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Effect of oxygen pressure on properties of $NdBa_2Cu_3O_{7-\delta}$ films on $SrTiO_3$ (100) substrates grown by pulsed laser deposition

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***Abstract*-- We report a successful fabrication of high-J_C $NdBa_2Cu_3O_{7-\delta}$ (NdBCO) films on (100) $SrTiO_3$ substrates by pulsed laser deposition (PLD) in high oxygen pressures ranging from 400 to 800 mTorr. Fabricated NdBCO films exhibited only *c*-axis orientation, good out-of-plane and in-plane textures, and also excellent superconducting properties, including critical temperature (T_C) and critical current density (J_C) of above 90 K and the highest of 3.1 MA/cm^2 at 77 K in self-field, implying that NdBCO is a perspective alternative to YBCO for coated conductor. In low oxygen pressures ranging from 100 to 200 mTorr, however, the films showed *a*-, *c*-mixed orientation and degraded $T_{C,zero}$ values due to the formation of $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$–type solid solutions with an excessive substitution of Nd^{3+} ions for the Ba^{2+} sites.**

1. INTRODUCTION

In comparison with $YBa_2Cu_3O_{7-\delta}$ (YBCO), NdBCO is known to have high J_C in high magnetic field in the case of bulk-type superconductors [1,2]. NdBCO films are also reported to have higher surface stability than YBCO films [3]. In spite of these advantages, reports on high-quality NdBCO films are much less than those on YBCO films at the moment. The reason is mainly attributed to a difficulty in preparing high-T_C NdBCO films with large J_C at 77 K reproducibly because of the tendency to form $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ –type solid solutions.

Since Badaye *et al.* [3] reported *c*-axis oriented NdBCO films prepared by the PLD method for the first time, many groups have studied the superconducting properties of NdBCO films as a function of PLD processing parameters such as deposition temperature, target composition, oxygen pressure, laser energy, and etc. [4-12]. Concerning the oxygen pressure during deposition, most reports argued that relatively low oxygen pressures (≤300 mTorr) with pure oxygen gas or much lower oxygen pressures (< 10 mTorr) with oxygen-argon mixed gas were necessary to fabricate high-quality NdBCO films having T_C over 90 K, implying that the processing window is rather limited compared with YBCO films. On the contrary to these reports, there are several papers reporting high-quality NdBCO films deposited using relatively high oxygen pressures over 300 mTorr[4,9,12]. Moon *et al.* [4] first reported a successful fabrication of high-quality NdBCO films with the oxygen pressures ranging from 800 to 1000 mTorr the highest J_C of 2 MA/cm^2 at 77 K. However, detailed microstructures and grain orientations for their films were not reported. Recently, Zama *et al.* [9] reported NdBCO films with T_C over 90 K at the oxygen pressures ranging from 450 to 900 mTorr while T_C values were gradually degraded to ~ 84 K with decreasing oxygen pressure down to 50 mTorr. More recently, Ochino *et al.* [12] reported that NdBCO films with T_C values above 90 K could be prepared at 1 Torr and only *c*-axis orientation could be achieved at relatively low substrate temperatures below 830°C. However, J_C values were not reported in refs. [9] and [12]. Therefore, it can be understood that superconducting properties of PLD-processed NdBCO films at relatively high oxygen pressures have never been fully studied. In addition, the deposition rate of YBCO films has been reported to be raised with increasing oxygen pressure [13]. These points motivated present study. In this paper, we report the effect of oxygen pressure ranging from 100 to 800 mTorr on the microstructures and superconducting properties of NdBCO films.

2. EXPERIMENTAL PROCEDURE

We first fabricated a highly dense and stoichiometric NdBCO target with the dimension of 2 inch diameter by the solid state reaction. The target had the relative sintered density of 93% on the basis of the theoretical density of NdBCO with the tetrahedral structure (6.5 g/cm^3).

NdBCO films were deposited on $SrTiO_3$ (100) substrates by PLD using a KrF excimer laser (LPX220i with wavelength 248 nm from Lambda Physik). Repetition rate and the pulsed energy of the laser beam were fixed to 10 Hz and 100 mJ, respectively. The laser energy density on the target calculated from the focused spot area (5×1 mm^2) was about 2 J/cm^2. The substrate to target distance was fixed to 6.5 cm. $SrTiO_3$ (100) substrates with the size of 10×3×0.5 mm^3 were attached on a stainless steel heater block with silver paste. Prior to the deposition, the chamber was evacuated to a base pressure of about 5×10^{-6} Torr. NdBCO films were grown under the ambient oxygen pressure ranging from 100 to 800 mTorr, while the substrate temperature was maintained at 800°C. After the deposition, the films were cooled to 500°C in the same oxygen pressure with a cooling rate of 20°C/min, and then the chamber was filled with 500 Torr of pure oxygen and held for 30 min for oxygen annealing, and subsequently cooled to 300°C with a cooling rate of 10°C/min, and finally cooled to room temperature.

