Preparation and Characterization of $NdBa_2Cu_3O_y$ Thin Films

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Abstract— *C*-axis oriented epitaxial $NdBa_2Cu_3O_y$ thin films on (100) $SrTiO_3$ substrates were prepared by off-axis rf sputtering. Thin films with T_{c0} =90K in a deviation of 0.5K were prepared reproducibly under the optimal depositing conditions. A parabolic relation of T_{c0} to *c*-axis lattice parameter corresponding to a typical electronic phase diagram for high-T_c superconductors was observed, indicating an optimal oxygen content for the best superconductivity. The oxygen out-diffusion and thermal expansion of the films were studied by an in-situ high temperature x-ray diffraction.

I. INTRODUCTION

For both foundation and application purposes of high-T_c superconductors, $YBa_2Cu_3O_y$ (YBCO) system has been studied extensively. On the other hand, not much attention has been paid to $NdBa_2Cu_3O_y$ (NBCO) system. Recently, NBCO has been suggested being superior to YBCO in some instances for device applications [1]. It has the highest superconducting transition temperature T_c and an enhanced critical current J_c in intermediate magnetic fields [2,3]. NBCO thin films had been prepared by molecular beam epitaxy (MBE) [4,5], liquid phase epitaxy (LPE) [6], laser ablation [7,8] and off-axis rf sputtering [9]. NBCO thin films with high zero resistance temperature T_{c0} (>92K) were occasionally reported. But it seems not very easy to obtain high-T_{c0} in NBCO thin films. The superconducting properties of the thin films were found to strongly depend on the deposition conditions. It is believed that the oxygen contents of thin films resulted directly from their deposition conditions affect on the superconducting properties strongly. However, there is currently no effective method to measure the oxygen content of the thin films precisely. For powder samples, it was found that the *c*-axis lattice parameter varies with the oxygen content linearly for orthorhombic YBCO[10]. The dependence of the c-axis lattice parameter on oxygen content for YBCO single crystal[11]. A similar relation in NBCO system was also reported by Shaked et al [12]. Thus, we can indirectly determine the oxygen content by measuring the *c*-axis lattice parameter of the thin films. To our knowledge, there is little work to investigate the relation between *c*-axis lattice parameter or oxygen content and superconducting properties for thin films, even in YBCO system. In this work, we aimed at preparation of high quality NBCO thin films and the relations between T_c and *c*-axis lattice parameter or oxygen content in NBCO thin films. The oxygen out-diffusion and thermal expansion of the films were studied by an in-situ high temperature x-ray diffraction.

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II. EXPERIMENT

NBCO thin films were deposited on STO substrates by an off-axis rf sputtering system [13]. The deposition temperature referred hereafter as the substrate temperature T_s, was measured by a thermocouple inserted into the stainless substrate heater. The substrate was stuck on the heater by silver paste. The deposition gas was a mixture of argon and oxygen with different ratios. First, the deposition conditions were optimised. Different oxygen contents of the grown films were obtained by slightly changing the substrate temperature T_s, the ratio of P_{Ar}/P_{O2} and the annealing process. To ensure the accuracy of *c*-axis lattice parameter of the different films, all films used in this study are deposited with the thickness about 2000Å, and the deviation of the film thickness for different films is smaller than 200Å.

The temperature dependence of resistance was measured by a standard DC four-probe method using a closed-cycled cryogenerator with a measuring current of 0.1mA. The temperature was determined by a Pt resistance thermometer. The cooling rate was controlled to be less than 1K/min by a computer program.

