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High-J_c $NdBa_2Cu_3O_{7-\delta}$ thin films on $SrTiO_3$ (100) substrates prepared by the PLD process

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Abstract-- **We report a successful fabrication of high J_c-$NdBa_2Cu_3O_{7-d}$ (NdBCO) films on $SrTiO_3$ (STO) (100) substrates by pulsed laser deposition (PLD) in a relatively wide processing window. Under various oxygen pressures controlled by either $1\%O_2/Ar$ mixture gas or pure O_2 gas, strongly *c*-axis oriented NdBCO films were grown at the substrate temperature (T_s) of 800°C in 800 mTorr with $1\%O_2/Ar$ gas and also in 400 and 800 mTorr with pure O_2 gas. These samples exhibited T_c values over 90 K and J_c values of 2.8-3.5 MA/cm^2 at 77K in self-field (77K, sf). On the other hand, J_c values over 1 MA/cm^2 were obtained at the temperature regions of 700-830°C in 800 mTorr with $1\%O_2/Ar$ gas at those of 750-830°C in 800 mTorr with pure O_2 gas. Unlike previous reports, present results support that the PLD processing window for high-Jc NdBCO films is not narrow.**

1. INTRODUCTION

In comparison with YBCO, NdBCO superconductors are known to have some critical advantages like higher J_c in high field [1,2] and higher surface stability [3]. Therefore, many researchers [3, 4-14] have tried to optimize the processing condition for NdBCO films, including T_s, target composition, oxygen partial pressure, laser energy (D_L), target to substrate distance (d_{T-S}), and *etc*. However, NdBCO films are known to have a serious drawback in the point that much narrower processing window is available to grow high-quality NdBCO films in comparison with YBCO films. Thus, only a few groups [4-5,7-8,9] could fabricate NdBCO films having J_c (77K, sf) values over 1 MA/cm^2. The first report on high J_c-NdBCO films was from Moon *et al.* [4] reporting J_c (77K, sf) of 1-2 MA/cm^2 and the field-dependence of J_c. Later, Cantoni *et al* [7-8] and Li *et al.* [5,9] reported the properties of NdBCO films possessing J_c (77K, sf) values higher than 3 MA/cm^2.

In the present study, we carefully studied the PLD processing window for NdBCO films which can produce high-J_c films on STO (100) single crystal substrates.

2. EXPERIMENTAL PROCEDURE

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The NdBCO target of 2-inch diameter was prepared by the solid-state reaction. The starting materials were Nd_2O_3, $BaCO_3$ and CuO compounds with high purities (≥ 99.9%). The precursors were accurately weighed and ball-milled in a polyethylene jar containing zirconia balls and ethanol as the medium for 24 h. After dried, the mixed powder were calcined three times at 880°C for 24 h in flowing purified-air with a flow rate of 5 l/min, with intermediate grinding and pelletizing. The XRD pattern of the calcined powder showed that a small amount of $BaCuO_2$ phase existed due to substitution of Nd^{3+} ions for Ba^{2+} sites. The powder was pre-sintered at 1000°C for 12 h in $1\%O_2/Ar$ gas with a flow rate of 300 ml/min to produce the powder with a single NdBCO phase. The pre-sintered powder was ball-milled for 24 h using ethanol as the medium. The milled powder was dried and pressed into pellet with the dimension of 62 mm diameter and 7 mm thickness, and then isostatically pressed at a pressure of 2000 kg/cm^2. The pellet was sintered at the same condition as pre-sintering. The target had a relative sintered density of 93%, on the basis of the theoretical density of NdBCO with tetragonal structure (6.5 g/cm^3).

