Absence of $\frac{1}{8}$ anomaly in strained thin films of $La_{2-x}Ba_xCuO_{4+\delta}$

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Compressive and expansive strain was induced into $La_{2-x}Ba_xCuO_{4+\delta}$ thin films with $x=0-0.35$ on $LaSrAlO_4$ and $SrTiO_3$ substrates, respectively. For the compressed films, the superconducting transition temperature (T_c) reached 44 K with $\delta\sim 0$ and 49 K with $\delta>0$, and the T_c-x phase diagram did not show a local minimum at $x\sim 0.125$, the so-called ''$\frac{1}{8}$ anomaly.'' For the expanded films, we observed strong reduction of T_c. We suggest that the absence of the ''$\frac{1}{8}$ anomaly'' in the compressed films is due to the *c*-axis expansion, as well as the in-plane compression, and suppression of the residual resistivity.

Since the discovery of high-temperature superconductivity in $La_{2-x}Ba_xCuO_{4+\delta}$ (LBCO),[1,2] this material has been extensively investigated[3–16] to clarify the correlation between superconductivity and crystal structure. In LBCO, a reduction of the superconducting transition temperature (T_c) is observed for the barium composition $x\sim 0.125$ ($\frac{1}{8}$),[3] where the low-temperature tetragonal (LTT) phase appears below 60 K.[4] It has been reported that application of hydrostatic pressures extinguishes the LTT phase[5] and restores the superconductivity in bulk ceramic samples of LBCO.[5–10] But the recovery of T_c seems to be incomplete; T_c remains around 15 K or lower.[5–10] Thus, it is still unclear whether the suppression of T_c at around $x=0.125$, the so-called ''$\frac{1}{8}$ anomaly,'' can be prevented only by structural modifications or not. Recently, it has been demonstrated that pressurized states can be induced into thin films by epitaxial growth of $La_{2-x}Sr_xCuO_{4+\delta}$ (LSCO).[17–21] In LSCO films, T_c increases[20,21] or decreases[17,18] with the compressive or expansive epitaxial strain due to lattice mismatch between films and substrates, respectively. In this paper, we applied the epitaxial strain to LBCO and observed the disappearance of the ''$\frac{1}{8}$ anomaly'' by the structural modification.

The (001)-oriented thin films of LBCO were grown by electron-beam coevaporation. The details of the growth were described in our previous report.[22] The film thickness was typically 300 Å. The films were grown on (001) $LaSrAlO_4$ (LSAO) and (100) $SrTiO_3$ (STO) substrates. After the evaporation, the films were cooled to temperatures lower than 150 °C in molecular oxygen or in a mixture of 10% ozone and molecular oxygen. The films cooled in oxygen have an oxygen composition close to 4 ($\delta\sim 0$), while those cooled in ozone contain excess oxygen ($\delta>0$).[23] The lattice parameters of the films were determined using four-circle and standard x-ray diffractometers, assuming a tetragonal structure. Resistivity was measured by the standard four-probe method. The electrodes were formed by evaporation of silver films with thickness of 500 Å. The contact resistance was lower than 10 Ω for a 2 mm^2 area. We defined T_c as the temperature below which the resistivity is less than 1% of the normal-state value.

Figure 1 shows the *a*- and *c*-axis lengths, a_0 and c_0, of the films at room temperature. Both the a_0 and c_0 for the films deviate from those for bulk samples,[11] indicating that the films are strained by the lattice mismatch between the films and substrates. On LSAO substrates, the a_0 for the films is close to the in-plane lattice parameter $a_s=3.756$ Å for the substrates, which is 0.03–0.05 Å smaller than a_0 for bulk LBCO.[11] The compression of a_0 results in the expansion of c_0 via the Poisson effect. In Fig. 1, the c_0 for the films with $\delta\sim 0$ and >0 is about 0.1 and 0.15 Å larger than that for the bulk,[11] respectively. The increase in the c_0 for the films with $\delta>0$ is expected to include the change caused by the excess oxygen as observed in bulk samples.[16] On the other hand, a_0 for the films on STO substrates is 0.035 Å larger than that for the bulk[11] in Fig. 1. This is consistent with $a_s=3.905$ Å for the STO substrates, which is larger than the a_0 for the bulk LBCO. In this case, the increase in a_0 results in a decrease in c_0 via the Poisson effect. In Fig. 1, the c_0 for the films on STO substrates is about 0.1 Å smaller than that for the bulk.[11]

