## Heteroepitaxial Growth of Strained Multilayer Superconducting Thin Films of Nd<sub>1.83</sub>Ce<sub>0.17</sub>CuO<sub>x</sub>/YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>

A. Gupta, R. Gross, E. Olsson, A. Segmüller, G. Koren, and C. C. Tsuei IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598 (Received 18 December 1989)

Heteroepitaxial growth of strained multilayer thin films of  $YBa_2Cu_3O_{7-\delta}/Nd_{1.83}Ce_{0.17}CuO_x$  by pulsed-laser deposition is reported. The coherency strain results in biaxial compression of the tetragonal  $Nd_{1.83}Ce_{0.17}CuO_x$  layers, whereas the biaxial tension in the  $YBa_2Cu_3O_{7-\delta}$  layers removes the orthorhombic distortion and makes the unit cell isotropic in the basal plane (a=b). Depending on their oxygen content, either the  $YBa_2Cu_3O_{7-\delta}$  or the  $Nd_{1.83}Ce_{0.17}CuO_x$  layers are superconducting in these multilayers. The strain-induced structural modification has a significant influence on the superconducting transition temperature of the  $YBa_2Cu_3O_{7-\delta}$  layers.

PACS numbers: 74.70.Jm, 74.70.Vy, 74.75.+t

The common structural feature of all the copper oxide superconductors is the presence of CuO<sub>2</sub> sheets which are believed to be essential for the occurrence of superconductivity in these systems. A consequence of the presence of these sheets is that the lattice constants in the basal plane (a and b) are quite similar in the different copper oxide systems. This offers the possibility of heteroepitaxial growth of multilayer structures of two different copper oxides, as has been recently demonstrated in the  $RBa_2Cu_3O_{7-\delta}$  (*R* = rare earth) system.<sup>1</sup> In this case, the two different rare-earth copper oxides (Y/Dy, Y/Pr) in the multilayers have the same orthorhombic unit cell, with very similar lattice constants, and the strain is easily accommodated without formation of defects. It is well known in the heteroepitaxial growth of semiconductor multilayers that significantly larger misfits can be coherently accommodated below a critical layer thickness. Here, the layers with the larger lattice undergo a biaxial compression, while those with the smaller lattice experience a biaxial tension.<sup>2-4</sup> The strain-induced structural modifications can significantly influence the electronic and optical properties of the semiconductors<sup>4</sup> and has been a field of very active research over the last few years. The high- $T_c$  superconductors show wide variation in properties with subtle structural and chemical changes. The growth of strained multilayers thus provides an opportunity to artificially tailor the properties of these materials.

In this Letter we report for the first time the growth of strained multilayer thin films of the hole-doped superconductor,  $YBa_2Cu_3O_{7-\delta}$  (YBCO), and the electrondoped superconductor,  $Nd_{1.83}Ce_{0.17}CuO_x$  (NCCO),<sup>5</sup> on (100) SrTiO<sub>3</sub> substrates.

The Nd<sub>1.83</sub>Ce<sub>0.17</sub>CuO<sub>x</sub>( $x = 4 + \delta'$ )/YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> multilayers were prepared by sequential deposition from separate ceramic targets of NCCO and YBCO using the pulsed-laser deposition technique<sup>6-8</sup> (KrF excimer laser, 248-nm wavelength). The films, starting with NCCO and ending with YBCO in the multilayer structure, were deposited on optically polished (100) SrTiO<sub>3</sub> substrates at 730 °C in 200 mTorr of oxygen. The number of pulses used for ablation from each target was adjusted to deposit alternating layers of thickness (*t* NCCO) and (*t* 

YBCO). The process was repeated for N cycles and the resulting multilayers are designated as  $(t \text{ NCCO})/(t \text{ YBCO}) \times N$ . At the end of the deposition cycle, the films were cooled in different concentrations of oxygen to control the oxygen stoichiometry in the two oxide layers. To fully oxygenate the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> layers ( $\delta \sim 0$ ), the films were cooled slowly in 700 Torr oxygen with a dwell time of 0.5 h at 400 °C.<sup>7</sup> On the other hand, to make the Nd<sub>1.83</sub>Ce<sub>0.17</sub>CuO<sub>x</sub> layers superconducting ( $x \sim 3.96$ ), the films were annealed at the deposition temperature under vacuum (10<sup>-5</sup> Torr) for 10-15 min and then slowly cooled down to room temperature.<sup>8</sup> By cooling the films under intermediate oxygen pressures, the oxygen stoichiometry in the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> layers could be adjusted anywhere between 6.0 and 7.0.

