Deposition and reduction of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ superconducting thin films

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Superconducting thin films of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (NCCO) were grown at 720–820 °C by pulsed laser deposition in N_2O atmosphere. The reduction subsequent to the deposition was found to be critical, and was studied systematically for various temperature, atmosphere, and duration. An ac susceptibility technique was used to stringently characterize the film quality. Very high quality films were made with optimized reduction conditions which showed a $T_c(R=0)$ of 22.4 K, with a transition width of 0.2 K and a J_c (4.2 K) of $8\times10^5/cm^2$ at zero field. Microwave surface resistance R_s was measured at 9.6 GHz and a value of ~3 mΩ was obtained at 4.2 K in a 5000 Å thick NCCO film.

A study of the superconducting properties of the electron-doped oxide $Nd_{2-x}Ce_xCuO_{4-y}$ (NCCO) is important for understanding the mechanism of superconductivity in copper oxides. It is desirable to have high quality single-crystalline NCCO thin films for this purpose and therefore the fabrication of NCCO thin films has drawn considerable effort during the past years.[1-3] One critical parameter for making NCCO films is the control of the Ce concentration, since superconductivity occurs only in a very narrow concentration range at $x=0.15$.[4,5] As demonstrated by Gupta *et al.* pulsed laser deposition is a suitable technique in this respect since it reproduces the target composition in the films. Another critical parameter is the oxygen content:[2,6] certain reduction is necessary to achieve superconductivity in NCCO, while excessive reduction renders it transparent and nonsuperconducting. In this letter, we report our experimental results on the reduction process in NCCO thin films grown by pulsed laser deposition. A N_2O atmosphere was used during the deposition, which was pointed out by Kussmaul *et al.* to produce higher quality NCCO films than using O_2.[7] Our results show that the optimized reduction can be achieved at different temperatures with different durations, indicating the diffusive nature of the reduction process. As a result, we were able to produce very high quality epitaxial NCCO thin films with high T_c and sharp transition, high J_c and low microwave surface resistance.

The basic pulsed laser deposition technique has been described previously.[8] The pellet in this work was made from NCCO ceramic sample with $x=0.15$. Pellets with other Ce concentrations gave poorer film qualities. This is consistent with the results of bulk samples[4,5] indicating that the pellet composition is indeed preserved in the films. Single crystals of (100) $SrTiO_3$ and (100) $LaAlO_3$ were used as substrates, which gave similar superconducting properties while the difference in the lattice match ($a=3.905$ Å for $SrTiO_3$ and 3.793 Å for $LaAlO_3$ as compared to $a=3.946$ Å for NCCO) resulted in different morphologies. Mainly the results on $SrTiO_3$ are presented in this letter. The films were deposited in 200 mTorr N_2O at a deposition rate of 0.3 Å/pulse and a repetition rate of 10 Hz. The substrates were held at different temperatures from 720–820 °C. After the deposition, different procedures were taken to cool the films to room temperature. They included: (a) cooling directly in 200 mTorr N_2O, (b) cooling after evacuating the chamber to 10^{-5} Torr, and (c) holding the films at the deposition temperature in a vacuum of 10^{-5} Torr for different time periods before cooling down. The films reported in this letter had a thickness of 5000 Å and we found that different film thickness requires 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, similar to that described in Ref. 9.

Before we proceed to describe different reduction procedures, we plot in Fig. 1 the resistance R versus temperature T and ac susceptibility results for a film made under the optimum conditions. The film has a T_c ($R=0$) of 22.4 K with a transition width of 0.2 K. The ratio of room-temperature resistance to the residual resistance is over 6 with a residual resistivity of 80 $\mu\Omega$ cm. X-ray diffraction shows that the film is grown primarily with c-axis perpendicular to the substrate surface with a small fraction of (110) orientation. Rocking curve (ω scan) through the (006) planes of this sample gives a full width at half maximum (FWHM) of 0.4°, indicating a superior growth characterized by narrow mosaic distributions. Note that the zero resistance temperature corresponds to the onset of the transition in the ac susceptibility measurement. Since the ac susceptibility, particularly the imaginary part, provides a sensitive means to detect the inhomogeneities such as multiphases in the films,[10] the ac susceptibility measurement was adopted as the characterization technique for films made with different reduction procedures.

