

La_{2-x}Sr_xCuO_y epitaxial thin films ($x=0$ to 2): Structure, strain, and superconductivity

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We have grown (001)-oriented thin films of La_{2-x}Sr_xCuO_y with strontium composition $x=0-2$ by reactive coevaporation and characterized them by x-ray-diffraction and resistivity measurements. A systematical change in the c -axis length indicates that single-phase films were obtained for the whole compositional range. The films with the oxygen composition $y\sim 4$ showed superconductivity for x between 0.06 and 0.30. For $x=0.15$, the superconducting transition temperature (T_c) was maximized to 44 K, due to a strain effect caused by the lattice mismatch between films and substrates. Around this composition, it is found that T_c for the films shows a good correlation with the c -axis length. For $x=0.30$, T_c for the films strongly depends on the residual resistivity [$\rho(0\text{ K})$]: higher T_c for lower $\rho(0\text{ K})$. The depression of T_c around $x=0.125$ is smaller than that for the bulk samples, suggesting that the strain suppresses the “1/8 anomaly.” The films with $y>4$ attained by cooling in ozone showed T_c between 40 and 48 K for $x<0.15$. For $x>0.30$, the compositional dependence of the resistivity is explained by both oxygen defects and a structural phase transition at $x=1.8$.

I. INTRODUCTION

It has been well established that the carrier concentration is one of the key parameters for the superconducting transition temperature (T_c) in cuprate high- T_c superconductors (HTSC's). In La_{2-x}Sr_xCuO_y (LSCO), the carrier concentration is easily controlled in a wide extent by the strontium composition x and the oxygen composition y . Hence the fabrication of high-quality thin films of LSCO with various compositions is important for fundamental investigations of HTSC's. Until recently, however, it has been difficult to grow LSCO thin films with good superconducting properties comparable to those of bulk single crystals. As revealed by several experiments,¹⁻⁵ the essential reason is the strain due to lattice mismatches between LSCO films and substrates, which strongly affects the T_c of LSCO films. With (100) SrTiO₃ (STO) substrates, a serious reduction in T_c is observed because of large unrelieved expansive strain.¹ Recently, it has been demonstrated that, using substrates of LaSrAlO₄ (LSAO) with a small and compressing lattice mismatch, T_c for LSCO films is improved,^{2,3} and even exceeds^{4,5} the values for bulk samples. To the best of our knowledge, exceeding of bulk T_c 's has not been reported so far for other HTSC's.

It is likely that the strain in thin films also affects the so-called “1/8 anomaly” for $x\sim 0.12$ (Refs. 6 and 7) in this system. This anomaly is expected to be correlated with structural distortions of the CuO₂ planes with rotations of CuO₆ octahedra.⁸ In the La_{2-x}Ba_xCuO₄ (LBCO) system, a long-

range order of the rotations takes place, resulting in a low-temperature tetragonal (LTT) phase.⁹ In LSCO, it has been suggested that the instability to the LTT phase is not sufficient to realize a long-range order, but instead causes local distortions of the CuO₂ planes.^{10,11} It is expected that the strain in thin films of LSCO may affect the distortions, allowing us to investigate the physical properties in this system free from the anomaly.

Another topic in the thin-film growth of LSCO-related material is the introduction of the excess oxygen by strong oxidation. Our recent report¹² on the physical properties of superconducting thin films of La₂CuO_{4+ δ} suggests that films oxidized using ozone have a much more homogeneous distribution of the excess oxygen than bulk samples oxidized by high-pressure annealing¹³ or electrochemical methods.¹⁴ The strong oxidation using ozone may also be effective for investigating the transport properties in LSCO with $x>0.3$, where it is known that oxygen vacancies in the CuO₂ planes are formed and compensate the carrier doping by Sr substitution for La.¹⁵⁻¹⁸

Furthermore, the strong oxidation may metallize orthorhombic Sr₂CuO₃ containing isolated CuO chains with sufficient doping of holes. The transport properties for this compound has been reported for bulk samples oxidized strongly,¹⁹ but not for thin films yet. In the case of Ba₂CuO₃ with the same structure as Sr₂CuO₃, the oxidation using ozone results in redistribution of oxygen atoms and leads to superconducting thin films of Ba₂CuO_{4- δ} , which has a tetragonal structure with CuO₂ planes instead of well-doped

CuO chains.²⁰ Although a tetragonal phase of $\text{Sr}_2\text{CuO}_{3+\delta}$ with oxygen vacancies in the CuO_2 planes has been reported for bulk samples by several groups,^{21–24} it has been claimed that this phase is nonsuperconducting.^{22–24}

In this paper, we report the growth of single-phase (001)-oriented thin films of LSCO with strontium composition $x = 0$ to 2. The films without excess oxygen showed superconductivity for $x = 0.06–0.30$. The maximum value of T_c observed for $x = 0.15$ exceeds 44 K due to the strain effect in the films on LSAO substrate. The strain also appears to be effective in suppressing the “1/8 anomaly.” The oxidation using ozone successfully introduces excess oxygen into the films with $x < 0.15$, but is not strong enough to fill up the oxygen vacancies in the CuO_2 planes for $x = 0.4–1.7$ nor to make the CuO chains metallic for $x = 1.8–2$.

