Structural characterization and microwave loss of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ superconducting thin films on yttria-stabilized zirconia buffered sapphire

S. N. Mao, X. X. Xi, Jian Mao, D. H. Wu, Qi Li, S. M. Anlage, and T. Venkatesan[a)]
Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742

D. Prasad Beesabathina, and L. Salamanca-Riba
Center for Superconductivity Research, Materials and Nuclear Engineering Department, University of Maryland, College Park, Maryland 20742

X. D. Wu
STC, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 19 October 1993; accepted for publication 16 November 1993)

We have grown superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (NCCO) thin films on $(1\bar{1}02)$ sapphire using a yttria-stabilized zirconia (YSZ) buffer layer, which has been demonstrated to be the best material for the growth of n-type superconducting NCCO thin films. The films are c-axis oriented, epitaxially grown with a small mosaic spread of 0.2° and a Rutherford backscattering spectroscopy channeling yield of ~9%. Cross-sectional transmission electron microscopy images reveal a sharp interface between NCCO and YSZ. The microwave surface resistance of NCCO films on YSZ buffered sapphire at 9.6 GHz is only 80 $\mu\Omega$ at 4.2 K in zero magnetic field, which is comparable to $Y_1Ba_2Cu_3O_{7-y}$ films at similar reduced temperature, as a consequence of the decrease of structural imperfection in the film. The temperature dependence of the surface resistance and magnetic penetration depth in these films further confirms the s-wave BCS nature of NCCO.

Sapphire is a favorable substrate for applications of high temperature superconducting thin films at high frequencies due to its low dielectric constant, good mechanical strength, and low loss tangent.[1–3] However, a suitable buffer layer is needed on the substrate to avoid interactions between sapphire and the cuprate thin films, as has been extensively explored with p-type $Y_1Ba_2Cu_3O_{7-y}$ (YBCO) thin films.[2–8] However, such systematic studies have not yet been performed in the n-type $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (NCCO) system, thereby limiting various important experiments on NCCO thin films, aimed at both practical applications such as microwave devices using superconducting p-n junctions,[9] and fundamental physics studies such as cyclotron resonance using infrared transmission for determining the sign of charge carriers and the physics of vortex dynamics in high T_c cuprates.[10] In this letter we report the fabrication of high quality NCCO films on sapphire by the use of a fluorite-type yttria-stabilized zirconia (YSZ) buffer layer.

It is well known that the buffer layer between the sapphire substrate and the high T_c films must be chemically stable at the deposition temperature for growing epitaxial thin films, and structurally matched with both sapphire and oxide superconductors.[2,3] $SrTiO_3$ (STO),[4] $LaAlO_3$ (LAO),[5] MgO,[7] YSZ,[2,6] $Pr_1Ba_2Cu_3O_{7-y}$ (PBCO),[8] and CeO_2[2] have been demonstrated to be good buffer layers for superconducting YBCO films grown on $(1\bar{1}02)$ sapphire. In this work, however, we have found that these results from YBCO cannot be directly extended to NCCO films. First, severe chemical reactions occur between NCCO and CeO_2 and MgO. Second, a considerable amount of a-axis NCCO growth occurs on PBCO or YBCO buffer layers. Third, the superconducting properties of the NCCO films on LAO, NGO, STO, and YSZ are also different, especially for thinner films, as discussed below. Therefore it is worth discussing the substrate effect on NCCO films before presenting the results on YSZ buffered sapphire.

Two different types of substrates were used to investigate the influence of lattice mismatch, interface chemical stability, and substrate physical properties on the transport and structural properties of the NCCO films. They are perovskite substrates such as (100) LAO, (100) $NdGaO_3$ (NGO), (100) STO, and fluorite substrate such as (100) YSZ. The difference in the lattice match and structure (a=3.793 Å for LAO, 3.85 Å for NGO, 3.905 Å for STO, and 5.14 Å for YSZ as compared to 3.94 Å for NCCO) resulted in different superconducting properties, especially for thinner films as discussed below. The NCCO films were made by pulsed-laser deposition in 200 mTorr N_2O reactive gas at 800 °C. Detailed descriptions of the deposition and reduction procedures and of various properties of our high quality films have been published elsewhere.[11–13] Generally, the superconducting transition temperatures for the thick films (>2000 Å) grown under optimized conditions are the same even for different substrates and only show slightly different transition widths. The normal state resistivity also varies slightly. However, the superconducting transition temperature (T_{c0}) of the films decreases significantly as the thickness of the films is reduced below 1000 Å. Figure 1 shows the best values of T_{c0} for 600 Å NCCO films grown on different substrates as a function of the misfit between the substrate and the film. It is clear that the T_{c0} of the films in all of the perovskite substrates is correlated with the lattice misfit. The difference betweem T_{c0}'s is resulted from strains caused by the lattice

---

[a)] Also at Department of Electrical Engineering, University of Maryland, College Park, Maryland 20742.