In Fig. 2, the imaginary part of the ac susceptibility is plotted for 5000 Å NCCO films which were deposited at different substrate temperatures and (a) cooled directly in 200 mTorr N_2O and (b) cooled after the deposition cham-

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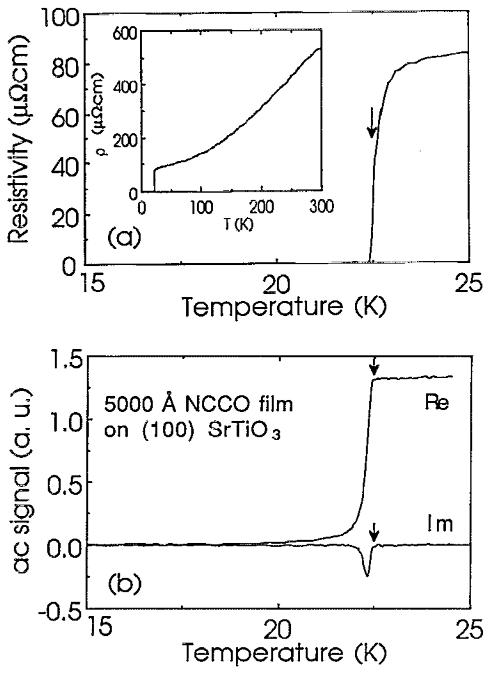

FIG. 1. (a) Resistance vs temperature and (b) ac susceptibility of a 5000 Å NCCO film on (100) $SrTiO_3$ substrate. Note that the zero resistance temperature (indicated by the arrows) corresponds to the onset in the ac susceptibility, which is a more stringent characterization of the film quality.

ber was evacuated at 10^{-5} Torr. Since the magnitude of the signal depends on the sample size the data are normalized and offset for the clarity of presentation. Surprisingly, the films cooled directly in N_2O are superconducting with T_c as high as 18 K [Fig. 2 (a)]. This is in sharp contrast to the films deposited in O_2 atmosphere where directly cooling in O_2 results in nonsuperconducting films. It indicates that a

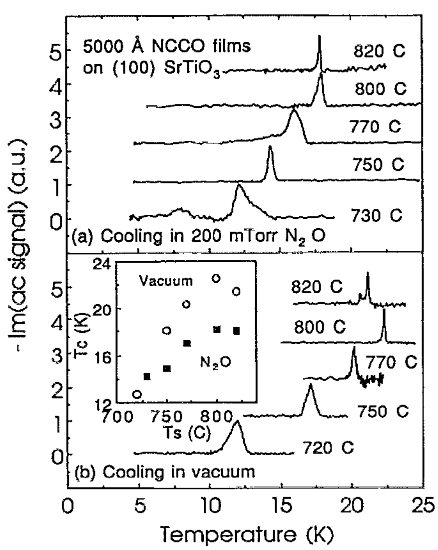

FIG. 2. Imaginary part of the ac susceptibility signal, normalized and offset for the clarity of presentation, for 5000 Å thick NCCO films deposited at different temperatures which were (a) cooled directly in 200 mTorr N_2O and (b) cooled after evacuating the chamber to 10^{-5} Torr. The insert shows T_c vs substrate temperature T_s for both N_2O and vacuum cooling.

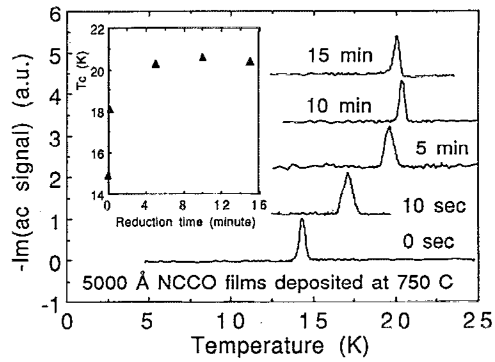

FIG. 3. Imaginary part of the ac susceptibility signal, normalized and offset, for 5000 Å thick films deposited at 750 °C followed by vacuum annealing at 10^{-5} Torr for different durations. The insert shows T_c vs reduction time.

certain amount of oxygen deficiency already exists in the films when they are deposited in N_2O. However, the reduction is not sufficient as T_c is low and cooling the films in vacuum further increases T_c as shown in Fig. 2 (b). The additional reduction may take place during the time the chamber was evacuated, which was ~10 s, and also when the film was cooled. In both N_2O and vacuum cooling, 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 temperatures. We attribute the temperature dependence primarily to the oxygen 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 and ununiform oxygen content in the films. It is also possible that local disorders develop with lowering 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] The optimized condition was obtained for 800 °C and vacuum cooling, which results in a high T_c and sharp transition as shown in Fig. 1.