II. EXPERIMENT

The thin films of LSCO were grown by electron-beam coevaporation from metal sources. The evaporation beam flux of each element was controlled by electron impact emission spectrometry via feedback loops to electron guns. Nominal flux was adjusted during the growth so as to keep the film surfaces free from precipitates of impurity phases in reflection high-energy electron diffraction (RHEED) monitoring.²⁵ The evaporants react at the substrate surfaces heated to 650–750 °C with a mixture of 10% ozone and molecular oxygen supplied with the flow rate 2.25 sccm through an alumina tube directed at the substrate from a distance of about 3 cm. The chamber pressure during growth was 3×10^{-5} Torr. The growth rate was typically 0.5–3 Å/s. The films were grown on (001) LSAO substrates except for the films with $x = 2$, which were grown on (100) STO substrates. For the films with $x = 0$ and 0.12–0.18, the both kinds of substrates were used. The thicknesses of the films were 150–4500 Å.

After the evaporation, the films were cooled to temperatures lower than 150 °C at a rate lower than 20 °C/min in 3×10^{-4} Torr molecular oxygen or in the same ozone flow as the film growth. For $x < 0.35$, two sets of films were prepared. One set was cooled in oxygen to obtain the oxygen composition y close to 4. The other was cooled in ozone to introduce the excess oxygen into the films. The films with $x = 0.4–2$ were cooled in ozone to compensate the oxygen deficiency reported in the literature for bulk materials.^{15–18}

The lattice parameters of the films were determined using four-circle and standard x-ray diffractometers. Resistivity was measured by the standard four-probe method using electrodes formed by Ag evaporation. We defined T_c as the temperature below which the resistivity is less than 1% of the normal-state value. Although the composition of the films was roughly determined by inductively coupled-plasma measurements, the strontium composition x was estimated from the nominal deposition rates assuming that T_c is maximum at $x = 0.15$. The oxygen composition y is an important parameter in this system. At present, however, we have no available method to determine the values of y in thin-film samples with enough accuracy. In this study, we estimate y qualitatively from the comparison of the lattice parameters and the resistivity data with those for bulk samples in the literature.^{6,7,15–18,26}

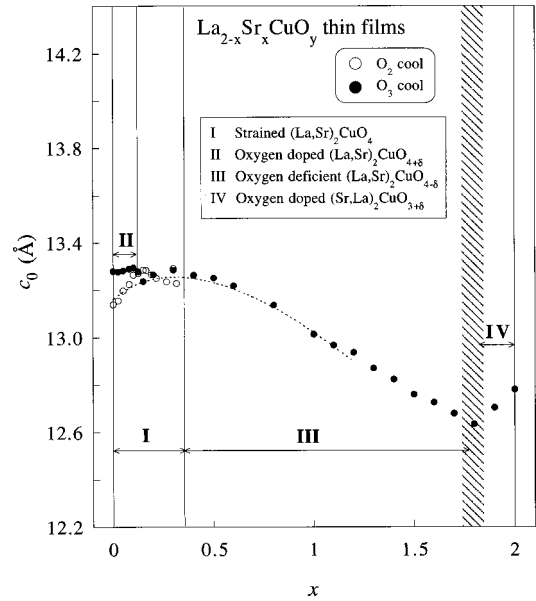


FIG. 1. Evolution of the c -axis length (c_0) with strontium composition x for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_y$ thin films. The films with $x < 2$ were grown on (001) LaSrAlO_4 substrates. The film with $x = 2$ was grown on a (100) SrTiO_3 substrate. Open and closed symbols are for films cooled in oxygen and ozone, respectively. The broken line represents the data for bulk ceramic samples annealed in oxygen (Ref. 15). Four compositional regions are denoted by I, II, III, and IV, whose details are described in the text.

III. RESULTS AND DISCUSSION

A. Lattice parameters

The x-ray diffraction patterns indicated that all of the films are single phase and c -axis oriented. Figure 1 shows the c -axis length (c_0) of the films of LSAO substrates with strontium composition $x < 2$ and the film on a STO substrate with $x = 2$. The systematic variation of c_0 indicates that a solid solution is formed in the entire compositional region. Furthermore, the overall behavior of c_0 , neglecting the strain effect for $x = 0–0.35$, shows a good agreement with the broken line reported for bulk samples with $x = 0–1.2$ annealed in oxygen.¹⁵ Below, we give detailed descriptions of the lattice parameter for the following four compositional regions: (1) $x = 0–0.35$, $y \sim 4$, (2) $x = 0–0.13$, $y > 4$, (3) $x = 0.35–1.8$, and (4) $x = 1.8–2$. The regions are denoted in Fig. 1 by I, II, III, and IV, respectively.