Phases were analyzed by x-ray diffraction (XRD). In-plane and out-of plane textures were characterized by φ scan of (102) peak and ω scan of (005) peak of NdBCO films. Microstructures of films were observed by a field emission scanning electron microscope (FE-SEM). Superconducting properties of T_C and J_C were measured by the standard four-probe method. For this measurement, Ag electrode with about 1 μm thickness was deposited on top of the NdBCO films by rf magnetron sputtering and then post-annealed at 450°C for 1 h by flowing pure oxygen gas with a flow rate of 400 ml/h.

3. RESULTS AND DISCUSSION

Cross-sectional SEM views for NdBCO films revealed that the film thickness was increased with increasing oxygen pressure. At the oxygen pressures of 400 and 800 mTorr, the film thicknesses were 250 and 270 nm, respectively, corresponding to deposition rates of 4.9 and 5.2 Å/s, respectively, while those were 210 and 220 nm at 100 and 200 mTorr, respectively, corresponding to 4.1 and 4.3 Å/s, respectively. The increase in the deposition rate might be related to denser plumes in higher oxygen pressure. Interestingly, the deposition rate of NdBCO at 800 mTorr with the laser repetition rate of 10 Hz is very similar to that of YBCO at 800 mTorr with the repetition rate of 40 Hz [14], which was obtained using the same PLD system, implying that the deposition rate of NdBCO is around 4 time faster than that of YBCO. We believe that this higher deposition rate will be advantageous in increasing the production rate of long-length coated conductors

Fig. 1 represents θ-2θ XRD patterns of NdBCO films

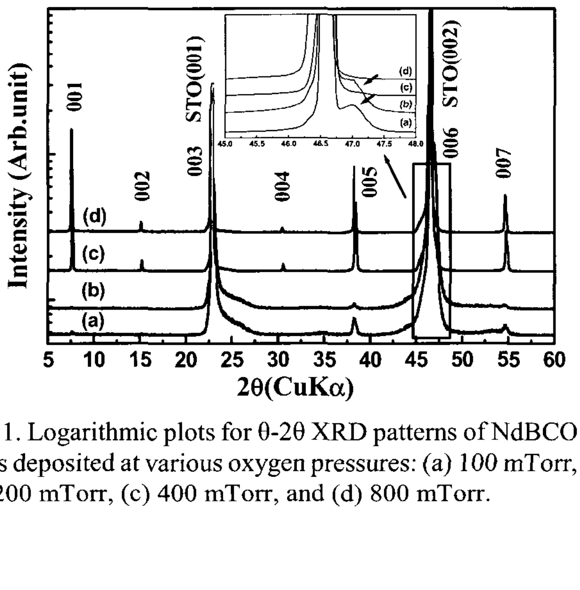

Fig. 1. Logarithmic plots for θ-2θ XRD patterns of NdBCO films deposited at various oxygen pressures: (a) 100 mTorr, (b) 200 mTorr, (c) 400 mTorr, and (d) 800 mTorr.

grown at various oxygen pressures. The films deposited in the oxygen pressure range of 100-200 mTorr show low intensities of (00*l*) peaks and the existence of (*h*00) peaks near (*h*00) peaks of $SrTiO_3$ substrates, indicating that the films possess *a*-, *c*-mixed orientation. On the other hand, the films deposited in the pressure range of 400-800 mTorr show the strong (00*l*) peaks without any (*h*00) peaks, representing only c-axis orientation.

In order to verify out-of- and in-plane texture of both films, (005) ω-scan and (102) φ-scan for the films were carried out, and their FWHM values were measured, as shown in Fig. 2. Both films have good out-of plane textures with low FWHM values of ω scan less than 0.2°. Especially the film deposited at 800 mTorr shows very low FWHM value of 0.08° which is similar to value of $SrTiO_3$ single crystal substrate. Low FWHM values of φ-scan between 0.6°-0.7° indicate that in-plane textures of both films are also excellent.