Figures 2(a)–2(d) show the temperature dependences of the resistivity for the LBCO films with $\delta\sim 0$ and $x=0.05-0.35$. The films are stable for both long-time air exposure and cooling cycles. The results after air exposure for more than three months is exactly the same as those for fresh films. Films of La_2CuO_4 ($x=0$, $\delta=0$) are semiconducting. This fact confirms that the LBCO films cooled in oxygen are free from the intercalation of the extra interstitial oxygen. With increasing *x*, the resistivity decreases, then the superconductivity appears at $x\sim 0.06$ as shown in Fig. 2(a). In Fig. 3, T_c increases to 40 K with increasing *x* to 0.10 for the films on LSAO substrates. For $x=0.10-0.15$, the increasing rate of T_c is lower than for $x=0.06-0.10$. At $x=0.15$, T_c is maximized to 44 K, which is higher than that observed in the bulk,[1–15] demonstrating the strain effect as in the LSCO films.[20] With increasing *x* beyond 0.15, T_c starts to decrease. For $x>0.30$, the superconductivity disappears, although the films stay metallic ($d\rho/dT>0$) down to 4.2 K. The compositional evolution is similar to that observed for LSCO.[24–26]

For $x=0.10-0.15$, the values of T_c distribute over a rather narrow range between 40 and 44 K in Fig. 3. This is quite different from the case for bulk samples of LBCO where the ''$\frac{1}{8}$ anomaly'' is observed as a pronounced T_c depression at around $x=0.125$ and T_c is lower than

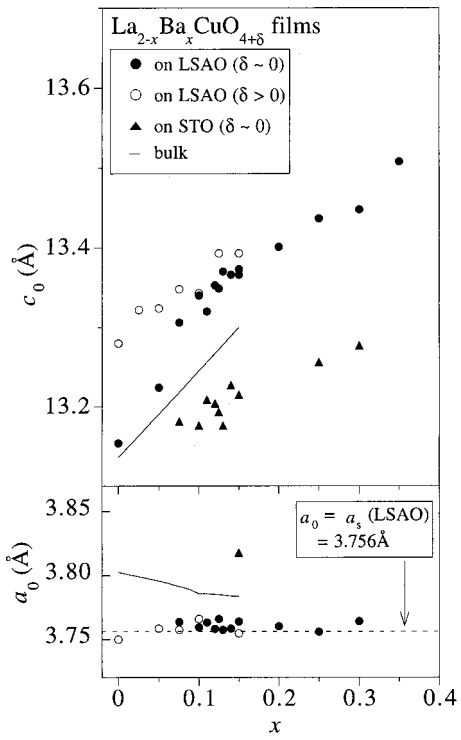

FIG. 1. Variations of the *a*- and *c*-axis lengths, a_0 and c_0, as functions of Ba concentration, *x*, for $La_{2-x}Ba_xCuO_{4+\delta}$ thin films. Open and closed circles are for films on (001) $LaSrAlO_4$ substrates with $\delta>0$ and ~ 0, respectively. Closed triangles are for films on (100) $SrTiO_3$ substrates with $\delta\sim 0$. The solid lines represent the data for polycrystalline samples with no excess oxygen (from Ref. 11). The broken line represents $a_0=3.756$ Å, the in-plane lattice parameter of $LaSrAlO_4$ substrates.

40 K.[3–13] It seems that the ''$\frac{1}{8}$ anomaly'' does not appear in LBCO films on LSAO substrates. Moreover, as seen in Fig. 2(b), the resistivity for the films on LSAO substrates with $x\sim 0.125$ does not exhibit a kink nor minimum above T_c, which are observed at around 60 K in bulk samples and interpreted as indications of some unclarified change in the electronic states related with the ''$\frac{1}{8}$ anomaly.''[12,13] The absence of the anomaly in the resistivity for the films also supports the disappearance of the ''$\frac{1}{8}$ anomaly'' by the compressive strain.[27]

On STO substrates, T_c is below 4.2 K and as low as 8 K for the films with $x=0.125$ and 0.15 as shown in Figs. 2(b) and 2(c), respectively. The resistivity values at low temperatures for the films on STO is more than two times larger than for the films on LSAO, suggesting a strain effect on the normal-state properties. In Fig. 3, it can be seen that T_c is below 8 K in the entire compositional range $x=0.10-0.15$. The T_c suppression is pronounced at around $x=0.125$ as in bulk samples,[3–13] suggesting that this suppression is related with the particular hole density.