Figure 1 shows a cross-section TEM micrograph of a NCCO/YBCO multilayer film in which the different layers can be clearly distinguished because of the high atomic-number contrast between the layers. It is seen that the two oxides grow heteroepitaxially with their basal planes parallel to each other and also parallel to



FIG. 1. Cross-section TEM micrograph of a (100 Å NCCO)/(50 Å YBCO) multilayer film showing that the layers are well defined over large length scales. The NCCO layers (dark bands) and the YBCO layers (light bands) are indicated in the figure. Inset: Sharpness of the interfaces between the layers.

the (100)  $SrTiO_3$  substrate. The images of individual layers within the two copper oxide materials are apparent in the micrograph (see inset in Fig. 1) and the interface between the oxide layers is observed to be sharp to within an unit cell. The multilayer structure is essentially free of major defects except for a few isolated regions where the YBCO locally extends into the NCCO layers. Defects which are believed to be stacking faults are also observed in a few regions in both layers. Auger analysis with argon-ion sputtering was performed to verify the composition modulation over relatively larger areas of the films. The periodic modulation in composition with depth was clearly observed for films with layer thicknesses down to 50 Å.

The multilayer structures were characterized in directions parallel to the interface using grazing-incidence xray diffraction (GID),<sup>9</sup> whereas normal Bragg-reflection geometry was used for probing the structure in the perpendicular direction. Figure 2 shows GID  $\theta$ -2 $\theta$ diffraction patterns for (a) (200 Å NCCO)/(200 Å YBCO) × 5 and (b) (400 Å NCCO)/(400 Å YBCO) × 5 multilayers. The data in Fig. 2(a) show only one diffraction line for all orders indicating that the individual layers are below the critical thickness and most of the misfit between the NCCO (I) and YBCO (II) layers is accommodated by strain [the broadening of the (400) peak suggests some relaxation]. The data in Fig. 2(b) show splitting of the higher orders into the lines of the component layers (I) and (II). [The (300) reflection for the NCCO layers is forbidden due to the body-centered tetragonal structure.] This indicates that the individual layers are above the critical thickness and the misfit strain between the two oxides is relaxed resulting in the formation of misfit dislocations. The normal Braggreflection patterns for the two films showed only the (001) peaks of the respective oxides, thus confirming their *c*-axis normal orientations. Weak satellites of the (001) and (002) reflections, characteristic of periodic chemical modulation, were observed for multilayers with smaller layer thicknesses of around 50 Å. The c-axis lattice constants in the (400 Å NCCO)/(400 Å YBCO)×5 multilayer film were calculated to be 11.68 and 12.08 Å for the YBCO and NCCO layers, respectively, which are close to the known values for these oxides. The lattice constants for the (200 Å NCCO)/(200 Å YBCO)×5 film were calculated to be 11.61 Å for the YBCO layers and 12.12 Å for the NCCO layers. Since this film is coherently strained, the in-plane strain causes a strain in the perpendicular c-axis direction which is tensile for the NCCO layers and compressive for the YBCO layers. This results in a contraction of the c axis for the YBCO layers and an expansion for the NCCO layers as compared to their relaxed values.

The in-plane lattice constants of NCCO ( $a=b\approx3.94$ Å) are larger than those of YBCO ( $a\approx3.83$  Å,  $b\approx3.88$ Å for  $\delta\sim0$ ) resulting in lattice mismatch of about 2.8% and 1.5% in the *a*- and *b*-axis directions, respectively. If



FIG. 2. GID  $\theta$ -2 $\theta$  scan data for (a) (200 Å NCCO (I))/ (200 Å YBCO (II))×5 and (b) (400 Å NCCO (I))/(400 Å YBCO (II))×5 multilayer films on (100) SrTiO<sub>3</sub> substrates prepared by cooling in 700 Torr O<sub>2</sub>.

the strain is symmetrically distributed between the two layers,<sup>4</sup> then for a multilayer film with equal thicknesses of each layer, an average in-plane lattice constant of 3.88 Å will minimize the strain energy in both layers assuming similar elastic properties for both the oxides. This is indeed what is found in the (200 Å NCCO)/(200 Å **YBCO**) $\times$ 5 film in Fig. 2(a). Strain symmetrization was also observed when the relative thicknesses of the layers were changed in the multilayer films. For example, the in-plane lattice constants increased to 3.90 Å for a (200 Å NCCO)/(100 Å YBCO)×5 film, and further to 3.92 Å for a (200 Å NCCO)/(50 Å YBCO)×5 film. Using the average elastic constants for YBCO (Young's modulus = 1500 kbar, Poisson's ratio = 0.25), the biaxial stress resulting from a 2% lattice mismatch is calculated to be 40 kbar.