$$(1) x = 0–0.35, y \sim 4.$$

For the films on LSAO substrates with $x = 0–0.35$ cooled in oxygen, c_0 around $x = 0.15$ deviates from that for bulk samples¹⁵ annealed under an oxygen pressure of 1 bar at 400 °C shown by a broken line in Fig. 1. The c axis for the thin films with $x = 0.15$ is about 0.05 Å longer than that for the bulk. This expansion in the c axis is due to the strain effect discussed in our previous report.⁴ In the films with $x = 0.15$ on LSAO substrates, the a axis is compressed by 0.4% due to the stress generated by the lattice mismatch between LSCO and LSAO. The stress is of a plane type because a film has no restriction in the direction perpendicular to the surface. This causes the expansion of the c axis in

the films due to the Poisson effect. The shrinkage of the a axis of 0.2–0.3% was also observed for the films with $x=0.08$ –0.125, confirming that the deviation of c_0 from the bulk values around $x=0.15$ is due to the strain effect. Thus, we suggest that the films in this region are strained (La, Sr)₂CuO₄ as shown in Fig. 1.

$$(2)x=0-0.13, y>4.$$

The cooling in ozone expanded the c axis further for the films with $x=0$ –0.13 in Fig. 1. Considering the report for bulk materials oxidized electrochemically,²⁶ this c -axis expansion indicates that the excess oxygen was successfully introduced into the films. The strength of the oxidation by cooling in ozone is enough to introduce the excess oxygen into the films with $x<0.15$. The oxygen composition of the films in this region is expected to be larger than 4. So we suppose the films in this region are oxygen-doped (La, Sr)₂CuO_{4+ δ} as shown in Fig. 1.

$$(3)x=0.35-1.8.$$

In the compositional region $x=0.35$ –1.8, the c axis shrinks with increasing x . The data for the films shows a good agreement with that for bulk samples with $x<1.3$ annealed in oxygen, which have a K₂NiF₄-type crystal structure with oxygen defects in the CuO₂ planes.^{15,16} These bulk samples were reported to have an oxygen deficiency of $x/2-d$ with $d\sim 0.11$ for $x=0.4$ –1 and $d\sim 0.33$ for $x=1.2$.¹⁵ The values of c_0 observed for the films with $x=0.4$ –1.3 suggests that the films also have oxygen deficiencies, the amounts of which are close to those in the bulk samples.

It has been reported that the stoichiometric compound LaSrCuO₄ has a large c -axis length of 13.27 Å.²⁷ The bulk samples of this compound were prepared under an oxygen pressure of 3 kbar. In this case, the amount of oxygen deficiency is very small. The c -axis length for our film with $x=1$ is 13.05 Å and much smaller than the value for the stoichiometric compound, suggesting a larger oxygen deficiency in the film.

The change in the c -axis length for the films with $x=1.3$ –1.8 coincides with the extrapolation line of that for the bulk samples with $x<1.3$. This suggests that the films with $x=1.3$ –1.8 are single phase and they also have the K₂NiF₄-type structure with oxygen defects in the CuO₂ planes. For the bulk samples with $x>1.34$, multiphase formation has been reported.¹⁶ The solid-solution region is wider in the thin-film synthesis with cooling in ozone than that in the bulk synthesis.

These results show that the oxidation by cooling in ozone is not strong enough to remove the oxygen deficiencies in the films with $x>0.4$. In this compositional region, the films are expected to be oxygen-deficient (La, Sr)₂CuO_{4- δ} as shown in Fig. 1.

$$(4)x=1.8-2.$$

The compositional evolution of the c -axis length for the films have a clear kink at $x=1.8$. We attribute this kink to the boundary between two structural phases, the tetragonal

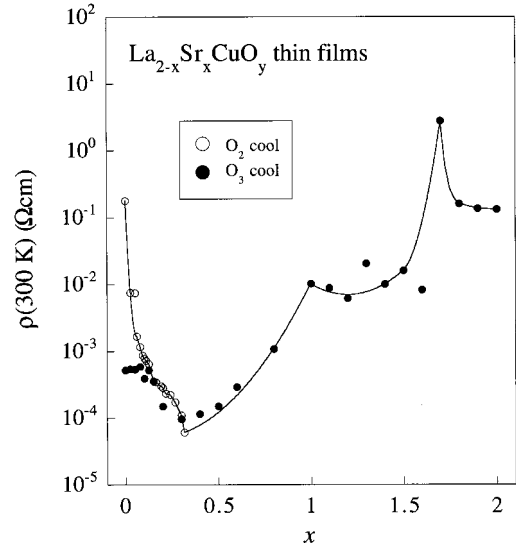


FIG. 2. Plot of the resistivity at 300 K [$\rho(300\text{ K})$] for La_{2-x}Sr_xCuO_y thin films with various strontium compositions x . The films with $x<2$ were grown on (001) LaSrAlO₄ substrates. The film with $x=2$ was grown on a (100) SrTiO₃ substrate. Open and closed symbols are for films cooled in oxygen and ozone, respectively. The solid line is a guide for the eye.

K₂NiF₄-type phase for $x<1.8$ and an orthorhombic Sr₂CuO₃-type phase for $x=1.8$ –2. The orthorhombic structure of the films with $x=1.8$ –2 appeared in RHEED patterns. For $x=1.8$ –2, the c -axis length increases with x systematically, indicating that a solid solution is formed also in this compositional region.

