OXIDATION AND REDUCTION DURING FABRICATION OF HIGH QUALITY $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ SUPERCONDUCTING THIN FILMS

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Abstract-Using pulsed-laser deposition and N_2O reactive gas, we have successfully fabricated very high quality c-axis n-type $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (NCCO) oxide superconducting thin films epitaxially grown on different substrates. The film shows a superconducting transition temperature T_c (R = 0 Ω) of 22.4K and a transition width of 0.2K from ac susceptibility measurement. The critical current density J_c is $8x10^5$ A/cm^2 at 4.2K in zero magnetic field. The microwave surface resistance measured at 9.6 GHz shows a value of 3 mΩ at 4.2K in 500 nm-thick NCCO film, the best result reported so far for NCCO thin films. The oxygen deficiency is necessary to achieve the superconductivity in NCCO and the oxygen reduction during and after film deposition is critical. The oxidation and reduction processes are studied systematically for various substrate temperature, atmosphere and annealing duration .

I. INTRODUCTION

Although extensive studies have been performed on the electron-doped oxide NCCO superconductor, some controversial experimental results (e. g., the sign of carriers determined from Hall measurements) on intrinsic transport properties still need to be clarified[1,2]. It is well known that vacuum annealing is necessary to get superconductivity in this electron-doped oxide system and this process of materials may cause the partial decomposition and lead to inhomogeneities such as multi-phases in the samples[3]. Thus it becomes difficult to obtain reliable and reproducible transport measurements. There are still some interesting fundamental issues unresolved, such as the nature of the carriers, the role of oxygen vacancies, the origin of the insulator-superconductor transition and the interaction between p-type and n-type superconductors [4]. It is desirable to have high quality single-crystalline NCCO thin films for these studies and therefore the fabrication and the characterization of NCCO films have drawn considerable effort [5,6,7]. The laser ablation technique is a superior one for the deposition of high Tc oxide superconducting films[8]. It reproduces the target composition in the films so that the Ce composition can be sustained which is especially important for NCCO superconductor[3].

In this paper, we report the fabrication process for NCCO films on different kinds of substrates using pulsed-laser deposition in N_2O or O_2 reactive gas. By fine control of the oxygen content in the film, very high quality films were made under optimized reduction conditions with a T_c (R=0) of 22.4K and a transition width of 0.2K. The value of J_c and microwave surface resistance are the best reported so far for NCCO films.

II. EXPERIMENTAL

The basic pulsed laser deposition technique has been described previously [8]. The pellet in this work was made from an $Nd_{2-x}Ce_xCuO_{4-y}$ ceramic sample with x = 0.15. Pellets with other Ce concentrations gave poorer film qualities. This is consistent with the results of bulk samples [3] indicating that the pellet composition is indeed preserved in the films. Single crystals of (100) $LaAlO_3$(LAO), (100)$NdGaO_3$ (NGO), (100)$SrTiO_3$ (STO) and (100)Y-ZrO_2 (YSZ) were used as substrates, while films on all substrates gave similar superconducting properties, the difference in the lattice match (a = 3.793 Å for $LaAlO_3$, 3.85Å for $NdGaO_3$, 3.905 Å for $SrTiO_3$ and 5.15Å for YSZ as compared to a = 3.946 Å for NCCO) resulted mainly in different surface morphologies. Mainly the results on $LaAlO_3$ are presented in this paper. The films were deposited in 200 mTorr N_2O or O_2 at a deposition rate of 0.5 Å/pulse and a repetition rate of 10 Hz. The substrates were held at different temperatures from 620°C - 820°C. After the deposition, different procedures were taken to cool the films down to room temperature (RT). They included: a) cooling directly in 200 mTorr N_2O, b) cooling after evacuating the chamber to 10^{-5} Torr, c) holding the films at the deposition temperature in a vacuum of 10^{-5} Torr for different time periods before cooling down and d) cooling or annealing in 200 mTorr-200Torr O_2 ambient. The films had a thickness of 1500Å-5000 Å and we found that different film thicknesses required different optimum reduction conditions. The films were then characterized for structural and superconducting properties using X-ray diffraction, dc resistance and ac susceptibility measurements. Microwave surface resistance R_s was measured at 9.6 GHz in a superconducting Nb cavity with a variable-temperature sample stage.