The x-ray diffraction (XRD) was performed on the Siemens D5000 x-ray diffractometer with CuK_α radiation. The *c*-axis lattice parameters of NBCO thin films were determined from the XRD patterns and refined by the least square method. The zero-point-shift of the diffractometer was corrected by using a high-purity silicon powder standard. The crystallinity of the film was examined by measuring the rocking curve of (005) diffraction peak. To investigate the oxygen out-diffusion, in-situ, high-temperature x-ray diffraction was performed. The sample was stuck on the Pt heating slice by silver paste, and a thermocouple was fixed on the opposite side of the Pt slice. The sample chamber was evacuated to $\sim 10^{-4}$mbar. The sample was heated and cooled at a rate of 50°C/min to a set of temperatures and held for two minutes before measuring. The temperature fluctuation during measurement was smaller than 1°C.

III. RESULTS AND DISCUSSION

The optimal deposition temperature and pressure for thin films with $T_{c0} \sim 89.5 - 90.5$K are 740°C < T_s < 780°C and 1.2 ~ 1.8×10^{-1} mbar with the ratio of P_{Ar}/P_{O2} = 4/1 ~ 2/1. Typical film thickness is ~2000Å. In the x-ray diffraction patterns only (001) peaks for NBCO and the STO substrate reflections are visible, indicating that the films are highly *c*-axis oriented. The full width at half maximum (FWHM) of (005) peak determined from the rocking curve is 0.2 ~ 0.3°, demonstrating a good crystallinity of our thin films.

Fig.1 shows a typical XRD pattern and a rocking curve of (005) peak.

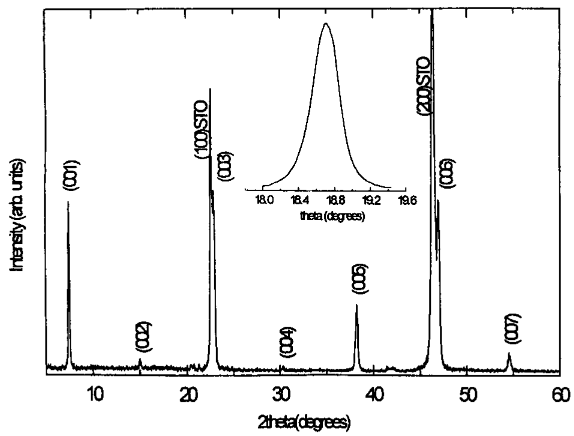

Fig.1. XRD pattern and rocking curve of (005) peak of a single-phase NBCO thin film.

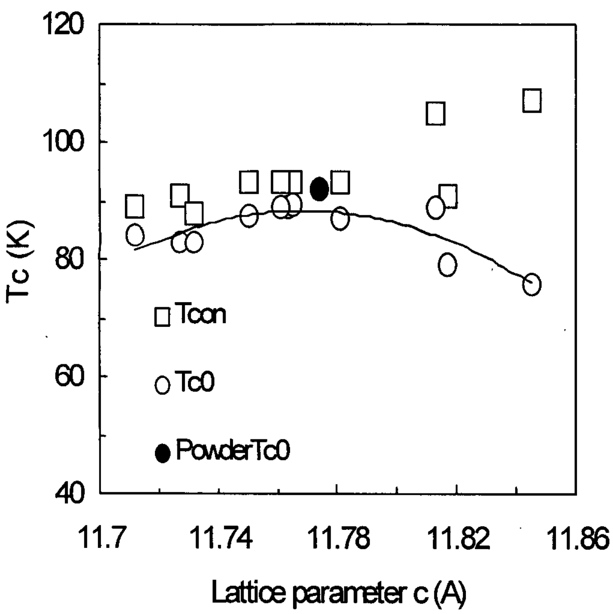

Fig.2. The dependence of superconducting transition temperature T_c on the c-axis lattice parameter.