With cooling in ozone, T_c for the films on LSAO substrates with $x=0-0.15$ exceeds 40 K regardless of *x* as shown in Fig. 3. The resistivity for these films (Fig. 4) is metallic ($d\rho/dT>0$) and similar to that for the films with $\delta\sim 0$ and $x=0.15$ in Fig. 2(b). The excess oxygen introduced into the films seems to result in the optimal doping of holes into the CuO_2 planes. For $x=0.075$, we attained the maximum T_c of 49 K, which is higher than the T_c reported

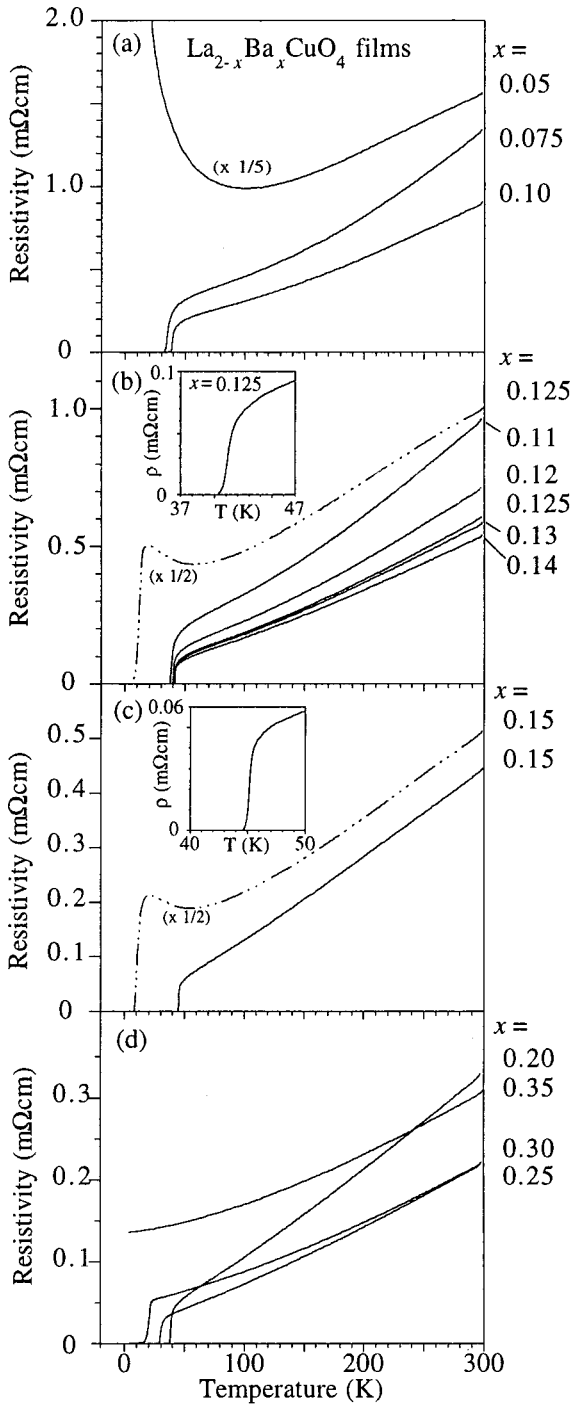

FIG. 2. Temperature dependences of resistivity for $La_{2-x}Ba_xCuO_4$ thin films with $x=$ (a) 0.05–0.10, (b) 0.11–0.14, (c) 0.15, and (d) 0.20–0.35. The solid and dashed lines are for the films on (001) $LaSrAlO_4$ and (100) $SrTiO_3$ substrates, respectively. The insets in (b) and (c) show the superconducting transitions for the films on $LaSrAlO_4$ with $x=0.125$ and 0.15, respectively. The resistivity data for films on $LaSrAlO_4$ with $x=0.05$ in (a) and on $SrTiO_3$ in (b) and (c) are scaled down by factors of 5 and 2, respectively.

for bulk samples,[16] indicating the strain effect again.