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III. RESULTS AND DISCUSSION

Before we start describing the oxidation and reduction in the fabrication of films, we present here the basic structural characterization of these NCCO thin films. Fig.1 is the θ-2θ X-ray diffraction from NCCO/LAO sample deposited at 800°C, and then cooled down directly to RT in vacuum. The diffraction pattern is well indexed by (00l) peaks, showing highly oriented c-axis growth with a small fraction of (110) orientation (of the order of 1%). The lattice constant calculated from (006) NCCO peak gives c=12.08 Å, which is consistent with single crystal results [3]. The full width at half maximunm (FWHM) of a rocking curve scan from (006) peak of NCCO/STO is 0.3° (NCCO/LAO is 0.4°) which shows highly oriented growth characterized by a narrow mosaic distributions. The films are optically observed to be black with mirror-like surfaces. Scanning electron microscope (SEM) images show the presence of spherical particulates , a common feature of the laser ablation process. Cross sectional TEM studies reveal a sharp interface with the substrate and a layered structure without apparent stacking defects like those observed in YBCO[8].

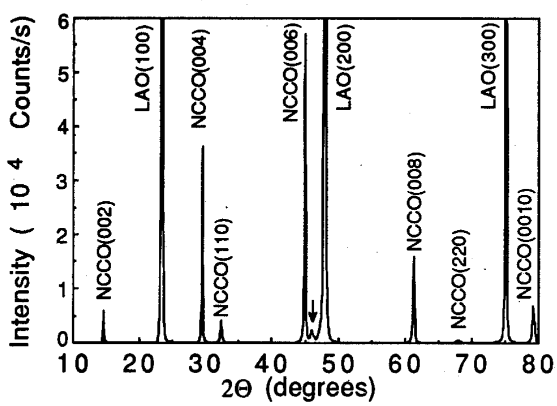

Fig. 1. X-ray diffraction of 4000Å-thick NCCO /LAO film. The diffraction for the films on other kinds of substrates is similar to this except without the (200) peak which appeared only on LAO (shown by the arrow).

The superconducting properties of the film are shown in Fig.2. The resistance measurement shows a Tc of 22.3K (22.4K) with sharp transition of 0.6K (0.2K) for NCCO/LAO (NCCO/STO). The ratio of the room temperature resistance to the residual resistance is over 6 with a residual resistivity of 85 μΩcm. Since the ac susceptibility is a much more stringent characterization technique which reveals the bulk properties of the film while the zero resistance can be achieved once a superconducting percolation path is formed, the ac susceptibility measurement was adopted as the characterization technique for all the films made with the different reduction procedures. For the clarity of presentation, we only give resistance measurement results later for other samples. Besides a high T_c and a sharp transition as well as a narrow FWHM in the ω-scan, the NCCO film made under the optimum conditions is also characterized by a high critical current density, J_c, at 4.2 K; A J_c value as high as 8 x 10^5 A/cm^2 was obtained at 4.2 K and zero field. The most stringent characterization of the film quality is the microwave surface resistance measurement. A sharp drop in R_s is seen at around 22K, unlike in poorer quality samples where multiple transitions are often found. The residual surface resistance is ~3 mΩ, the best result reported so far for NCCO thin films. The good microwave property is a clear indication of a high crystalline quality and homogeneity of the superconducting properties in the sample [7,9].

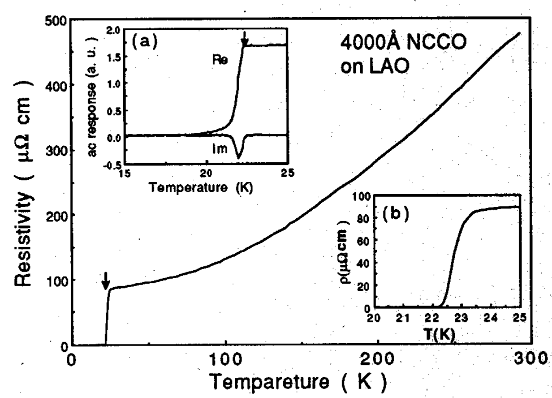

Fig. 2. Transport properties of the film, (a) ac susceptibility and (b) resistivity measurement of a 4000 Å NCCO film on (100) LaAlO3 substrate. Note that the zero resistance temperature (indicated by the arrows) corresponds to the onset in the ac susceptibility, which is a more stringent characterization of the film quality.