Figure 3 shows the resistivity (calculated using the total thickness of the film) as a function of temperature for three multilayers with different YBCO and NCCO layer thicknesses. The films were prepared by slow cooling in 700 Torr of oxygen. The resistivity versus temperature curves for single-layer films of YBCO and NCCO, prepared under the same conditions, are also shown for comparison. The YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> ( $\delta$ ~0) [Fig. 3(a)] exhibits metallic behavior in the normal state and has a sharp superconducting transition with zero-resistance temperature of 92.5 K. The Nd<sub>183</sub>Ce<sub>0.17</sub>CuO<sub>x</sub> film [Fig. 3(b)] has excess oxygen, and although it shows an initial decrease in resistivity on cooling, localization sets in at lower temperatures with no evidence of superconductivity down to 5 K.<sup>8</sup> The (50 Å NCCO)/(50 Å YBCO) ×20 multilayer film [Fig. 3(c)] shows metallic behavior in the normal state with somewhat higher normal-state resistivity values than a single-layer YBCO film, as would be expected for a parallel resistive network of NCCO and YBCO layers. The film has a sharp super-

conducting transition (< 1 K), with somewhat lower onset and zero-resistance (89 K) temperatures than the single-layer YBCO film. We attribute this to the biaxial strain in the YBCO layers which expands the in-plane lattice and removes the orthorhombic distortion. A similar reduction in transition temperature has been observed by Kamigaki et al. for a 100-Å-thick YBCO film deposited on (100) SrTiO<sub>3</sub>,<sup>10</sup> which we believe is also due to elastic strain. By increasing the strain in the YBCO layers, which is achieved by decreasing the relative thickness of the YBCO layers with respect to the NCCO layers, the normal-state resistivity increases further and the superconducting onset and zero-resistance temperatures shift to even lower values as seen in Figs. 3(d) and 3(e). While the (200 Å NCCO)/(100 Å YBCO)×5 multilayer in Fig. 3(d) shows metallic behavior in the normal state and a relatively sharp transition  $[T_c(R=0)=84]$ K], the behavior changes significantly for the (200 Å NCCO)/(50 Å YBCO)×5 multilayer film [Fig. 3(e)]. The normal-state resistivity of this film is significantly higher than the other multilayers and is nonmetallic, with a broad superconducting transition  $[T_c(R=0)=30]$ K]. Interfacial disorder or intermixing may be partly responsible for this broadening. However, it should be noted that the film with similar YBCO layer thickness (but with lower strain) exhibits a much sharper transition [Fig. 3(c)]. The decrease in transition temperature was very similar for different strained multilayers with the same relative layer thicknesses [e.g., (200 Å NCCO)/(100 Å YBCO)×5 and (100 Å NCCO)/(50 Å YBCO) $\times$ 10], and the transition temperature returned back to above 90 K in the thicker multilayers where the strain was relaxed. This provides additional evidence that the observed changes in the transition temperature are primarily related to strain in the YBCO layers.

A reduction in transition temperature due to the proximity effect is not expected because of the very short



FIG. 3. Resistivity vs temperature of (a) 1000 Å YBCO, (b) 1000 Å NCCO, (c) (50 Å NCCO)/(50 Å YBCO)×20, (d) (200 Å NCCO)/(100 Å YBCO)×5, and (e) (200 Å NCCO)/(50 Å YBCO)×5 films. Note that the resistivity scale for the film in (e) is  $\times$ 5 the ordinate scale.