Microstructures of NdBCO films are shown in Fig. 3. In the oxygen pressure range of 100-400 mTorr, the films

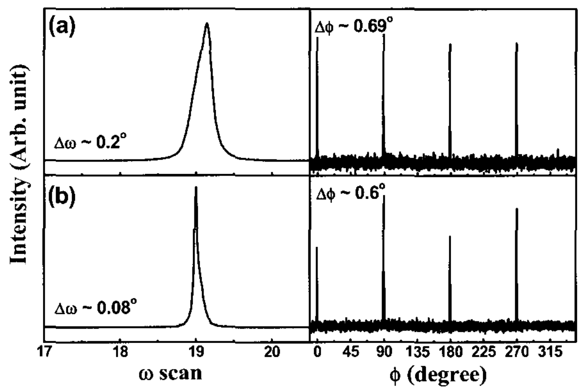

Fig. 2. (005) ω scans and (102) φ scans of the NdBCO films deposited at the oxygen pressures of (a) 400 mTorr and (b) 800 mTorr.

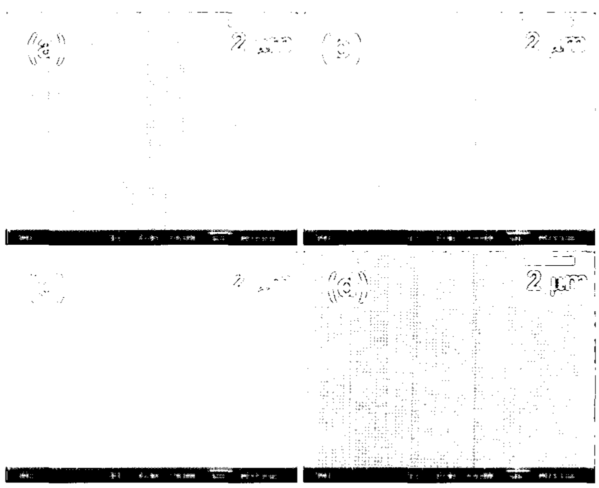

Fig. 3. Microstructures of the NdBCO films deposited at various oxygen pressures: (a) 100 mTorr, (b) 200 mTorr, (c) 400 mTorr, and (d) 800 mTorr.

have very smooth surface morphologies. Rarely observed submicron-sized surface particles seem to slightly increase with increasing oxygen pressure. Unlike these films, a lot of outgrowth particles with the particle size from several tenth to 1 μm exist in the film deposited at 800 mTorr. Higher density of outgrowths in higher oxygen pressure has also been reported for the NdBCO film by Ochino *et al.* [12]. Outgrowths in high oxygen pressure are generally known to be produced by a non-stoichiometric deposition due to a difference in kinetic energies of the ablated atoms in the plume. SEM-EDS analyses for the outgrowths shown in Fig. 3(d) exhibited a Cu-excess composition, which has also been reported by Proyer *et al.* [15]. However, we could not identify the phase and accurate composition of the outgrowths because of their small size. Further analysis with TEM-EDS is under progress. Fig. 4 shows the T_C values of the NdBCO films deposited in various oxygen pressures. The films deposited in the pressure range of 400-800 mTorr exhibit high T_C values above 90 K and very sharp superconducting transition with the transition widths of less than 1 K while the films deposited in the pressure range of 100-200 mTorr show low T_C values near 80 K and broad transition widths of 3~4 K. Present results are in good agreement with previous report from Zama *et al.* [9]. However, our results are somewhat contradictory to other reports [4,5], in that they commonly obtained depressed T_C values at 400 mTorr. Here, it should be noted that this discrepancy could be originated from somewhat longer target-to-substrate distance employed for their experiments. Degradation in T_C for NdBCO films is generally resulted from two major factors [16,17]; one is the oxygen deficiency (δ) and the other is the amount of substitution Nd^{3+} ions for Ba^{2+} sites, i.e., x in $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$. Since all samples were *in-situ* annealed and subsequently post-annealed after the deposition of Ag electrode with the same oxygen annealing condition, T_C degradation in low oxygen pressures of 100 and 200 mTorr are not attributable to oxygen deficiency. Instead, an excessive substitution of Nd^{3+} ions for Ba^{2+} sites must be the most probable origin for T_C degradation. To clarify this point, compositional analyses with EPMA were performed for our films. The results are represented in Fig. 5. In accordance with our speculation, the samples deposited in the pressure range of 100-200 mTorr show x values higher than 0.1. Referring to ref. [15], it can be seen that T_C abruptly decreases below 90 K when x exceeds 0.1. Consequently, degradation in T_C values for the films deposited at 100 and 200 mTorr is obviously caused by excessive substitution of Nd^{3+} ions for the Ba^{2+} sites.