NdBCO films were deposited onto STO (100) substrates by PLD using a KrF excimer laser (LPX220i with wavelength 248 nm from Lambda Physik). The substrates were attached on the stainless steel heater block with silver paste. Prior to the deposition, the chamber was evacuated to a base pressure of ~5×10^{-6} Torr. Repetition rate and the pulsed energy of the laser beam were fixed to 10 Hz and 100 mJ. The laser energy density on the target calculated from the focused spot area (5×1 mm^2) was 2 J/cm^2. The substrate to target distance was also fixed to 6.5 cm. Either $1\%O_2/Ar$ mixture gas or pure O_2 gas were used to adjust deposition oxygen pressure. The films were grown at various oxygen pressures and substrates temperatures. Deposition pressures with either $1\%O_2/Ar$ mixture gas or pure O_2 gas were varied from 100 to 800 mTorr, where T_s was fixed at 800°C. T_s was varied from 650 to 830°C in the deposition pressure of 800 mTorr with either $1\%O_2/Ar$ mixture gas or pure O_2 gas. After the deposition, the films were cooled to 500°C with a cooling rate of 20°C/min. Subsequently, the chamber was filled with 500 Torr pure

O_2 gas and held for 40 min for oxygen annealing, cooled to 300°C with a cooling rate of 10°C/min, and finally cooled to room temperature. The number of laser shots used to grow films was varied from 5,000 to 10,000, depending on the thickness of NdBCO film. The thicknesses of the films were 200~300 nm, corresponding to growth rates of 2-2.5 Å/s (1%O_2/Ar gas) and 4-5 Å/s (pure O_2 gas).

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, respectively. 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 purpose, Ag electrodes with ~1 μm thickness were deposited on the NdBCO films by rf magnetron sputtering and post-annealed at 450°C for 1 h in pure oxygen gas.

3. RESULTS AND DISCUSSION

3.1. NdBCO films grown under various deposition pressures.

The θ-2θ XRD patterns of NdBCO films grown in deposition pressures of 100-800 mTorr are shown in Fig. 1. One can see that the film orientation is sensitive to deposition pressure. When 1%O_2/Ar mixture gas was used, fully *c*-axis oriented films were grown only at 800 mTorr while *a*-axis oriented grains were also grown at lower pressures of 100-400 mTorr. When pure O_2 gas was used, on the other hand, fully *c*-axis oriented films were grown in 400 mTorr as well as 800 mTorr. Fig. 1 also implies that the deposition pressure to grow fully *c*-axis oriented NdBCO films is higher than those to grow *c*-axis oriented PLD-YBCO films, even though the deposition pressure with 1%O_2/Ar mixture gas to grow *c*-axis oriented film were unequal to that with pure O_2 gas. Referring to previous papers [3,5,10,13-14], the deposition pressures to grow *c*-axis oriented NdBCO films can be affected by the growth temperatures. Early literatures [3,5] reported that the deposition pressure to grow the *c*-axis oriented NdBCO films was in range of 100-300 mTorr similar to those of PLD-YBCO films, however, the growth temperature of NdBCO (> 850 °C) was much higher than those of YBCO. On the contrary, recent reports from Zama *et al.* [10] and Ichino *et al.* [13-14] showed that fully *c*-axis oriented NdBCO films could be grown at the temperatures lower than 830°C under high deposition pressure of ~ 1 Torr.

Both the deposition pressure and the type of processing gas affect the microstructures of NdBCO films, as shown in Fig. 2. As shown in Fig. 2, the microstructure of the film grown in 800 mTorr is quite different from those of the films grown in 100 to 400 mTorr. The samples grown in low pressures normally exhibit a smooth surface without outgrowths. When 1%O_2/Ar mixture gas was used, the samples grown in 100 and 200 mTorr, however, show

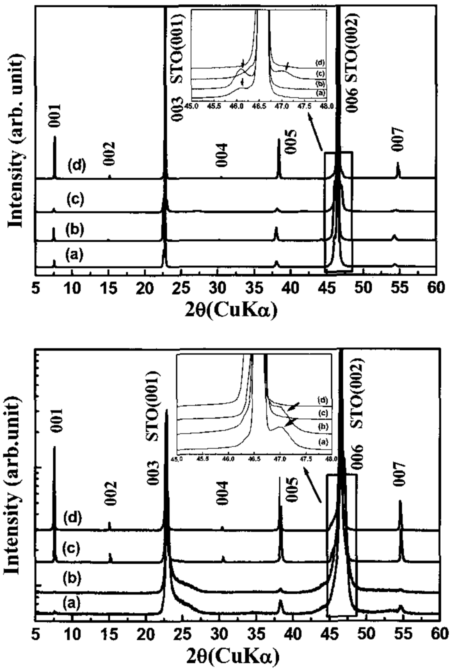

Fig. 1. The θ-2θ XRD patterns of NdBCO films grown on STO (100) substrates under various deposition pressures: (a) 100 mTorr, (b) 200 mTorr (c) 400 mTorr and (d) 800 mTorr, when either 1%O_2/Ar mixture gas (top) or pure O_2 gas (bottom) was used. The arrow indicates the peak due to *a*-axis oriented grains.