coherence length in these materials along the c-axis direction. The application of hydrostatic pressure is known to increase the superconducting transition temperature of YBCO.<sup>11</sup> A decrease in the transition temperature with expansion of the lattice is, therefore, to be expected. However, because of the highly anisotropic nature of the copper oxide superconductors, the biaxial stress resulting from coherency strain in the layers would not necessarily have the same effect on the superconducting properties as the application of isotropic pressure. Indeed, the observed decrease in transition temperature is significantly larger than what would be predicted on the basis of results obtained from hydrostatic-pressure experiments.<sup>11</sup> A large anisotropy in the pressure dependence of  $T_c$ , for pressure applied parallel and perpendicular to the CuO<sub>2</sub> planes, has been predicted by Marsiglio and Hirsch<sup>12</sup> on the basis of their hole-pairing mechanism of superconductivity. Strain-induced structural modification has previously been observed in superconducting Mo-V superlattices with short modulation wavelength of the layers, and has been correlated with the anomalously sharp drop in transition temperature observed for the coherently strained layers.<sup>13</sup> For the NCCO/YBCO multilayers, small changes in stoichiometry or ordering of the oxygen in the lattice, in the presence of strain, could also lead to a decrease in the transition temperature. Despite the decrease in the transition temperature, the multilayers can sustain high critical currents, which in some cases are higher than the values observed for single-layer YBCO films. Critical current density as high as  $10^{7}$  A/cm<sup>2</sup> at 77 K in zero magnetic field has been obtained by direct transport measurements. Details, along with the current-voltage characteristics, will be discussed in a separate publication.<sup>14</sup>

The transition temperature of the multilayers also varies with oxygen content, as shown in Fig. 4 for three (200 Å NCCO)/(200 Å YBCO)×5 films cooled under different oxygen pressure after deposition. In the film which is cooled in 700 Torr  $O_2$  [Fig. 4(a)], the YBCO layers are superconducting and the resistivity behavior is very similar to the film in Fig. 3(c), with almost identical superconducting onset and zero-resistance temperatures. A similarly deposited film when annealed and cooled in vacuum, instead of in O<sub>2</sub>, shows a resistive transition at a much lower temperature (10 K) due to superconductivity in the NCCO layers [Fig. 4(c)]. This was confirmed by depositing a NCCO film under similar conditions, whose resistivity showed much the same behavior and also a superconducting transition temperature of 10 K. The compressive strain in the NCCO layers in the multilayers does not seem to have a significant influence on its transition temperature, similar to what has been observed by the application of hydrostatic pressure.<sup>15</sup> The YBCO layers, prepared under the reducing conditions required to make the NCCO layers superconducting, would lose all the oxygen in the chains and be nonsuperconducting. Under partly reducing conditions some of



FIG. 4. Resistivity vs temperature of (200 Å NCCO)/(200 Å YBCO)×5 films cooled under different oxygen pressures: (a) 700 Torr, (b) 10 mTorr, (c) < 0.01 mTorr.

the chain oxygen can be retained and the multilayers show interesting behavior under such conditions. The temperature dependence of the normal-state resistivity of a multilayer film cooled in 10 mTorr O<sub>2</sub> [Fig. 4(b)] shows characteristics in between those of the films in Figs. 4(a) and 4(c), and also has a relatively sharp superconducting transition at an intermediate temperature  $[T_c(R=0)=46 \text{ K}]$ . Films of NCCO and YBCO (1000 Å) prepared under identical conditions are, however, not superconducting and show localization behavior at temperatures below 100 K. Strain-induced perturbations in the electronic or phonon properties may be responsible for the observed superconductivity in the multilayer film which is close to the superconducting phase boundary. Indeed, hydrostatic-pressure studies on  $EuBa_2Cu_3O_{7-\delta}$ have shown significantly larger pressure effects on the oxygen-deficient phases as compared to the 90-K phase.<sup>16</sup> It is also possible that superconductivity is induced due to subtle changes in the oxygen stoichiometry or ordering when the two oxides, with different affinities for oxygen, are layered together.

In conclusion, we have shown that it is possible to heteroepitaxially grow strained multilayer films of structurally different copper oxide superconductors  $(Nd_{1.83}Ce_{0.17}CuO_x \text{ and } YBa_2Cu_3O_{7-\delta})$ . Depending on oxygen concentration, either the YBCO or the NCCO layers can be made superconducting in these films. The coherency strain removes the orthorhombic distortion in the YBCO layers, and the lattice parameters in the basal plane can be changed by varying the relative thicknesses of the two oxides. The biaxial expansion of the YBCO layers has been observed to have a more pronounced effect on its transition temperature than the application of isotropic pressure. On the other hand, the biaxial compression does not have a significant influence on the transition temperature of the NCCO layers. Straininduced changes in oxygen stoichiometry, or increased structural disorder with decreasing layer thicknesses may be responsible for some of the observed behavior.