The c -axis length of the film with $x=2$ is 12.78 Å, which is longer than the value of 12.706 Å reported for bulk samples of orthorhombic Sr₂CuO_{3.01}.¹⁹ It is likely that the larger c -axis length for the film comes from excess oxygen introduced by the cooling process in ozone. An increase in the c -axis length with increasing oxygen content has been reported for bulk samples,¹⁹ which supports the above speculation. On the other hand, the c -axis length of 12.54–12.57 Å has been reported for a tetragonal phase of Sr₂CuO_{3+ δ} .²³ This value is far from that for our thin films with $x=2$. So we speculate that the films in this compositional region are oxygen-doped orthorhombic (Sr, La)₂CuO_{3+ δ} as shown in Fig. 1.

B. Resistivity and transition temperature

Figure 2 is a plot of the resistivity at 300 K for the LSCO films with the various strontium composition x , which gives a perspective view of the results of the resistivity measurements reported in this paper. Here we displayed the data for the films grown on LSAO substrates with $x<2$ and the film grown on a STO substrate with $x=2$. The resistivity for the films cooled in oxygen decreases with increasing x from 0 to 0.32, suggesting that the substitution of Sr for La introduces holes into the CuO₂ planes in this compositional region. The slope of the curve changes at around $x=0.06$ where the superconductivity appears. A monotonic decrease of the resistivity from $x=0.06$ –0.32 indicates that the oxygen composition y is maintained close to 4 in these films cooled in oxygen as it is in well-oxidized bulk ceramics.²⁸ The resis-

tivity starts to increase at $x=0.4$, suggesting the formation of the oxygen deficiency starts at this composition, even though the films with $x>0.35$ were oxidized by the cooling in ozone. The increase is intensified at 0.6 and continue to 1. In the compositional region $x=1-1.6$, the resistivity at 300 K is almost independent of x . The resistivity shows a strong enhancement for $x=1.7$ close to the structural phase boundary between K_2NiF_4 -type and Sr_2CuO_3 -type structures as suggested by the structural data discussed above. The resistivity is almost independent of x again for $x=1.8-2$ with the orthorhombic Sr_2CuO_3 -type structure.

As we did in the previous section for the lattice parameter, we describe below the details of the results of the resistivity measurements for the following four compositional regions. (1) $x=0-0.35$, $y\sim 4$, (2) $x=0-0.13$, $y>4$, (3) $x=0.35-1.8$, and (4) $x=1.8-2$.

$$(1)x=0-0.35, y\sim 4.$$

Figures 3(a), 3(b), and 3(c) show the temperature dependences of the resistivity for the films cooled in oxygen on LSAO substrates with $x=0-0.05$, $0.06-0.15$, and $0.15-0.32$, respectively. As seen in Fig. 3(a), the films of La_2CuO_4 ($x=0$) are semiconducting in the whole temperature region. With increasing x , the resistivity decreases rapidly, more than an order of two in magnitude. The films for $x=0.025$ and 0.05 show a similar temperature dependence. Both are metallic ($d\rho/dT>0$) at temperatures between 100 and 300 K, and semiconducting ($d\rho/dT<0$) below 100 K.

The superconductivity appears at $x=0.06$ as shown in Fig. 3(b). As seen in the figure, the resistivity decreases with increasing x monotonically. On the other hand, the compositional dependence of T_c is not simple as shown in Fig. 4. With increasing x from 0.06 to 0.10, T_c rapidly increases from 10 to 40 K. In the compositional region $x=0.10-0.15$, the increasing rate of T_c is lower than $x=0.06-0.10$. For $x=0.10-0.15$, the values of T_c distribute over a rather narrow range between 40 and 44 K. The maximum T_c of 44 K is obtained for the films on LSAO substrates with $x=0.15$, which are considered to be ‘‘optimally’’ doped. This value of T_c is significantly higher than that observed in bulk samples.

In our previous report, we explained this increase in T_c by a strain effect due to lattice mismatch between films and substrates.⁴ The uniaxial strain dependences $dT_c/d\epsilon_i$ ($i=a, b$ and c) for LSCO have been deduced by Gugenberger *et al.* from high-resolution dilatometry experiments using the Ehrenfest relationship.²⁹ Their result gives positive $dT_c/d\epsilon_a=250$ K and $dT_c/d\epsilon_b=400$ K, and a negative $dT_c/d\epsilon_c=-1090$ K. Using these values, we can estimate the increase in T_c from the observed strain in the films. The a -axis compression of 0.4% and the c -axis expansion of 0.5% in the films with $x=0.15$ are expected to give increases in T_c of +2.6 and +5 K, respectively. The total value of 7.6 K is consistent with the observed T_c enhancement of 4–7 K. It may be noteworthy that the c -axis expansion has a significant contribution to the T_c gain.