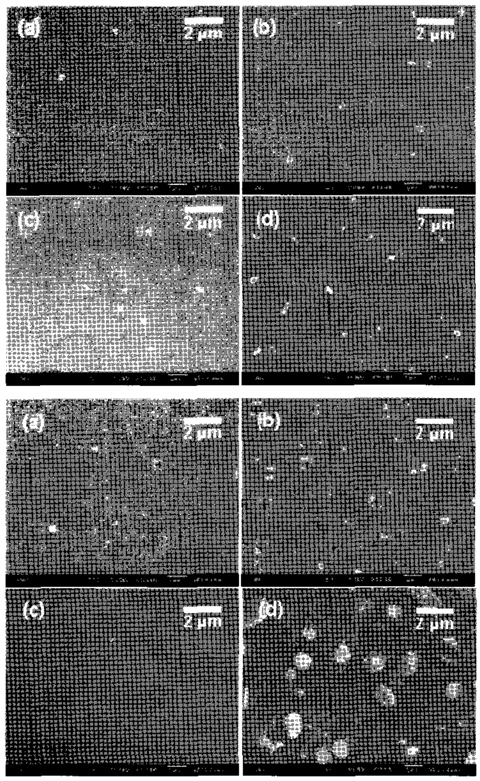

Fig. 2. FE-SEM micrographs of NdBCO films grown in various deposition pressures: (a) 100 mTorr, (b) 200 mTorr (c) 400 mTorr, and (d) 800 mTorr, when either 1%O_2/Ar gas (top) or pure O_2 gas (bottom) was used.

pinholes on the film surface. The pinholes in these films are most probably due to a selective re-sputtering of the ablated atoms, which is usually occurred when the substrate is touched with a visible plasma plume [16]. As usual, the plasma plume size of NdBCO in low pressures is larger than that in high pressures. When pure O_2 gas was used, the substrates were located out of the plumes even though the deposition pressure was as low as 100 mTorr. When $1\%O_2/Ar$ mixture gas was used, however, the substrates were located within the plumes in low pressures of 100 and 200 mTorr although the substrates were located out of the plumes in high pressures of 400 and 800 mTorr. On the other hand, the sample grown in 800 mTorr exhibit much higher number of outgrowths on the film surface, compared to those grown in lower pressures. The outgrowths are known to easily form under high deposition pressure because of a non-stoichiometric deposition caused by a difference in kinetic energies of the ablated atoms in the plume [17]. Fig 3 shows the cross-sectional TEM image of the sample shown in fig. 2 (d, top). It is observable that the outgrowth begins to nucleate at the film thickness about 20 nm. The composition of the outgrowth was roughly estimated to have Ba:Cu = 1:3 by EDS analyses.

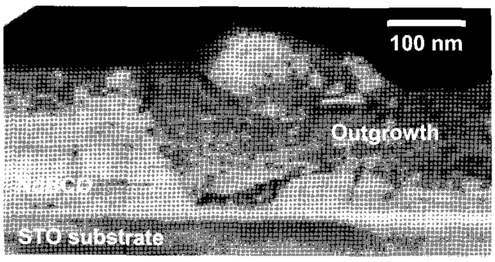

Fig. 3. Cross sectional TEM image of NdBCO film shown in fig. 5-1-2(top, d).

