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<td><strong>Citation</strong></td>
<td>IEEE Transactions on Applied Superconductivity, 1999, v. 9 n. 2, p. 1590-1593</td>
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<td><strong>Issued Date</strong></td>
<td>1999</td>
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<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10722/43270">http://hdl.handle.net/10722/43270</a></td>
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Preparation and Characterization of NdBa$_2$Cu$_3$O$_y$ Thin Films

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Abstract—C-axis oriented epitaxial NdBa$_2$Cu$_3$O$_y$ thin films on (100) SrTiO$_3$ substrates were prepared by off-axis rf sputtering. Thin films with $T_{co} = 90$K in a deviation of 0.5K were prepared reproducibly under the optimal deposition conditions. A parabolic relation of $T_{co}$ 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$_2$Cu$_3$O$_y$ (YBCO) system has been studied extensively. On the other hand, not much attention has been paid to NdBa$_2$Cu$_3$O$_y$ (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 $T_{co}$ (>92K) were occasionally reported. But it seems not very easy to obtain high-$T_{co}$ 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.

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 $P_{O_2}/P_{Ar}$ 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 ~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 $T_{co}$ ~ 89.5 - 90.5K are 740°C $< T_s < 780°C$ and 1.2 $\sim$ 1.8x10$^4$ mbar with the ratio of $P_{O_2}/P_{Ar}$ = 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 the superconducting transition 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 ($T_{c0} > 100K$) 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 $T_{c0}^{on}$ were treated by quick annealing or direct quenching after deposition. Thus, a possible explanation is to say that the superconducting phase with the higher-$T_{c0}^{on}$ 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 $T_{c0}^{on}$ phase is difficult to be reproduced. Although we had observed this phase in several films, we failed in fabricating pure higher-$T_{c0}^{on}$ films. Nevertheless, this data suggests a possibility to obtain films with $T_{c0} > 95K$.

Fig. 3. The temperature dependence of the resistance for a single-phase thin film of $T_{c0} \sim 90K$ (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$_2$Cu$_3$O$_y$ 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

$$c = 12.674 - 0.132y$$  \hspace{1cm} (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 $T_c - c$ 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.

$$T_c = T_{c0} - A(n_o - n)^2$$ \hspace{1cm} (2)

where $T_{c0}$ is the maximum superconducting transition temperature $T_c$ corresponding to an optimal carrier concentration $n_o$. $A$ is a constant.

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$_x$Ba$_2$Cu$_3$O$_7$ 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 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$_x$Ba$_2$Cu$_3$O$_7$ 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.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$_2$Cu$_3$O$_y$ 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 < $T$ < 780°C) and pressure (1.2 – 1.8x10$^{-1}$ mbar, $P_{oxygen}/P_{total}$ = 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 $T_s$ for high-Tc 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.

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