Since we are going to discuss the oxidation and reduction during materials preparation, we are more concerned about curvature of the resistance curve, resistance ratio before the transition to that at room temperature (RR) and Tc rather than the absolute resistivity for the study of insulator-superconductor transition[4]. The normalized resistance R(T)/R(295K) is used for simplicity of presentation. In Fig. 3, the normalized resistance is plotted for 400 nm NCCO films which were deposited at different substrate temperatures in 200 mTorr N_2O and cooled after the deposition chamber was evacuated to 10^{-5} Torr. Both the Tc and RR decreased with decreasing substrate temperature(Ts) and the curvature of the resistance curve changed from metallic to semiconductor-like or insulator-like behavior (curves 1-8). The reduction took place during the time the chamber was evacuated and also when the the film was cooled. T_c depends on the substrate temperature and the optimum temperature is ~800 °C. The signal peak is broader and sometimes shows multiple transitions for lower deposition temperatures. We attribute the temperature-dependence primarily to the oxygen stoichiometry effects since no major structural change is detected by X-ray diffraction within this temperature range except for a slight increase of the (110) reflection for lower temperatures. The poor superconducting properties for low deposition temperatures indicate insufficient reduction, due to both higher equilibrium oxygen pressure at low temperature [10] and lower oxygen diffusion coefficients. There is also another possible reason that the local disorder develop with decreasing temperature which affect the reduction, similar to the case of $YBa_2Cu_3O_7$ films where the disorder in the apical oxygen position strongly affects the superconductivity [11].

Fig.4 shows the dependence of superconductivity of the films on the deposition and cooling ambient for the films deposited at same temperature (800°C) in different reactive gas(N_2O or O_2) and different cooling atmosphere pressure. As shown in curves 1 to 5 for the films made in N_2O, the Tc decreased with the more entry of oxygen to the film, and the RR decreased too. Surprisingly the film cooled in 200 Torr pure O_2 turns out to have a Tc of 12K , with a RR of about 2 (curve 4). Finally, the film annealed in 200 Torr O_2 for 10 minutes becomes insulating. The films deposited in oxygen atmosphere where directly cooled in O_2 results in non-superconducting films(curve 6) and those directly cooled in vacuum show a Tc of 13K(curve 7). It seems that there are two ways to achieve Tc=12K superconducting films: 1) depositing film under N_2O and cooling down in 200 Torr O_2; 2) depositing films under O_2 and cooling down in vacuum (10^{-5}Torr.). The possible reason for this is that the initial oxygen content in the film as-grown from the two processes is different, as mentioned by Kussmaul et. al. [6], in order to get the same final oxygen composition (indicated by Tc and RR), one should take some oxygen from the film made in the first method(reduction) and put some oxygen in the film made in

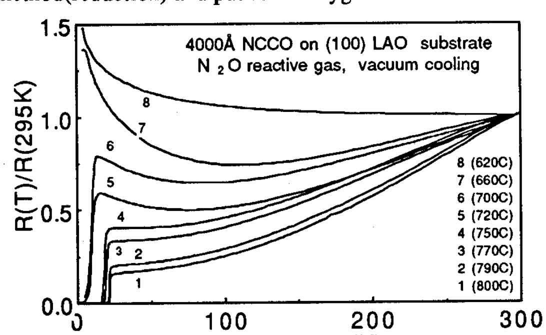

Fig. 3. Normalized resistance vs. temperature for NCCO films at different substrate temperature(Ts). Note curve 8 is reduced by cubic root for the presentation.

the second method(oxidation). But there are still some differences between these two methods. Detailed studies are under way. on the variation of the curvature and the surface morphologies.

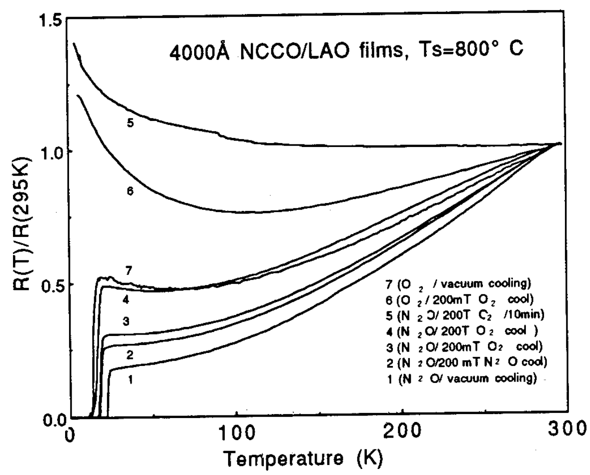

Fig. 4. Resistance measurement for different sample treatment processes. Curve 5 is reduced by cubic root.