Fig. 4 shows the T_c values (T_c's) of NdBCO films grown in various deposition pressures. When $1\%O_2/Ar$ gas was used, T_c's increase from 67 to 91.2 K with increasing pressure from 100 to 800 mTorr, respectively. On the other hand, when pure O_2 gas was used, the samples deposited in 400 and 800 mTorr exhibit high T_c's of 91.5 and 91.2 K, respectively, while the samples grown in 100 and 200 mTorr show depressed T_c's near 80 K. Degradation of T_c in NdBCO films generally result from two major factors [18,19]; 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 $Nd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$ film. Since all samples were *in-situ* oxygen annealed, and subsequently post-annealed after the deposition of Ag electrode with the same oxygen annealing condition, T_c degradation is 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, the quantitative compositional analyses of the samples were performed using EPMA. The results are shown in Fig. 5. When pure O_2 gas was used, in accordance with our speculation, the samples deposited in the pressure range of 100-200 mTorr show x values higher than 0.1. It has been reported [19] that T_c abruptly decreases below 90 K when x exceeds ~0.1. Consequently, T_c degradation in the films deposited at 100 and 200 mTorr is obviously caused by an excessive substitution of Nd^{3+} ions for Ba^{2+} sites. However, different results are observed in the samples deposited using $1\%O_2/Ar$ mixture gas. The x values of the samples grown in the pressure range of 200-800 mTorr are very small in the range of 0.01-0.03, indicating that small amount of substitution of Nd^{3+} ions for Ba^{2+} sites has occurred. In addition, although the sample deposited in 100 mTorr shows somewhat large x value of 0.07, this amount of substitution is not large enough to cause the T_c degradation down to ~67 K. Consequently, factors other than the amount of substitution must be responsible for the T_c degradation of these samples grown in the pressure range of 100-400 mTorr with $1\%O_2/Ar$ gas. One possible factor is grain boundary occupation of $BaCuO_2$ phase, hindering oxygenation of NdBCO grains, which, however, requires further identification with TEM.

I-V characteristics of the samples, exhibiting a strong *c*-axis orientation as well as high T_c's over 90 K, are represented in Fig. 6. When $1\%O_2/Ar$ gas was used, high J_c (77K, sf) of 3.5 MA/cm^2 is only obtained from the sample grown in 800 mTorr. When pure O_2 gas was used, J_c's values (J_c's) (77K, sf) of 2.8 and 3.1 MA/cm^2 were

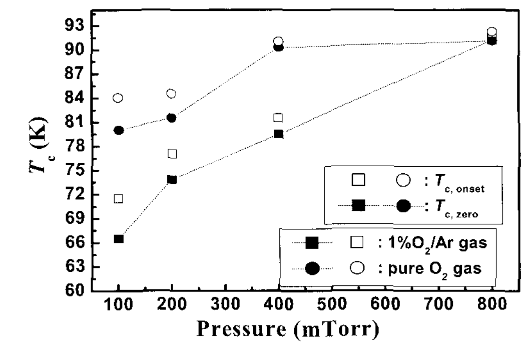

Fig. 4. T_c's of NdBCO films as a function of deposition pressure.

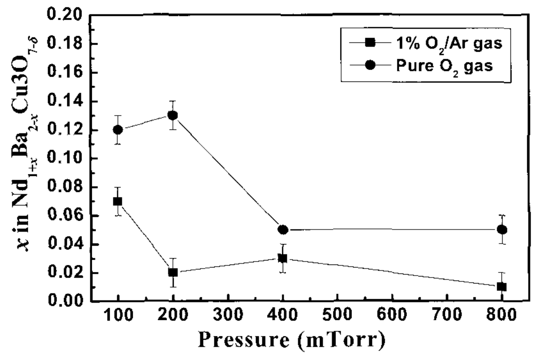

Fig. 5. The x values in $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$, the amount of Nd^{3+} substituted for the Ba^{2+} sites for the NdBCO film as a function of deposition pressure.

obtained from the film deposited in 400 and 800 mTorr, respectively. These high J_c values at 77 K are comparable to record high values reported by Cantoni *et al.* [7-8] and Li *et al.* [5,9]

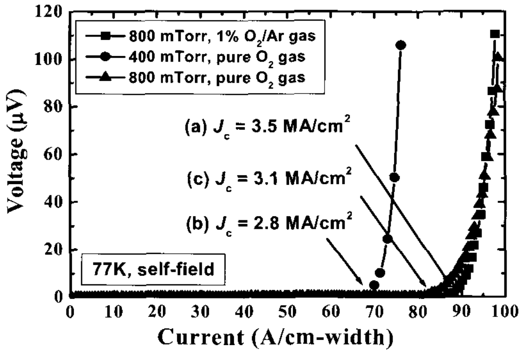

Fig. 6. *I-V* curves of NdBCO films grown at (a) 800 mTorr with $1\%O_2/Ar$ mixture gas, (b) 400, and (c) 800 mTorr with pure O_2 gas.