Fig.2 shows the dependence of the superconducting temperature T_c on the c-axis lattice parameter. These films were obtained by slightly shifting the deposition conditions from the optimal conditions or by quenching directly to room temperature after deposition. It is interesting to note that the zero resistance temperature T_{c0} exhibits a parabolic relation of the c-axis lattice parameter. From Fig.2 it is found that the maximum T_{c0} for thin films approaches the data for the powder samples. A higher onset of the superconducting transition temperature ($T_c^{on} > 100$K) was observed in the thin films with longer c-axis lattice parameter. Fig.3 shows the temperature dependence of the resistance for a single-phase film (a)and thin films containing the high-T_c phase (b), respectively. The resistance curves vs temperature of these films (Fig.3b) indicate that there exist two superconducting phases in these films. However, from their XRD patterns, no any detectable second phase in these films was found. Their rocking curves also give almost the same value of FWHM as that for the optimal films. Thus we believe both superconducting phases belong to orthorhombic Re-123 structure. Their difference comes from the different oxygen content or oxygen occupation. We noted that all films with higher T_c^{on} were treated by quick annealing or direct quenching after deposition. Thus, a possible explanation is to say that the superconducting phase with the higher-T_c^{on} corresponds to a severe oxygen-depletion phase. But for the normal superconducting phase, oxygen-depletion will result in a lower T_{c0}. That is a contradiction between these two superconducting phases. It should be pointed that the higher T_c^{on} phase is difficult to be reproduced. Although we had observed this phase in several films, we failed in fabricating pure higher-T_c^{on} films. Nevertheless, this data suggests a possibility to obtain films with $T_{c0} > 95$K.

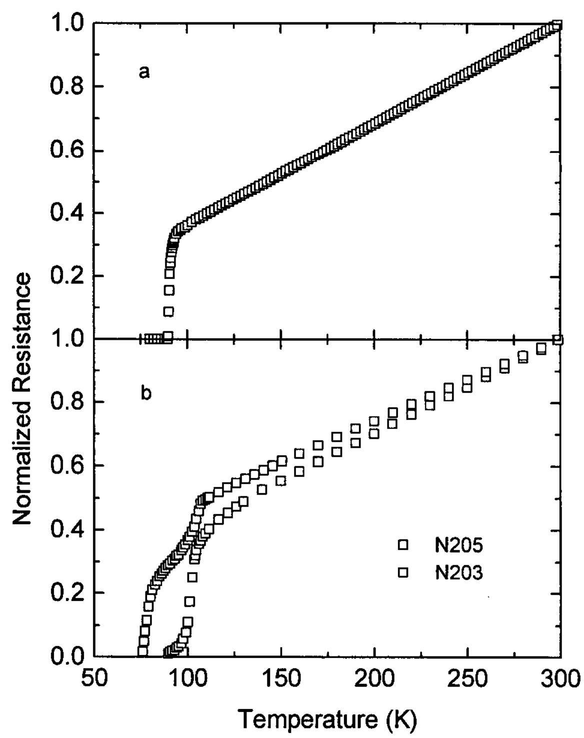

Fig.3. The temperature dependence of the resistance for a single-phase thin film of $T_{c0} \sim 90$K (a) and films containing the high-T_c phase (b).

Does the above mentioned parabolic relation in Fig.2 T_{c0} - c represent the general electronic phase diagram of T_c - n (where n is the carrier concentration) for high-T_c cuprate superconductors? For powder $NdBa_2Cu_3O_y$ samples, the *c*-axis lattice parameter increases with decreasing of oxygen content *y* [12]. By fitting the experimental data from the present work, an approximate linear relation can be given as

$$c = 12.674 - 0.132y \qquad (1)$$

Thus the *c*-axis lattice parameter directly takes a measurement of the oxygen content. Briefly speaking, the oxygen content is in proportion to the carrier concentration *n*. The parabolic relation of T_{c0} - *c* seems to agree well with the electronic phase diagram of T_c - *n* for other high-T_c cuprate superconductors. Such a T_c - *n* phase diagram indicates that there exists an optimal carrier concentration *n* between under- and over- doping regions. The following parabolic $T_c(n)$ relation is suggested.

$$T_c = T_{co} - A(n_o - n)^2 \qquad (2)$$

where T_{co} is the maximum superconducting transition temperature T_c corresponding to an optimal carrier concentration n_o, *A* is a constant.

