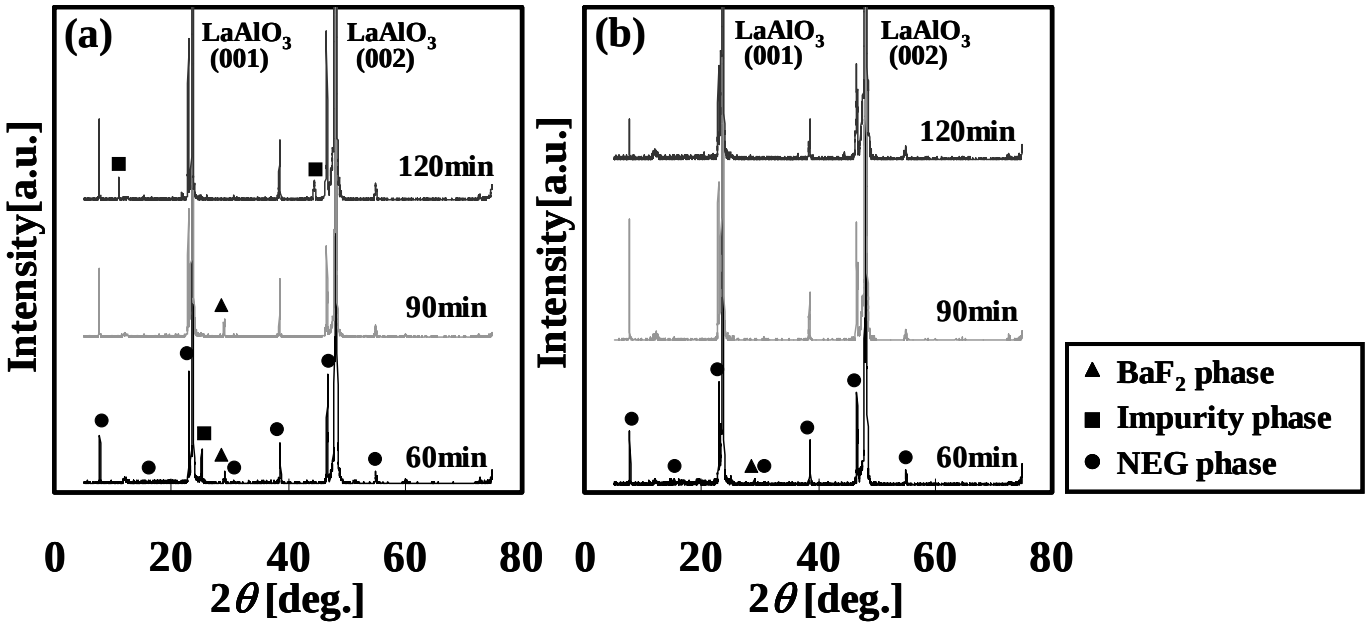

Fig.4 WTP-19 / ISS2008