3.2. NdBCO films grown at various substrate temperatures in 800 mTorr

The samples were grown at the substrate temperatures ranging from 700 up to 830°C which is the upper limit of the PLD heater used in this study. Fig. 7 shows the θ-2θ XRD patterns of NdBCO films grown at various substrate temperatures. The strong *c*-axis oriented films could be obtained at the temperature regions of 700-830°C when $1\%O_2/Ar$ mixture gas was used and 750-830°C when pure O_2 gas was used. FWHM values of (102) φ-scans and (005) ω-scans for the samples exhibiting the strong *c*-axis orientation are shown in Fig. 8. All films have excellent in-plane and out-of-plane textures with FWHM values of 0.55-0.65° and 0.06-0.2°, respectively, implying that the degree of textures for NdBCO films grown on the STO (100) substrates are insensitive to the growth temperature when the substrate temperature is higher than that for the strong *c*-axis oriented NdBCO film.

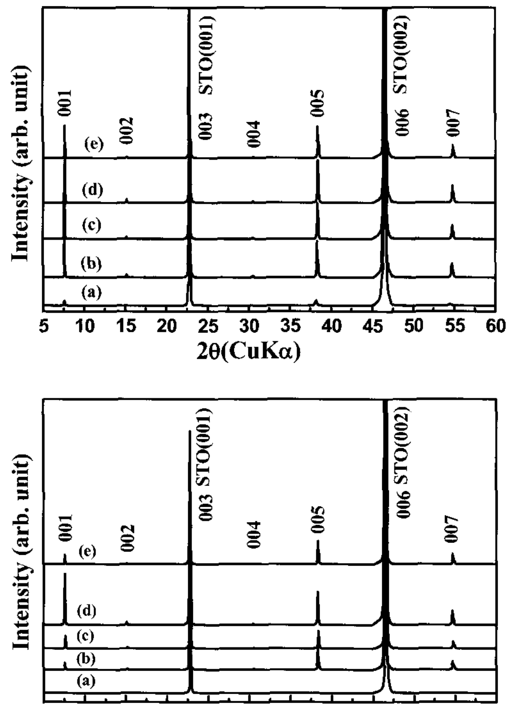

Fig. 7. The θ-2θ XRD patterns of NdBCO films grown on STO (100) substrates at (a) 650°C, (b) 700°C, (c) 750°C, (d) 800°C, and (e) 830°C, when $1\%O_2/Ar$ mixture gas was used (top) and grown at (a) 700°C, (b) 750°C, (c) 775°C, (d) 800°C, and (e) 830°C, when pure O_2 gas was used (bottom).

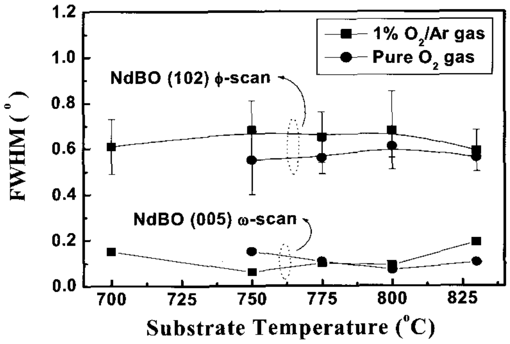

Fig. 8. FWHM values of (005) ω-scans and (102) φ-scans for NdBCO film as a function of the substrate temperature.