For the composition around $x=0.15$, we obtained films with various values of T_c by varying the growth conditions on LSAO and STO substrates. Figure 5 is a plot of T_c with the c -axis length for those films with $x=0.12-0.18$. This

figure shows a correlation between T_c and c_0 , confirming that the expansion in the c -axis direction is essential for the enhanced T_c in the films, as discussed above. The coefficient dT_c/dc_0 obtained by a least-squares fit of the correlation is about 200 K/Å. In a recent report of an anisotropic-pressure study for LSCO single crystals,³⁰ a correlation between T_c and c_0 has been also observed. For the single crystals, the coefficient dT_c/dc_0 was 280 K/Å,³⁰ which is close to the value obtained in this work for the films.

The resistivity for the films cooled in oxygen on LSAO substrates still decreases with increasing x from 0.15 to 0.32 as shown in Fig. 3(c), indicating the increase in the carrier concentration as established using bulk samples.²⁸ In this ‘‘overdoped’’ compositional region, T_c decreases with increasing x and the superconductivity disappears at $x=0.32$. For the nonsuperconducting metallic film on an LSAO substrate with $x=0.32$, the resistivity is about 60 $\mu\Omega$ cm at 300 K and 6 $\mu\Omega$ cm at 4.2 K. These values are much lower than those reported so far for bulk single crystals.

The superconductivity for the overdoped films on LSAO substrates with $x=0.30$ appears to be very sensitive to the residual resistivity, $\rho(0$ K) as shown in Fig. 6. We define $\rho(0$ K) as the extrapolated value at $T=0$ K of the third-order polynomials ($a+bT+cT^2+dT^3$) determined by least-squares fitting of the resistivity data above T_c . The upper bound of the temperature region for the fitting was fixed at 200 K. The lower bound was chosen from the temperature range between 4.2 and 60 K for each sample to avoid the effect of the superconducting fluctuation. In Fig. 6, the film with the lowest $\rho(0$ K) of 16 $\mu\Omega$ cm shows $T_c=16$ K, whereas the film with $\rho(0$ K) of 31 $\mu\Omega$ cm does not show the superconducting transition down to 4.2 K. Figure 7 is a plot of T_c with $\rho(0$ K) for the films with $x=0.15$ and 0.30. It can be seen that the increase of $\rho(0$ K) reduces T_c for $x=0.30$ more strongly than for $x=0.15$. For $x=0.30$, $\rho(0$ K) of about 30 $\mu\Omega$ cm is enough to extinguish the superconductivity. On the other hand, T_c as high as 20 K was still observed for $x=0.15$ even with $\rho(0$ K) of about 150 $\mu\Omega$ cm. For $x=0.15$, the correlation between T_c and $\rho(0$ K) is reached at around $\rho(0$ K)=280 $\mu\Omega$ cm by an extrapolation to $T_c=0$ K with a linear line obtained by least-squares fitting. This value is about 10 times larger than the critical value of 30 $\mu\Omega$ cm for $x=0.30$, at which the superconductivity disappears. This strong reduction of T_c with increasing $\rho(0$ K) in the overdoped compounds has also been reported for Zn-substituted single crystals of LSCO.³¹

We speculate that the sample dependence of T_c , c_0 , and $\rho(0$ K) for the films in Figs. 5 and 7 is mainly caused by the strain relaxation. Although the strain relaxation mechanism has not been understood well, it seems to be affected by the substrate surface conditions as well as the growth conditions including the cation stoichiometry and the oxidation. Depending on these conditions, the critical thickness for relaxation ranged from a thickness less than 50 Å to that more than 5000 Å. Some thick films exceeding the critical thickness show values of T_c higher than 40 K, but finite (nonzero) values of $\rho(0$ K). Such a result can be explained by considering that relaxation of strain causes a structural gradation in a film along the direction normal to the surface. Namely, even if the LSCO layers close to the surface are relaxed, the layers close to the substrate are still strained. The gradation