We are grateful to R. G. Schad for the Auger analysis. We also thank C. C. Chi, D. R. Clarke, A. Kleinsasser, F. Legoues, T. M. Shaw, and E. Spiller for helpful discussions. This work was supported in part by the U.S. Department of Advanced Projects Agency under Contract No. N00014-89-C-0112, and the Swedish Board for Technical Development.

<sup>1</sup>J.-M. Triscone, M. G. Karkut, L. Antognazza, O. Brunner, and  $\emptyset$ . Fischer, Phys. Rev. Lett. **63**, 1016 (1989); C. T. Rogers, A. Inam, M. S. Hegde, B. Dutta, X. D. Wu, and T. Venkatesan, Appl. Phys. Lett. **55**, 2032 (1989).

<sup>2</sup>J. W. Matthews and A. E. Blakeslee, J. Cryst. Growth 27, 118 (1974).

<sup>3</sup>D. B. McWhan, in *Synthetically Modulated Structures*, edited by L. L. Chang and B. C. Giessen (Academic, Orlando, FL, 1985), pp. 43-74.

<sup>4</sup>E. Kasper, in *Physics and Applications of Quantum Wells and Superlattices*, edited by E. E. Mendez and K. von Klitzing, NATO Advanced Study Institutes Ser. B, Vol. 170 (Plenum, New York, 1987), pp. 101–131.

<sup>5</sup>H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989); Y. Tokura, H. Takagi, and S. Uchida, Nature (London) **337**, 345 (1989).

<sup>6</sup>A. Inam, M. S. Hegde, X. D. Wu, T. Venkatesan, P. England, P. F. Miceli, E. W. Chase, C. C. Chang, J. M. Tarascon, and J. B. Wachtman, Appl. Phys. Lett. **53**, 908 (1988); B. Roas, L. Schultz, and G. Endres, Appl. Phys. Lett. **53**, 1557 (1988); J. Fröhlingsdorf, W. Zander, and B. Stritzker, Solid State Commun. **67**, 965 (1988).

<sup>7</sup>G. Koren, A. Gupta, E. A. Giess, A. Segmüller, and R. B. Laibowitz, Appl. Phys. Lett. **54**, 1054 (1989).

<sup>8</sup>A. Gupta, G. Koren, C. C. Tsuei, A. Segmüller, and T. R. McGuire, Appl. Phys. Lett. **55**, 1795 (1989).

<sup>9</sup>A. Segmüller, Thin Solid Films 154, 33 (1987).

<sup>10</sup>K. Kamigaki, H. Terauchi, T. Tereshima, Y. Bando, K. Iijima, K. Yamamoto, and K. Hirata, Physica (Amsterdam) **159**C, 505 (1989).

<sup>11</sup>H. A. Borges, R. Kwok, J. D. Thompson, G. L. Wells, J. L. Smith, Z. Fisk, and D. E. Peterson, Phys. Rev. B **36**, 2404 (1987); R. Griessen, Phys. Rev. B **36**, 5284 (1987); M. W. McElfresh, M. B. Maple, K. N. Yang, and Z. Fisk, Appl. Phys. A **45**, 365 (1988).

<sup>12</sup>F. Marsiglio and J. E. Hirsch, Physica (Amsterdam) **162-164C**, 1451 (1989).

<sup>13</sup>J.-M. Triscone, D. Ariosa, M. G. Karkut, and Ø. Fischer, Phys. Rev. B 35, 3238 (1987).

<sup>14</sup>R. Gross, A. Gupta, E. Olsson, A. Segmüller, and G. Koren (to be published).

<sup>15</sup>C. Murayama, N. Mori, S. Yomo, H. Takagi, S. Uchida, and Y. Tokura, Nature (London) **339**, 293 (1989); C. L. Seaman, N. Y. Ayoub, T. Bjørnholm, E. A. Early, S. Ghamaty, B. W. Lee, J. T. Market, J. J. Neumeier, P. K. Tsai, and M. B. Maple, Physica (Amsterdam) **159C**, 391 (1989).

<sup>16</sup>C. W. Chu, Z. J. Huang, R. L. Meng, L. Gao, and P. H. Hor, Phys. Rev. B **37**, 9730 (1988).



FIG. 1. Cross-section TEM micrograph of a (100 Å NCCO)/(50 Å YBCO) multilayer film showing that the layers are well defined over large length scales. The NCCO layers (dark bands) and the YBCO layers (light bands) are indicated in the figure. Inset: Sharpness of the interfaces between the layers.