The FE-SEM micrographs of NdBCO films grown at various substrate temperatures are represented in Figs. 9 and 10. When $1\%O_2/Ar$ mixture gas was used, while the film deposited at 650°C exhibits rectangular particles with sizes of ~0.2×~0.5 μm², those grown at T_s ranging from 700 to 830°C have typical microstructures composed of outgrowths on the smooth surface. The densities and shapes of outgrowths are, however, somewhat altered when T_s is increased. Irregular-shaped outgrowths with the densities of $0.7\text{-}1.4\times10^6$ cm^{-2} are observed in the films deposited at

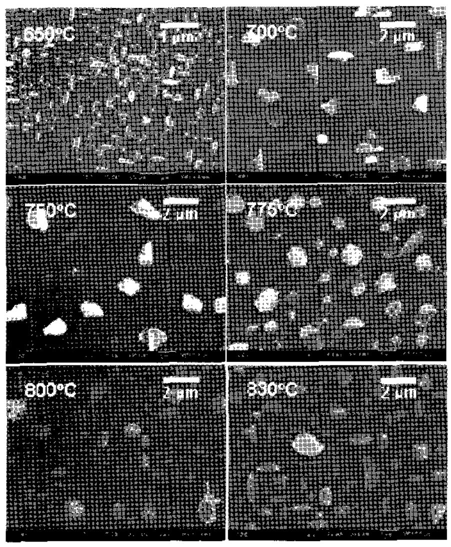

Fig. 9. FE-SEM micrographs of NdBCO films grown at various substrate temperatures when $1\%O_2/Ar$ mixture gas was used.

T_s region of 700-750°C. Although shapes of outgrowths are rather different from those grown at T_s region of 700-750°C, irregular-shaped outgrowths with much higher particle density of $3\text{-}5\times10^6$ cm^{-2} are observed in the films grown at T_s ranging from 775 to 830°C. In addition, a-axis oriented grains, which are hardly observed in other films, exist in the films grown at T_s of 800 and 830°C. When pure O_2 gas was used, on the other hand, while the film grown at 700°C has smooth surface morphology, those grown at T_s ranging from 750 to 830°C have outgrowths on the film surfaces. Further detailed observation indicates that the film grown at 750°C has quite a few irregular-shaped outgrowths, whereas, the films grown at T_s region of 775-830°C have many polygonal-shaped outgrowths with densities of $3\text{-}5\times10^6$ cm^{-2}.

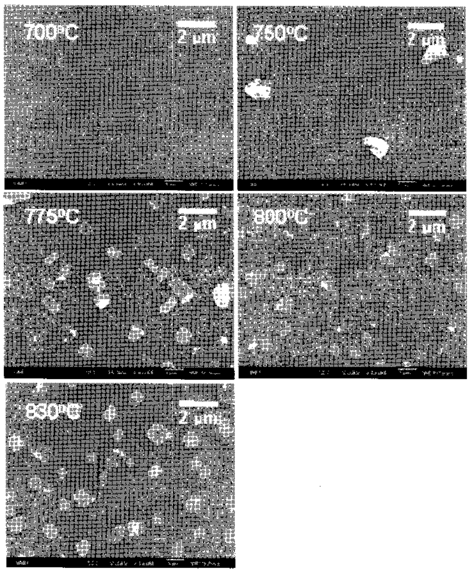

Fig. 10. FE-SEM micrographs of NdBCO films grown at various substrate temperatures when pure O_2 gas was used.

Fig. 11 shows the T_c's of NdBCO films grown at various substrate temperatures. When either $1\%O_2/Ar$ mixture gas or pure O_2 gas are used, the samples grown at T_s of 650 and 700°C show depressed T_c values of 68 K for $1\%O_2/Ar$ mixture gas and of lower than 56 K for pure O_2, where 56 K is lower temperature limit of cryo-cooler system used in this study. In the case of the films grown at the temperature regions of 700-830°C ($1\%O_2/Ar$ mixture gas) and 750-830°C (pure O_2), all NdBCO films exhibit high T_c's of 89-91.5 K. These results suggest that high quality NdBCO films having stoichiometric composition can be obtained at the wide T_s region in high deposition pressure of 800 mTorr with either $1\%O_2/Ar$ mixture gas or pure O_2 gas. Indeed, quantitative compositional analyses using EPMA (not presented here) revealed that these NdBCO films possessed a very small amount of substitution with the x values of 0.01-0.03 in $Nd_{1-x}Ba_{2+x}Cu_3O_{7-\delta}$.