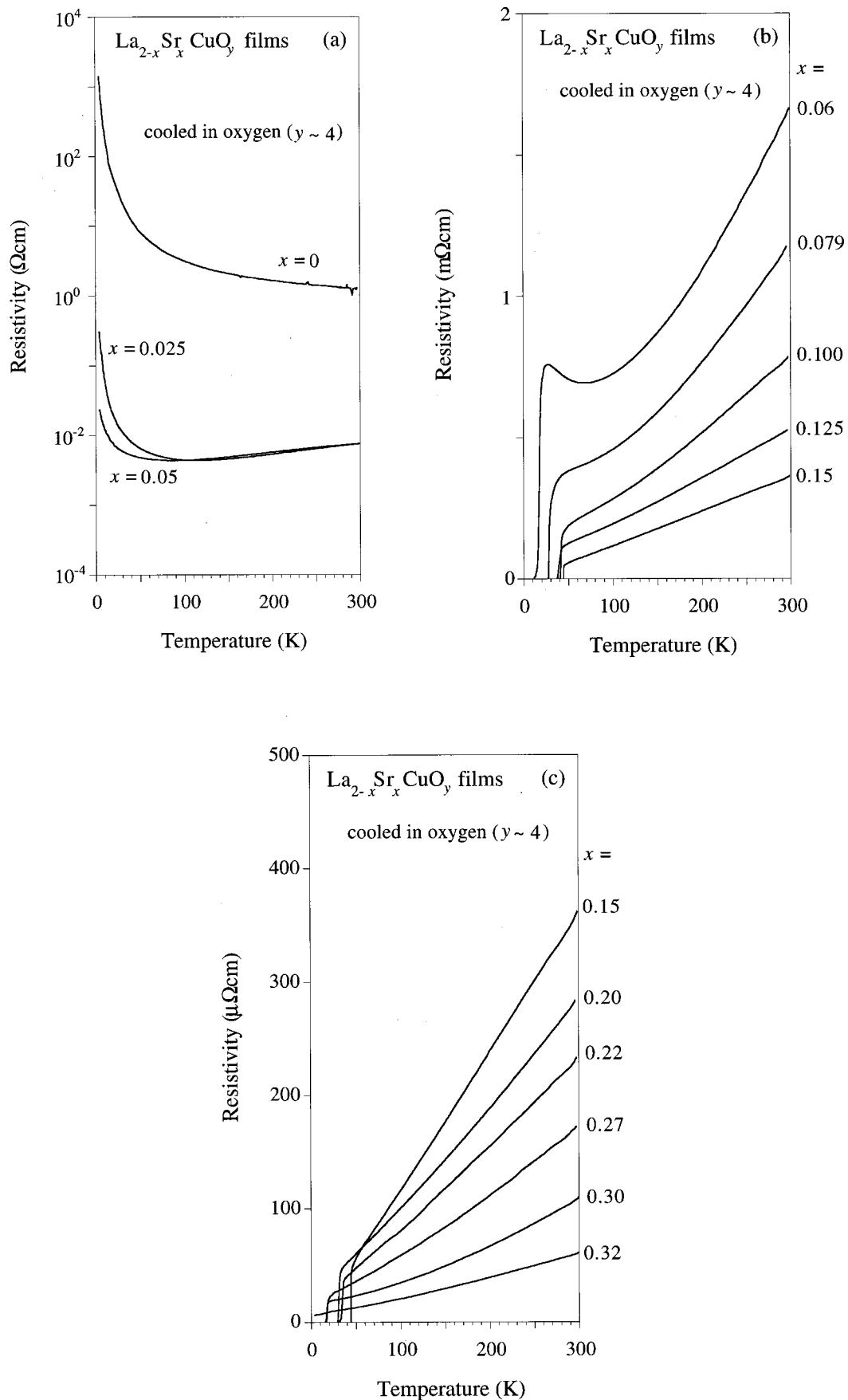


FIG. 3. Temperature dependences of the resistivity for La_{2-x}Sr_xCuO_y thin films cooled in oxygen on (001) LaSrAlO₄ substrates: (a) $x=0-0.05$, (b) $x=0.06-0.15$, and (c) $x=0.15-0.32$. The thicknesses of the films are 900–1800 Å for $x=0-0.22$, 4500 Å for $x=0.27, 0.32$, and 300 Å for $x=0.30$.

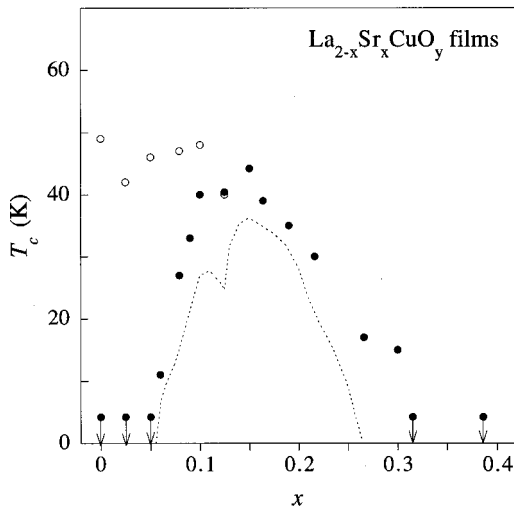


FIG. 4. Composition dependences of T_c for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_y$ thin films on (001) LaSrAlO_4 substrates. Closed and open symbols are for films without and with excess oxygen, respectively. The broken line represents the data for bulk polycrystalline samples (Ref. 32).

pattern depends on the critical thickness. Such partially relaxed (thick) films will disturb the T_c correlations with c_0 and $\rho(0\text{ K})$, leading to a large scatter of data in Figs. 5 and 7.