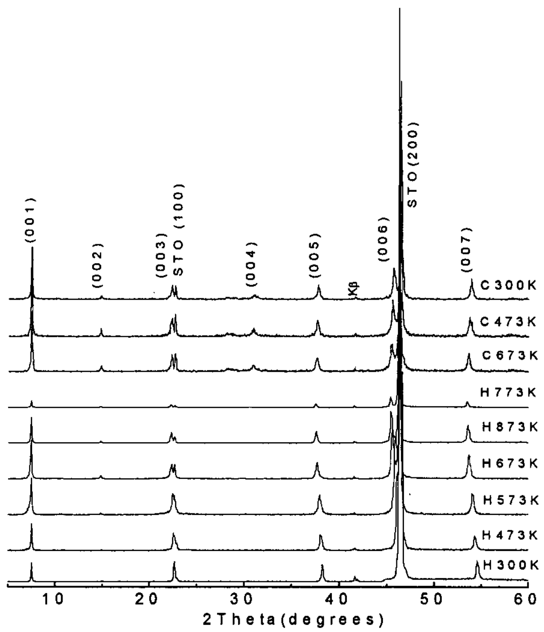

Fig.4. The in-situ high temperature x-ray diffraction patterns of the NBCO thin film.

Most experimental results suggest that the Re-123 system is likely to be in the overdoped region of the T_c - *n* phase diagram. The above $T_c(n)$ seems to contradict with the general belief that T_c should increase with increasing carrier concentration n. In fully oxygenated $Gd_{1-x}Y_xBa_2Cu_3O_7$ system, Fernandes et al [14] found that its T_c decreases linearly with increasing x, indicating that for a fixed carrier concentration n, T_c decreases with decreasing radius of the Re-ion *r*. Ramesh and Hedge [15] reported that the valence of Cu(2) increases with decreasing of radius of the Re ion *r*. i.e. the carrier concentration n increases with decreasing of *r*. Thus, the combination of Fernandes et al's experimental and Ramesh and Hedge's calculated results could give rise to a conclusion that T_c can decrease with increasing of n in Re-123 system. For NBCO system, its pressure coefficient dT_c/dP=1.21K/Gpa is the highest among all ReBCO systems [2]. In other words, its size effect on T_c is strongest in all ReBCO systems. The T_c of NBCO exhibits a clear parabolic relation, indicating that there exists an optimal carrier concentration n. T_c is sensitive to the carrier concentration *n*. That is why the T_c of NBCO thin films depends strongly on the depositing conditions.

Fig.4 shows the in-situ, high-temperature x-ray diffraction patterns. It is clearly found that the shift of diffraction peaks varies with the temperature. The XRD patterns indicate that the film are single phase and *c*-axis oriented. The *c*-axis lattice parameter was refined by the least square method. The results are presented in Fig.5. The lattice parameter of STO exhibits a linear temperature relation. By fitting the experiment data, the thermal expansion coefficient of STO is $6.6x10^{-6}$/K, which is close to the reported value of $8.6x10^{-6}$/K [16]. For the NBCO film, the *c*-axis lattice parameter shows a nonlinear variation in the heating process, however, a linear relation was obtained in the cooling process. The linear relation indicates the total thermal effect. The thermal expansion coefficient of NBCO was determined being $12.4x10^{-6}$/K by the linear fitting, which is comparable with the data of YBCO (10 ~ 15 $x10^{-6}$/K)[17]. The nonlinear relation are the combination effect of the thermal expansion and the oxygen out-diffusion. By removing the thermal expansion effect, a clear oxygen out-diffusion effect was given. It is evident that the oxygen out-diffusion only occurs below 770K. The oxygen out-diffusion is very small as the temperature is higher than 670K.