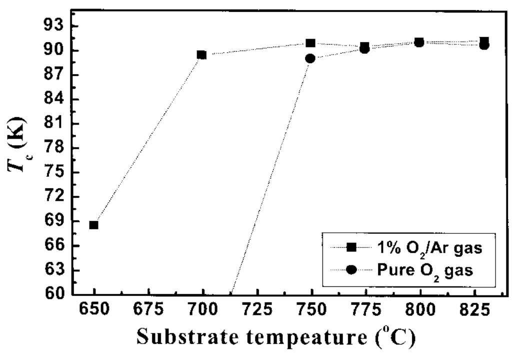

Fig. 11. T_c's of NdBCO films as a function of substrate temperature.

Fig. 12 shows J_c (77K, sf) dependency on T_s for NdBCO films. It can be seen that when either $1\%O_2/Ar$ mixture gas or pure O_2 gas are used, high J_c's over 1 MA/cm^2 are obtainable from the samples grown at wide temperature regions of 700-830°C for $1\%O_2/Ar$ mixture gas or 750-830°C for pure O_2 gas. As previously mentioned, these samples exhibit excellent textures and dense microstructures as well as high T_c's of 89-91.2 K. In particular, J_c's (77K, sf) above 3 MA/cm^2 could be achieved from the samples grown at 800°C, regardless of the type of processing gas.

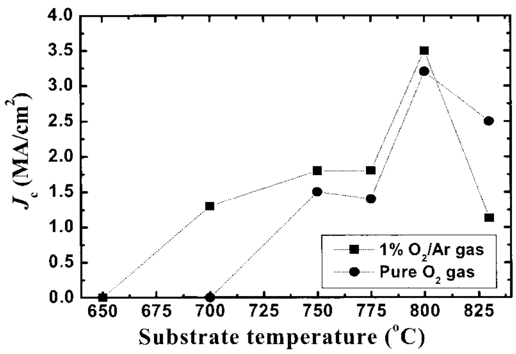

Fig. 12. J_c's (77K, sf) of NdBCO films as a function of substrate temperature.

4. SUMMARY

The effects of PLD-deposition parameters on the structural and superconducting properties of NdBCO films on STO (100) substrates were systematically investigated. The strong c-axis oriented NdBCO films having high T_c's over 90 K and J_c's (77K, sf) over 3 MA/cm^2 could be successfully fabricated in the high deposition pressure of 800 mTorr with either $1\%O_2/Ar$ mixture gas or pure O_2 gas at T_s of 800°C. In the deposition pressure region of 100-400 mTorr, however, the sample grown in 400 mTorr with pure O_2 gas exhibited strong c-axis orientation and high J_c (77K, sf) of 2.8 MA/cm^2, while the other samples had a-axis oriented gains in addition to c-axis oriented grains and depressed T_c's. Quantitative composition analyses indicated that the origin of depressed T_c was attributable to an excessive substitution of Nd^{3+} ions for Ba^{2+} sites when pure O_2 gas was used. However, the cause of T_c degradation when 1%O_2/Ar mixture gas was used has not been clarified yet. Under the high deposition pressure of 800 Torr with either 1%O_2/Ar mixture gas or pure O_2 gas, the strong *c*-axis oriented NdBCO films could be obtained at wide T_s regions of 700-830°C (1%O_2/Ar mixture gas) and 750-830°C (pure O_2 gas). Regardless of the type of processing gas, J_c's (77K, sf) above 3 MA/cm^2 could be achieved from the samples grown at 800°C in 800 mTorr with either 1%O_2/Ar mixture gas or pure O_2 gas. In conclusion, under high deposition pressure of 800 mTorr with either 1%O_2/Ar mixture gas or pure O_2 gas, NdBCO films having high J_c's (77K, sf) over 1 MA/cm^2 can be successfully grown on STO (100) substrates at the wide substrate temperature region, suggesting that the PLD processing window to obtain high J_c-NdBCO films is much wider than those of previous reports.

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