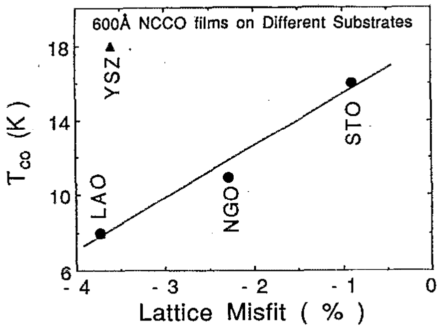

FIG. 1. The highest superconducting transition temperatures ($R=0\Omega$) for 600 Å NCCO films grown on different substrates as a function of lattice misfit $[(a_{\mathrm{film}}-a_{\mathrm{sub}})/a_{\mathrm{sub}}]$ between substrate and film. For YSZ substrate the misfit is obtained after correcting for the Nd(Ce)ZrCuO intermediate layer as discussed in Ref. 13. The solid line is to guide the eye.

mismatch and it is seen that larger the compressive strain, the smaller the value of T_{c0}.[13] On the other hand, the films grown on YSZ show the highest T_{c0} even though the lattice mismatch is as large as LAO. The differences between LAO and YSZ substrates can be attributed to different film-substrate atomic structure at the interface. Namely, in the case of a fluorite-type structure (YSZ), a one-to-one correspondence of oxygen atoms is possible across the substrate-NCCO interface since {001} planes containing only oxygen atoms are common along the growth direction in both materials. This configuration also satisfies the condition of interfacial charge neutrality and minimum energy. In contrast, none of the {001} planes of NCCO have as good a fit with the {001} planes of perovskite LAO or STO substrates with respect to charge neutrality.[13] The charge imbalances at the interface could create strains and/or strain-induced distortions that extend far into the film and decrease T_{c0}.

The YSZ buffer layer, which is identified above as the best candidate for NCCO growth, was epitaxially grown on $(1\bar{1}02)$ sapphire at optimal conditions for depositing the NCCO layer to reduce any possible contamination and also to be compatible with multilayer processing. The NCCO layer was subsequently *in situ* deposited. Grains with (111) orientation appeared in the YSZ layer at lower ambient pressure of N_2O, similar to the case of using O_2.[2] A typical x-ray θ-2θ spectrum of NCCO films on YSZ buffer layer on a sapphire substrate is very similar to that of NCCO on bare YSZ substrates.[13] The film is aligned with the c axis perpendicular to the surface of (1102) sapphire, with a small variation of ~0.2° as measured by rocking curve scan. X-ray ϕ scans and cross-sectional transmission electron microscopy (TEM) revealed the in-plane epitaxial relationship to be (110)NCCO//(001)YSZ, i.e., the NCCO film is rotated by 45° with respect to YSZ. Four clean peaks in the x-ray ϕ-scan spectrum indicate that the NCCO film on the YSZ buffer is of single domain in contrast to the case of YBCO on YSZ, where multiple-in-plane orientations exist.[14] High resolution TEM shows that the NCCO films do not contain any stacking faults and the interface between NCCO and YSZ is quite sharp, similar to the case of NCCO on YSZ substrates.[13] Similar concentrations of insulating $Ce_{0.5}Nd_{0.5}O_{1.75}$(CNO) grains still exist in films grown on YSZ compared to films grown on LAO.[13,15] The best Rutherford backscattering spectroscopy (RBS) channeling yield of ~9% was observed from the film grown on YSZ/sapphire, whereas a higher value of 24% was obtained for the film grown on LAO substrate, which is also microwave compatible.

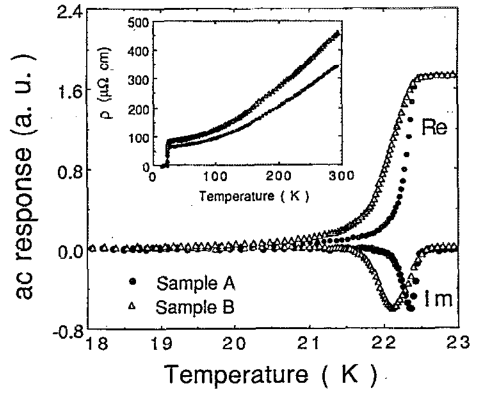

FIG. 2. ac susceptibility and dc resistivity measurements for 3000 Å NCCO films on YSZ buffered sapphire (sample A). The results on 5000 Å NCCO film on LAO substrate (sample B) is also presented for comparison. The dc resistivity before superconducting transition are 60 and 85 $\mu\Omega$ cm for samples A and B, respectively.