The film quality can be also optimized through vacuum annealing for a longer period at low temperatures. Figure 3 shows the imaginary part of the ac signal 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 becomes higher and the transition gets sharper until an optimum is reached at ~10 min. The highest T_c thus obtained is lower than the best results probably due to the local disorders 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 diffusion of oxygen out of the films during the reduction. For given diffusion parameters, it takes longer time at low temperatures to achieve certain oxygen deficiency in the NCCO film than at high temperatures. A more detailed study on the diffusion of oxygen in NCCO films will be reported elsewhere.

For NCCO thin films, there tends to be a more uni-

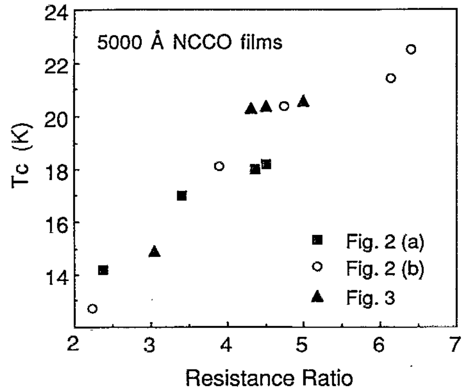

FIG. 4. T_c vs the resistance ratio for the samples from Figs. 2(a), 2(b), and 3. The three sets of data all overlap with each other, indicating that one single parameter controls the normal state and superconducting transport properties of these samples, likely the local oxygen content in the films.

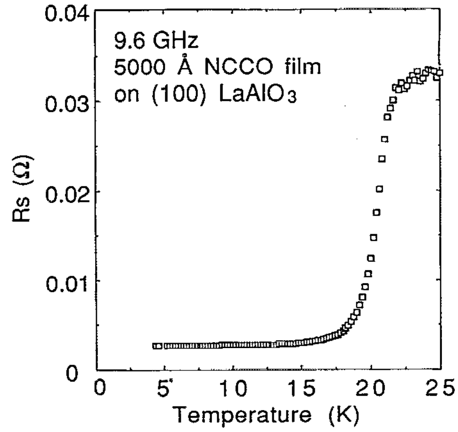

FIG. 5. Microwave surface resistance R_s vs temperature for a 5000 Å NCCO films on $LaAlO_3$ substrate measured at 9.6 GHz. A residual R_s value of ~ 3 mΩ was observed at $T=4.2$ K.

form distribution of the oxygen deficiency than in the bulk samples and single crystals. Therefore, a good correlation between T_c and resistance ratio could be established. In Fig. 4, T_c as a function of the resistance ratio is plotted for the samples of Figs. 2(a), 2(b), and 3, which were made under completely different reduction conditions. The three sets of data all overlap with each other, indicating that one single parameter controls the normal state and superconducting transport properties of these samples, which is 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 and hence a larger residual resistance and lower resistance ratio than in the films made at the optimum conditions, and on the other hand, it also results in a lower T_c and a broader or multiple transition in the film.

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.[2] At 4.2 K, a J_c value as high as 8×10^5 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. In Fig. 5, R_s as a function of T is shown for a 5000 Å NCCO film on $LaAlO_3$ substrate. A sharp drop in R_s is seen at T_c, unlike in poorer quality samples where multiple transitions are often found, and the residual surface resistance is ~ 3 mΩ. The good microwave property is a clear indication of a high crystalline quality and homogeneity of the superconducting properties in the sample. The R_s value is higher than that observed in $YBa_2Cu_3O_7$ thin films, probably due to some intrinsic inhomogeneities related to NCCO.

In conclusion, very high quality films were produced by fine control of the reduction process subsequent to the deposition of NCCO films by pulsed laser deposition. The systematic study shows that the reduction involves the diffusion of oxygen out of the films, which can be achieved at different temperatures and time periods. The superior quality thus obtained will allow a variety of fundamental and applied researches using NCCO superconducting thin films.

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