The main result of this work is the complete disappearance of the ''$\frac{1}{8}$ anomaly'' in LBCO attained by a structural modification due to the compressive epitaxial strain. Hydrostatic pressures extinguished the LTT phase in bulk ceramic samples of LBCO (Ref. 5) but do not recover T_c

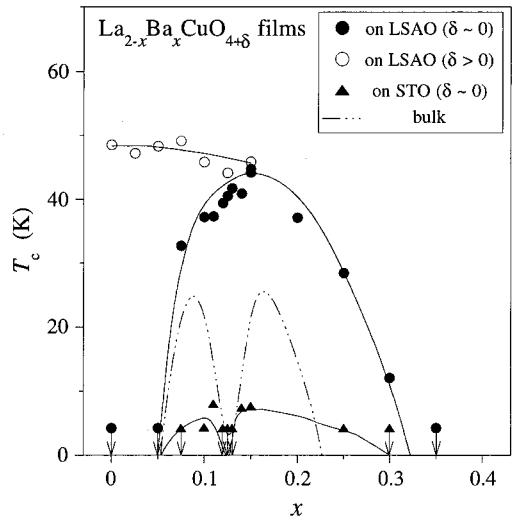

FIG. 3. Dependence of T_c on Ba concentration, x, for $La_{2-x}Ba_xCuO_{4+\delta}$ thin films. Open and closed circles are for films on (001) $LaSrAlO_4$ substrates with $\delta>0$ and ~ 0, respectively. Closed triangles are for films on (100) $SrTiO_3$ substrates with $\delta \sim 0$. The dashed line represents the data for polycrystalline samples with no excess oxygen (from Ref. 9). T_c for the films is defined as the temperature at which the resistivity is 1% of the normal-state value. The solid lines are guides for the eye.

completely.[5–10] T_c remains around 15 K and shows saturating behavior at pressures above around 1.5 GPa.[5] High-pressure studies have suggested that there exist other unknown origins of the ''$\frac{1}{8}$ anomaly,'' which are not directly related to the structural features of the LTT phase.[5,9] Our result contrasts with these results for bulk samples,[5–10] and seems to strongly suggest that the origin of the ''$\frac{1}{8}$ anomaly'' is related to the crystal structure.

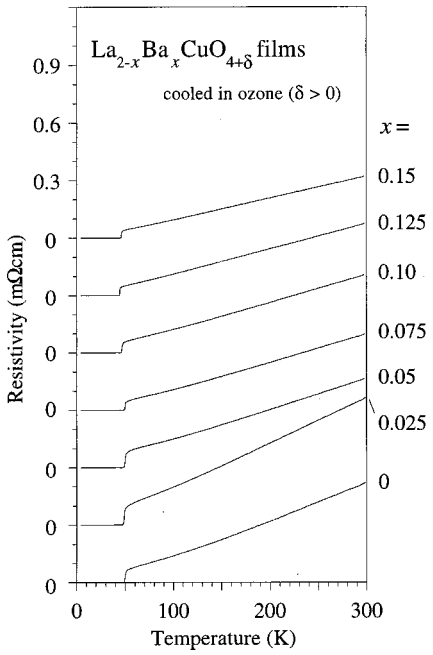

FIG. 4. Temperature dependences of resistivity for $La_{2-x}Ba_xCuO_{4+\delta}$ thin films on (001) $LaSrAlO_4$ substrates with $x=0-0.15$ and $\delta>0$.

It is likely that the difference between our result and the results for bulk samples under hydrostatic pressures[5–10] is due to the difference in the structural changes in the c-axis direction. The hydrostatic pressures suppress the formation of the LTT phase by the in-plane compression of the CuO_2 planes, but also suppress T_c by the compression in the c-axis direction. On the other hand, the films on LSAO substrates are also compressed in the in-plane directions but expanded in the c-axis direction under the anisotropic pressure of a plane type generated by the epitaxial strain, as seen in Fig. 1. It is expected that the low-temperature structure of the strained films on LSAO substrates is low-temperature orthorhombic (LTO) or high-temperature tetragonal (HTT) (Ref. 4) with expansion in the c-axis direction. This interpretation is consistent with our preliminary low-temperature structural analyses for the films on LSAO and STO substrates.[28]