We summarize the overall behavior of T_c for the films cooled in oxygen on LSAO substrates in Fig. 4, which plots the maximum value obtained so far for each composition. In the entire compositional region, T_c for the films is higher than that for the bulk.³² For $x=0.06-0.15$, the enhancement of T_c for the films comes from the epitaxial strain effect. For $x>0.15$, the enhancement of T_c may have different origins other than the strain effect. The c -axis length starts to approach the bulk value with increasing x from 0.15, suggesting that the strain effect is less effective in this overdoped compositional region. This is consistent with the fact that the lattice mismatch between LSCO and LSAO decreases with increasing x . Moreover, the superconductivity disappears at

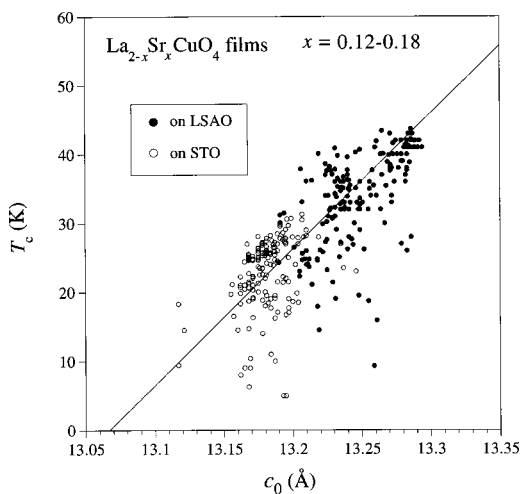


FIG. 5. Plot of T_c with the c -axis length (c_0) for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ thin films with $x=0.12$ to 0.18 . The thickness of the films ranges from 150 to 4500 Å. Closed and open symbols are for films on (001) LaSrAlO_4 and (100) SrTiO_3 substrates, respectively. The solid line represents the result for a linear fit to the data points.

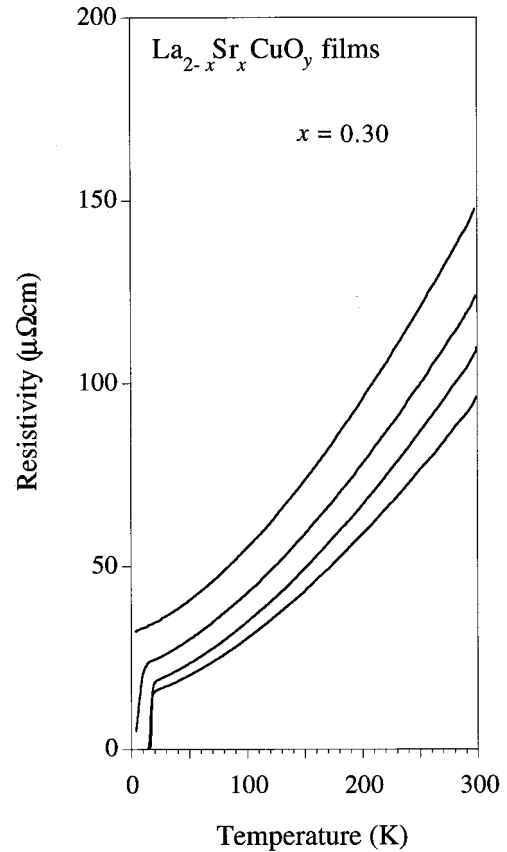


FIG. 6. Temperature dependences of the resistivity for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_y$ thin films on (001) LaSrAlO_4 substrates with $x=0.30$. The thicknesses of the films are 170 Å.

around $x=0.32$ for the films, while it disappears at around $x=0.25-0.30$ for the bulk.³³ As discussed above, the superconductivity in the overdoped region is very sensitive to the residual resistivity in the samples. The small $\rho(0\text{ K})$ in the thin-film samples results in the higher T_c in this compositional region and allows the superconductivity to survive until $x=0.30$.

It might be argued that the smaller $\rho(0\text{ K})$ in the films is, at least, partially due to the more homogeneous distribution of La and Sr atoms and the smaller amount of oxygen deficiency in the CuO_2 planes. More importantly, however, it should be noticed that the strain in the films also affects $\rho(0\text{ K})$, because we observed a clear difference in $\rho(0\text{ K})$ between the films on LSAO and STO substrates in our previous study.⁴ The compressive strain on LSAO substrates seems to be effective to reduce $\rho(0\text{ K})$ as seen in the resistivity data for the films with $x=0.15$ and $\delta>0$ in Figs. 3(b) and 8, respectively. We suppose that the larger $\rho(0\text{ K})$ in the bulk samples of the LSCO (Ref. 7) may come from scattering due to local antiferromagnetic domains, which cause the incommensurate magnetic peaks observed in neutron-scattering measurements.³⁴ The small values of $\rho(0\text{ K})$ are common with some other cuprates, for example, $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$, where the incommensurate dynamic spin fluctuations are not observed^{35,36} as clearly as in the LSCO crystals.³⁴ The reduced $\rho(0\text{ K})$ in our films may indicate the reduced local-spin fluctuation. Then the strong correlation between $\rho(0\text{ K})$ and T_c seems to suggest that the local antiferromagnetic spin fluctuation has a negative effect on the superconductivity in LSCO.