We measured I-V curves for our films. The results are illustrated in Fig. 6. It is shown that J_C values of the films deposited at the pressures of 400 and 800 mTorr are 2.8 and 3.1 MA/cm^2 at 77 K in self-field, respectively. Within the best of our knowledge, these J_C values are the record high ones ever reported for the NdBCO films prepared at relatively high oxygen pressures. Theses high J_C values of our samples are attributed to excellent out-of- and in-plane textures as-shown in Fig. 2 in addition to their high T_C values. On the other hand, the films deposited in the pressure range of 100-200 mTorr exhibited almost zero J_C values, which is definitely attributed to depressed T_C values and *a*-, *c*-mixed orientation.

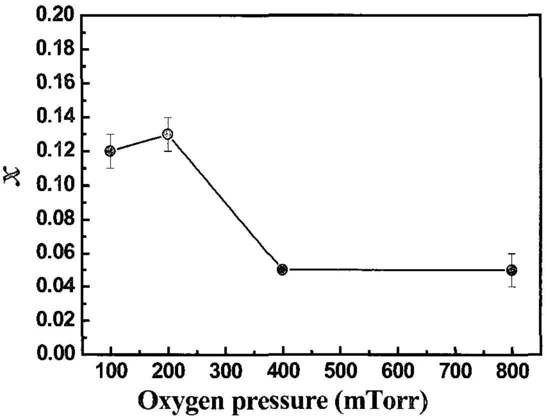

Fig. 5. Relationship between composition x values and oxygen pressure of the NdBCO films.

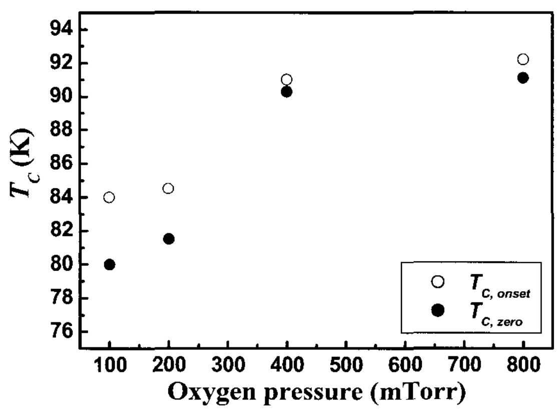

Fig. 4. TC,onset and TC,zero values of the NdBCO films deposited in the various oxygen pressures.

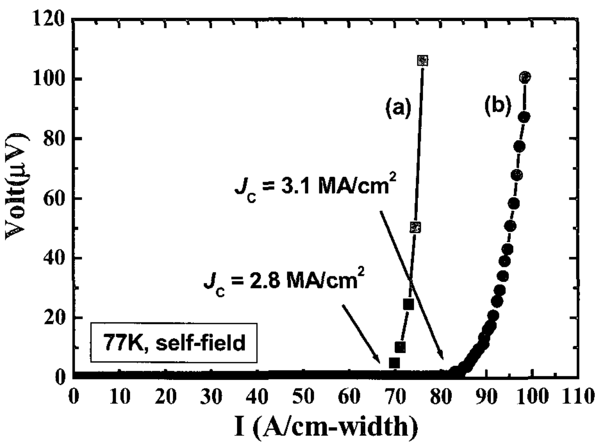

Fig. 6. I-V curves of the NdBCO films deposited at the oxygen pressures of (a) 400 mTorr and (b) 800 mTorr. Estimated JC values are also represented.

4. SUMMARY

We have systematically investigated the effect of oxygen pressure on the textures, microstructures, and superconducting properties of NdBCO films in the oxygen pressure rage of 100-800 mTorr while other important processing parameters were fixed like the following; laser repetition rate = 10 Hz, laser energy = 2 J/cm^2, target-to-substrate distance = 6.5 cm, and substrate temperature = 800°C. The films deposited in the relatively low oxygen pressure range of 100-200 mTorr exhibited low T_C values near 80 K and J_C values of almost zero because excessive substitution of Nd^{3+} ions for Ba^{2+} sites and *a*-, *c*-mixed orientation. However, the films deposited at high oxygen pressure range of 400 and 800 mTorr possessed high T_C above 90 K and large J_C values of 2.8 and 3.1MA/cm^2, respectively. High T_C values are attributed to an effective suppression of Nd^{3+} substitution for the Ba^{2+} sites, and large J_C values are attributed to strong *c*-axis orientation with excellent out-of- and in-plane textures in addition to high T_C values. In conclusion, high-J_C NdBCO films are obtainable using relatively high oxygen pressures ranging from 400 to 800 mTorr. This fact and higher deposition rate compared with YBCO definitely support that NdBCO is a strong alternative to YBCO for coated conductors.

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