The mechanism of the T_c suppression in the LTT structure is still not clear. Recently, it was suggested that the LTT structure seems to be favorable for pinning a horizontal stripe phase, which was proposed based on superlattice peaks in neutron diffraction for a single crystal of $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$.[29] In the model based on the stripe phase, the disappearance of the ''$\frac{1}{8}$ anomaly'' may be interpreted as the charge stripe becoming dynamical. However, dynamical charge stripes have not been experimentally observed yet. So we will resort to a simpler interpretation. We think that the T_c reduction is due to some structural features in the LTT phase, for example, the shorter bond length between Cu and oxygen in the apical site, which was reported from the extended x-ray absorption fine structure in LSCO crystals.[30] Then the charge redistribution caused by the changes in the positions of the atoms results in the T_c reduction. In this sense, we suppose that the ''$\frac{1}{8}$ anomaly'' is another aspect of the strain or pressure effects in LBCO. The experimental results demonstrated that the expansion and compression of the c axis increases and decreases T_c, respectively. We suggest that the transition from LTO to LTT is equivalent to a compression of the c axis.

We also note that the enhancement of T_c in the compressed films is related to the smaller residual resistivity (ρ_0). As seen in Figs. 2(b), 2(c), and 4, our films with the enhanced T_c show smaller ρ_0, defined by the extrapolation of the resistivity to 0 K with the third order polynomials ($a+bT+cT^2+dT^3$). For example, we obtained $\rho_0=10\,\mu\Omega$ cm for the film with $x=0.15$ and $\delta\sim 0$ in Fig. 2(c) and 2 $\mu\Omega$ cm for that with $x=0.15$ and $\delta>0$ in Fig. 4. The small values of ρ_0 are common in some other cuprates, for example, $YBa_2Cu_5O_{6.9}$, but not with bulk single crystals of the La-214 compounds.[14,15,31,32]

The larger ρ_0 in the La-214 crystals might be due to random potential caused by partial substitution of alkaline-earth cations for La ions. This argument is excluded by the lower ρ_0 in the films, which also have randomly distributed Ba ions in the La sites. Another possible origin of ρ_0 might be oxygen vacancies. This is also unlikely, because the bulk crystals annealed in oxygen partial pressures of about 1 bar are expected to contain oxygen vacancies not more than the films cooled from the growth temperatures to room temperature in oxygen partial pressures of 10^{-4} Torr.

As another possible candidate of the origin of ρ_0, we

suggest locally distributed antiferromagnetic domains, which causes the incommensurate magnetic peaks in inelastic neutron-scattering experiments for bulk crystals of La-214 compounds.[33] The incommensurate peaks have been observed not so clearly in $YBa_2Cu_3O_{6.9}$,[34,35] in which small values of ρ_0 are generally obtained as in the compressed LBCO films. The reduced ρ_0 in our films may indicate reduction of the local antiferromagnetic fluctuation, which may be related to the enhancement of T_c. In this scenario, the origin of the incommensurate peaks may have a negative contribution to the superconductivity in La-214 materials.

In summary, we observed disappearance of the ''$\frac{1}{8}$ anomaly'' in LBCO films under compressive epitaxial strain. The expansion of the c axis is possibly essential for the enhanced T_c. The reduced ρ_0 in the films may also correlate with the T_c enhancement.

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[27] Here we discuss about the possibility of the presence of the extra oxygen in the compressed films cooled in 10^{-4}-Torr oxygen, which might affect on the present results. We have no available analysis methods to determine the oxygen composition of films with thicknesses as small as 300 Å with enough accuracy to judge the possibility. However, we conclude that the amount of excess oxygen is negligible based on the following facts described in the text. (1) La_2CuO_4 films cooled in oxygen are semiconducting. This fact means the films do not contain significant amount of excess oxygen. (2) With increasing x from 0 to 0.25, the resistivity for the LBCO films cooled in oxygen decreases systematically as seen in Fig. 2. This fact means the hole concentration is mainly controlled by Ba doping as in the bulk samples with no excess oxygen [B. Batlogg *et al.*, Physica C **235–240**, 130 (1994)]. (3) With increasing x from 0, the superconductivity appears at around $x=0.06$ and T_c is maximized at $x=0.15$. These two characteristic compositions coincide with those for the bulk samples with no excess oxygen [K. Oh-ishi and Y. Syono, J. Solid State Chem. **95**, 136 (1991)].
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