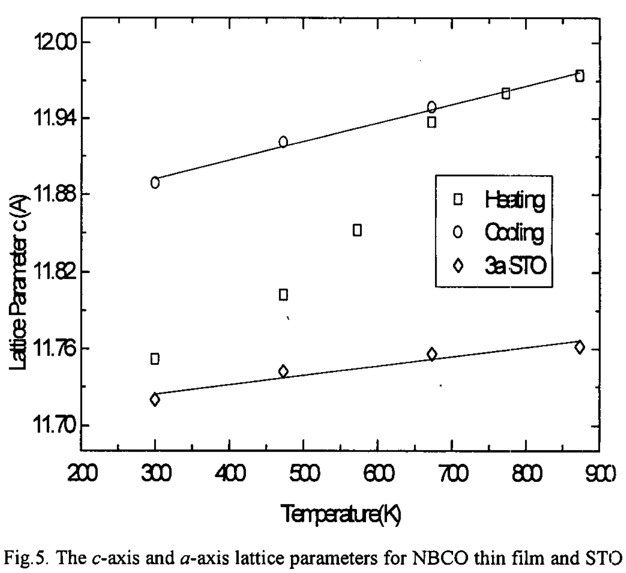

Fig.5. The *c*-axis and *a*-axis lattice parameters for NBCO thin film and STO substrate, the solid lines represent the linear fitting result.

IV. CONCLUSIONS

C-axis oriented $NdBa_2Cu_3O_y$ thin films on (100) $SrTiO_3$ substrates were prepared by an off-axis rf sputtering method under different conditions. Under the optimal deposition temperature (740°C < T_s < 780°C) and pressure (1.2 ~ $1.8x10^{-1}$ mbar, P_{Ar}/P_{O2} = 4/1 ~ 2/1), thin films with T_{c0} = 90±0.5K were prepared reproducibly. A parabolic relation of T_{c0} to c-axis lattice parameter corresponding to a typical electronic phase diagram of T_c – n for high-T_c superconductors was observed. The oxygen out-diffusion was investigated by an in-situ high-temperature x-ray diffraction. The result suggested that oxygen out-diffusion occurred below 770K and resulted in an expansion of the c lattice parameter.

REFERENCES

[1]. M. Badaye, J.G. Wen, K. Fukushima, N. Koshizuka, T. Morishita, T. Nishimura, and Y. Kido, `Superior properties of $NdBa_2Cu_3O_y$ over $YBa_2Cu_3O_x$ thin films' Supercond. Sci. Tech. vol.10, pp.825-830, 1997

[2].J.G. Lin, C.Y. Huang, Y.Y. Xue, C.W. Chu, C.W. Cao, and J.C. Ho, `Origin of the R-ion effect on T_c in $RBa_2Cu_3O_7$', Phys. Rev. B vol.51, pp.12900-12903, 1995

[3]. S.I. Yoo, N. Sakai, H. Takaichi, T. Higuchi, and M. Murakami, `Melt processing for obtaining $NdBa_2Cu_3O_y$ superconductors with high T_c and large J_c', Appl. Phys. Lett. vol.65 pp.633-635, 1994

[4]. H. Nonaka, T. Shimizu, and K. Arai, `Preparation $NdBa_2Cu_3O_{7-y}$ films in ultrahigh vacuum with a NO2 supersonic molecular beam', Appl. Phys. Lett. vol.57, pp.2850-2852, 1990

[5]. H. Nonaka, T. Shimizu, and K. Arai, `Growth behavior of $YBa_2Cu_3O_{7-d}$ and $NdBa_2Cu_3O_{7-d}$ thin films observed by electron diffraction' Appl. Phys. Lett. vol.59, pp.600-602, 1990

[6]. A. Takagi, U. Mizutani, and Y. Yamada, `Superconducting properties of Nd-Ba-Cu-O thick films prepared by liquid phase epitaxial growth', IEEE Trans. on Appl. Supercond. vol.7, pp.1388-1391, 1997