The transport properties were measured by standard dc resistive and ac inductive methods[11,12] as shown in Fig. 2 for a 3000 Å film grown on a YSZ buffered sapphire (sample A). The sharp transition width of 0.2 K obtained from the ac susceptibility and the low residual dc resistivity of 60 $\mu\Omega$ cm at 25 K indicate a high degree of homogeneity and purity. A comparison of these results with the ones obtained from the films grown on LAO substrates (sample B) shows the importance of the choice of the right substrate and/or buffer layer for NCCO films.

The most stringent evaluation of the quality of superconducting thin films is surface resistance (R_s).[11] Figure 3 shows the microwave loss at 9.6 GHz measured on sample A(NCCO/YSZ/sapphire) and sample B(NCCO/LAO) using a Nb cavity which has the resolution of $\sim 10\ \mu\Omega$.[16] It should

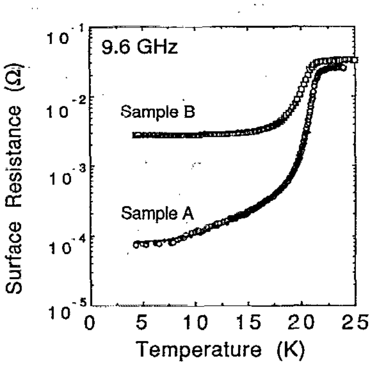

FIG. 3. Microwave surface resistance R_s at 9.6 GHz vs temperature for samples A and B. A residual R_{s0} value of $\sim 80\ \mu\Omega$ was observed at $T=4.2$ K for sample A, the value comprable to that of YBCO at the same reduced temperature. The measurement on sample B shows very high residual R_{s0} of 2500 $\mu\Omega$ cm. The solid lines are the best fit using BCS formula $R_s = CT^{-1}\exp(-\Delta(T)/KT)+R_{s0}$ with $2\Delta(0)/KT_c=4.1$ (Ref. 23).

be mentioned that all the samples used for microwave measurements in this work are as-fabricated, without any surface post-treatment. The surface resistance of the sample A at 4.2 K and in zero external magnetic field is only 80 $\mu\Omega$ which is close to the best values of YBCO films,[17,18] whereas the sample B shows much higher microwave loss of 2.5 mΩ at the same temperature. Since both samples A and B had the same concentration of insulating CNO phase the higher value of R_s in sample B is not the result of the impurity phase. The mosaic spread of c-axis grains for these two samples is the same ($\sim$0.4° by rocking curve measurement), and the in-plane orientation is also locked with respect to the YSZ layer (by x ray ϕ scan),[13] so the grain boundary effect (weak link)[18] is not the dominant factor responsible for the microwave losses in samples A and B. The main structural difference between samples A and B is the lattice perfection, indicated by the RBS channeling yields[19] of 9% and 24% for samples A and B, respectively, due to misfits and charge balance effect as discussed earlier. Although the origin of the residual losses in the microwave measurement, both intrinsic and extrinsic, in HTS is still unclear, the difference of R_s between samples A and B is speculated to be largely due to disordering of both Ce^{4+} and O^{2-} ions. This distributed local atom disordering[18] increases scattering of normal carriers which consequently increases the normal state resistivity and the residual resistivity as shown in Fig. ^{4}. The higher residual resistivity leads to the higher microwave surface resistance which is consistent with results on conventional superconductors like Nb[20] and also with that of p-type YBCO films,[18] but in contrast with results on very clean YBCO single crystals.[21]

The fact that the residual microwave losses in NCCO films have been substantially reduced with only modest effort by increasing the lattice perfection using the right substrate suggests that NCCO, with a relatively long coherence length of 80 Å, may become a promising low-loss high temperature oxide superconductor in future microwave applications. It also should be mentioned that in previous work we observed an s-wave BCS-type behavior from the penetration depth (frequency shift) measurement using sample B although with very high residual R_s.[16] With the observation, Lee has pointed out that a d-wave superconductor may exhibit an activated exponential behavior if the sample contains a large degree of disorder, and further questioned our observations of s-wave behavior on the NCCO because it showed a high residual R_s.[22] Interestingly, with the sample A of which the residual R_s is two orders of magnitude lower than that of sample B, we have observed the same exponential behavior in the temperature dependent penetration depth with the same reduced energy gap value of $2\Delta(0)/kT_c=4.1$.[23] Further, as can be seen in Fig. 3, the temperature dependence of R_s both for samples A and B is also consistent with the BCS s-wave behavior. This indicates that the activated behavior is not sensitive to disorder, implying the NCCO is more like a conventional s-wave BCS superconductor.