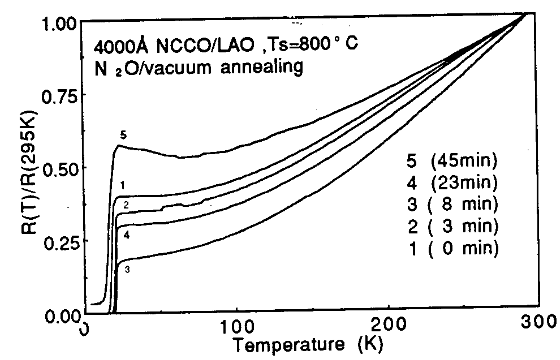

Fig. 5. The normalized resistance for 4000Å NCCO films deposited at 750 °C followed by vacuum annealing at 10^{-5} Torr for different durations.

The film quality can be also optimized through vacuum annealing for a longer period at low temperatures. Fig. 5 shows R(T)/R(295K) for films deposited at 750°C and annealed in a vacuum of 10^{-5} Torr for different durations. When the annealing time increases, T_c and RR become higher and the transition gets sharper until an optimum is reached at ~10 minutes(curve 3). Over-reduction renders some partial decomposition showing up as a degradation of Tc and RR(curve 4) and even the zero resistance cannot be achieved(curve 5, no ac signal either). Further reduction makes the film totally transparent and insulating. The highest T_c thus obtained is lower than the best results obtained at 800°C probably due to the local disorder as mentioned above. Similar experiments at higher temperatures require much shorter annealing time for the best T_c. These results can be explained by the change of diffusion mobility of oxygen out of the film at different temperature during the reduction. For given diffusion parameters, it takes a longer time at low temperatures to achieve certain oxygen deficiency in the NCCO film than at high temperatures.

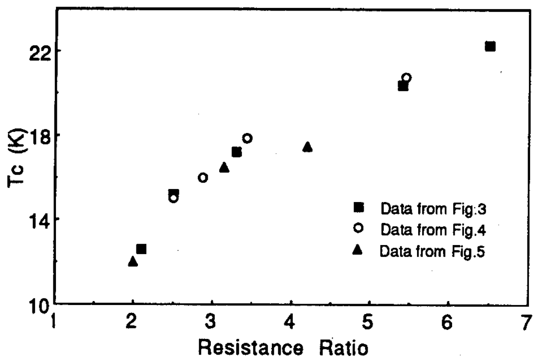

Fig. 6. Tc vs. resistance ratio for the 4000Å-thick NCCO films on LAO substrate.

For NCCO thin films, there tends to be a more uniform distribution of the oxygen deficiency than in the bulk samples and single crystals. Therefore, a good correlation between T_c and resistance ratio (RR) could be established. In Fig. 6, T_c as a function of the resistance ratio is plotted for the samples of Fig. 3 - 5, which were made under completely different reduction or oxidation conditions. The three sets of data all overlap with each other with small fluctuations, indicating that one single parameter controls the normal state and superconducting transport properties of these samples, which is more likely to be the oxygen content. An incomplete reduction, either due to the low temperature or due to the short annealing time, causes inhomogeneities in local oxygen content. It leads to more scattering centers (disordering) [4] and hence a larger residual resistance and lower resistance ratio. On the other hand, it also results in a lower T_c and a broader or multiple transition in the film.

IV. SUMMARY

High quality n-type $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ oxide superconducting thin films were successfully fabricated using pulsed laser deposition and N_2O reactive gas with T_c ($R=0\ \Omega$) of 22.4K and a transition width of 0.2K. The critical current density J_c is 8×10^5 A/cm^2 at 4.2K in zero magnetic field. The microwave surface resistance measured at 9.6 GHz shows a value of 3 mΩ at 4.2K in a 500 nm-thick NCCO film. The systematical study of the oxidation and reduction processes for various substrate temperature, atmosphere and annealing duration reveals the diffusive nature of oxygen reduction. Because of the superior quality, the superconducting NCCO films are suitable for a definitive study of intrinsic properties and potential applications involving n-type high Tc SuFET or other devices using both p- and n-type high-Tc superconductors.

V. ACKNOWLEDGEMENT

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