[7]. M. Badaye, F. Wang, Y. Kanke, K. Fukushima, and T. Morishita,`High-quality c-axis oriented superconducting $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ thin films deposited by laser ablation method', Appl. Phys. Lett. vol.66, pp.2131-2133, 1995

[8]. S.H. Moon and B. Oh,`Superconducting $NdBa_2Cu_3O_{7-\delta}$ thin films prepared by the laser ablation method', IEEE Trans. on Appl. Supercond. vol.7, pp.1185-1188, 1997

[9]. I.S. Kim, K.W. Lee, Y.K. Park, and J.C. Park, `Properties of $NdBa_2Cu_3O_{7-\delta}$ thin films prepared by off-axis sputtering', Appl. Phys. Lett. vol.68, pp.1859-1861, 1996

[10]. R.J. Cava, B. Batlogg, C. H. Chen, E.A. Rietman, S.M. Zahurak, and D. Werder, `Single- phase 60-K bulk superconductor in annealed $Ba_2YCu_3O_{7-\delta}$ ($0.3<\delta<0.4$) with correlated oxygen vacancies in the Cu-O chains' Physical Review B vol.36, pp5719-5722

[11]. H. Claus, U. Gebhard, G. Linker, K. Rohberg, S. Riedling, J. Franz, T. Ishida, A. Erb, G. Muller-Vogt, H. Wuhl,` Phase separation in YBa2Cu3O7-d single crystals near d=0', Physica C vol.200, pp.271-276, 1992

[12]. H. Shaked, B.W. Veal, J. Faber,Jr., R.L. Hitterman, U. Balachandram, G. Tomlins, H. Shi, L. Morss, and A. P. Paulikas,`Structural and superconducting properties of oxygen-deficient $NaBa_2Cu_3O_{7-\delta}$', Phys. Rev. B vol.41, pp.4173-4180, 1990

[13].J. Gao, W.H. Wong, and J. Xhie,`Formation of outgrowths at the growing stage of $YBa_2Cu_3O_x$ ultrathin films on $ZrO_2$ substrates', Appl. Phys. Lett. vol.67, pp.2232-2234, 1995; J. Gao, B. Hauser, and H. Rogalla, `High critical current density ultrathin $YBa_2Cu_3O_x$ films made by a modified rf-magnetron sputtering technique', J. Appl. Phys. vol.67, pp.2512-2515, 1990

[14]. A.A.R. Fernandes, J. Santamaria, S.L. Bud'ko, O. Nakamura, J. Guimpel, and Ivan K. Sckuller, `Effect of physical and chemical pressure on the superconductivity of high-temperature oxide superconductors', Phys. Rev. B vol.44, pp.7601-7606, 1991

[15]. S. Ramesh and M.S. Hedge, `Bond-valence analysis of the charge distribution and internal stresses in the $RBa_2Cu_3O_{7-d}$ system (R=rare earth)', Physica C vol.230, pp.135-140, 1994

[16]. R. Ramesh, A. Inam, W.A. Bonner, P. England, B.J. Wilkens, B.J. Meagher, L. Nazar, X.D. Wu, M.S. Hegde, C.C. Chang, T. Venkatesan, and H. Padamsee, `Ferrimagnetic rare-earth orthoferrites: A new, magnetic substrate for the growth of epitaxial Y-Ba-Cu-O thin films', Appl. Phys. Lett. vol.55, pp.1138-1140, 1989

[17]. X. D. Wu, A. Inam, M. S. Hegde, B. Wilkens, C. C. Chang, D. M. Hwang, L. Nazar, T. Venkatesan, S. Miura, S. Matsubara, Y. Miyasaka, N. Shohata, ` High critical currents in epitaxial YBa2Cu3O7-x thin films on silicon with buffer layers' Appl. Phys. Lett. vol.54, pp.754-756, 1989