To summarize, high quality NCCO superconducting thin films with low microwave surface resistance of 80 $\mu\Omega$ at 4.2 K were made on sapphire using YSZ buffer layer. The fluorite-type substrate or buffer layer is favorable for the growth of NCCO film, giving better structural and superconducting properties. The exponential temperature dependence of both surface resistance and penetration depth in films with very different residual surface resistance by near two orders of magnitude indicates the insensitiveness of the thermal activation of quasiparticles to the disorder in the film.

The authors would like to thank Professor D. Drew and Professor R. L. Greene for useful discussions and Dr. J. L. Peng for the preparation of the target. Very helpful interactions with M. Pambianchi, E. Choi, F. Dunmore, Wu Jiang, and M. Rajeswari are also appreciated. L. S.-R. acknowledges support from the National Science Foundation under Grant No. DMR-9020304. S.M.A. acknowledges support by NSF through NYI Grant No. (DMR-9258183) and NSF DMR-9123198.

[1] R. W. Simon, Proc. SPIE **1187**, 1 (1989).
[2] X. D. Wu *et al.*, Appl. Phys. Lett. **58**, 304 (1991).
[3] X. D. Wu, R. C. Dye, R. E. Muenchausen, S. R. Foltyn, M. Maley, A. D. Rollett, A. R. Garcia, and N. S. Nogar, Appl. Phys. Lett. **58**, 2165 (1991).
[4] J. J. Kingston, F. C. Wellstood, P. Lerch, A. H. Miklich, and J. Clark, Appl. Phys. Lett. **56**, 189 (1990).
[5] A. E. Lee, C. E. Platt J. F. Burch, R. W. Simon, J. P. Goral, and M. M. Al-Jassim, Appl. Phys. Lett. **57**, 2019 (1990).
[6] D. K. Fork, D. B. Fenner, R. W. Barton, J. M. Phillips, G. A. N. Connel, J. B. Boyce, and T. Geballe, Appl. Phys. Lett. **57**, 1161 (1990).
[7] A. B. Berezin, C. W. Yuan, and A. L. de Lozanne, Appl. Phys. Lett. **57**, 90 (1990).
[8] C. T. Roger, A. Inam, M. S. Hedge, B. Dutta, X. D. Wu, and T. Venkatesan, Appl. Phys. Lett. **55**, 2032 (1989).
[9] S. N. Mao *et al.*, Appl. Phys. Lett. **62**, 2425 (1993).
[10] K. Karrai, E. Choi, F. Dunmore, S. Liu, X. Ying, Qi Li, T. Venkatesan, H. D. Drew, Q. Li, and D. B. Fenner, Phys. Rev. Lett. **69**, 355 (1992).
[11] S. N. Mao *et al.*, Appl. Phys. Lett. **61**, 2365 (1992).
[12] S. N. Mao *et al.*, IEEE Trans. Appl. Supercond. **3**, 1552 (1993).
[13] S. N. Mao, X. X. Xi, Qi Li, T. Venkatesan, D. Prasad Beesabathina, L. Salamanca-Riba, and X. D. Wu, J. Appl. Phys. (to be published).
[14] D. K. Fork, S. M. Garrison, M. Hayley, and T. H. Geballe, J. Mater. Res. **7**, 1641 (1992).
[15] D. P. Beesabathina, L. Salamanca-Riba, S. N. Mao, X. X. Xi, and T. Venkatesan, Appl. Phys. Lett. **62**, 3022 (1993).
[16] D. H. Wu, J. Mao, S. N. Mao, J. L. Peng, X. X. Xi, T. Venkatesan, R. L. Green, and S. M. Anlage, Phys. Rev. Lett. **70**, 80 (1993).
[17] N. Newman, K. Char, S. M. Garrison, R. W. Barton, R. C. Taber, C. B. Eom, T. H. Geballe, and B. Wilkens, Appl. Phys. Lett. **57**, 520 (1990).
[18] S. S. Laderman *et al.*, Phys. Rev. B **43**, 2922 (1991).
[19] J. A. Davies, *Channeling: Theory, Observation and Applications*, edited by D. V. Morgan (Wiley–Interscience, New York, 1973), Chap. VIII, p. 330.
[20] J. P. Turneaure and I. Weissman, J. Appl. Phys. **39**, 4417 (1968); T. Van Duzer and C. W. Turner, *Principles of Superconductor Devices and Circuits* (Elsevier, New York, 1981), p. 137.
[21] K. Zhang, D. A. Bonn, R. Liang, D. J. Baar, and W. N. Hardy, Appl. Phys. Lett. **62**, 3019 (1993).
[22] Patrick A. Lee, Phys. Rev. Lett. **71**, 1887 (1993).
[23] S. M. Anlage, D. H. Wu, J. Mao, S. N. Mao, J. L. Peng, X. X. Xi, T. Venkatesan, R. L. Greene (unpublished).