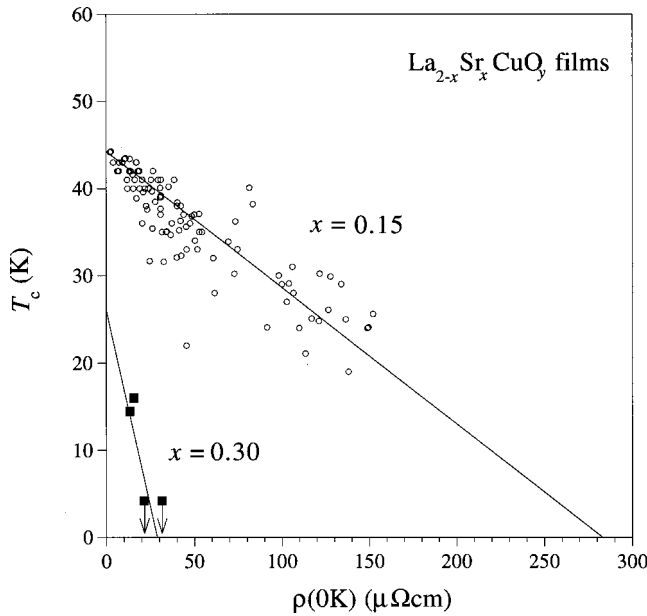


FIG. 7. Plot of T_c with $\rho(0\text{ K})$ for La_{2-x}Sr_xCuO_y thin films on (001) LaSrAlO₄ substrates. The thickness of the films ranges from 150 to 4500 Å. Open and closed symbols are for the films with $x = 0.15$ and 0.30 , respectively. The solid lines represent the results of linear fits to the two data sets.

Another feature of Fig. 4 is that the composition dependence of T_c around $x = 0.125$ is smaller than that for the bulk samples. This suggests that the strain in the films suppresses the “1/8 anomaly,” which appears in the reduction and disappearance of T_c in bulk samples of LSCO (Ref. 6) and

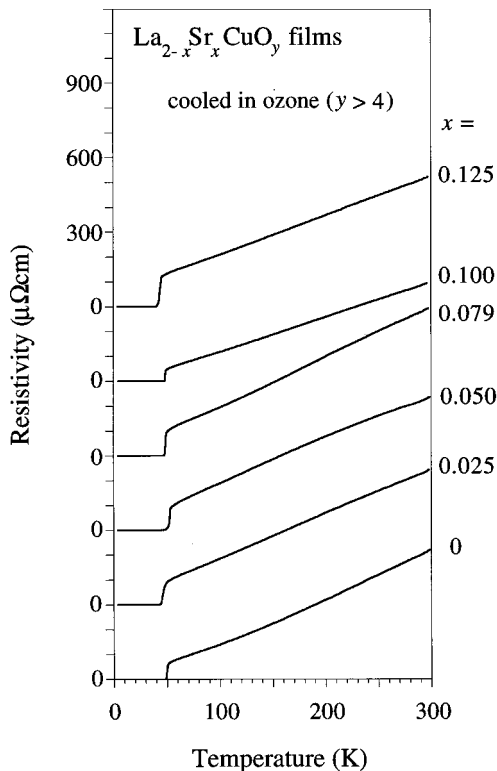


FIG. 8. Temperature dependences of the resistivity for La_{2-x}Sr_xCuO_y thin films on (001) LaSrAlO₄ substrates with $x < 0.15$ cooled in ozone. The thicknesses of the films are 450 Å.

LBCO,⁹ respectively. It is likely that the in-plane compressive strain in the films suppresses the local distortions of the CuO₂ planes,¹¹ which is expected to be closely related with the “1/8 anomaly” in the bulk samples. It may be noteworthy that the temperature dependences of the resistivity also suggest the suppression of the “1/8 anomaly” by the strain in the LSCO films. In Fig. 3(b), the resistivity for the films with $x = 0.10$ and 0.125 does not show upturns or saturating behaviors in the temperature range below 100 K, which have been reported for bulk single crystals with x close to 0.125 as evidence of the “1/8 anomaly.”⁷ The strain effect in the films is qualitatively consistent with high-pressure studies for bulk samples. It has been reported that an application of hydrostatic pressure suppresses the “1/8 anomaly,” from both the superconducting and normal-state properties in bulk samples of LSCO (Ref. 37) and LBCO.³⁷⁻³⁹

$$(2)x = 0 - 0.013, y > 4.$$

With cooling in ozone, T_c for the films on LSAO substrates with $x < 0.15$ exceeds 40 K regardless of x as shown in Fig. 4. The temperature dependence of the resistivity for these films in Fig. 8 is metallic and similar to that for the films cooled in oxygen with $x = 0.15$ in Fig. 3(b). In this compositional region, the excess oxygen is introduced into the films by cooling in ozone, resulting in nearly optimal doping of holes into the CuO₂ planes. For these films, the oxygen composition y is expected to be larger than 4. The maximum T_c of 48 K has been achieved for $x = 0$ and 0.10 . These values of T_c are comparable or higher than those reported for bulk samples oxidized by an electrochemical method.²⁶

The enhancement of T_c in the films cooled in ozone on LSAO substrates may be explained by the strain effect as in the case for the films with x around 0.15 cooled in oxygen. This argument is supported by the substrate dependence of T_c and the lattice parameters for La₂CuO_{4+δ} films cooled in ozone.¹² For the films on STO substrates, T_c is remarkably lower than that for the films on LSAO substrates; whereas T_c for the films on LSAO has reached 48 K, that for the films on STO has never exceeded 30 K. A clear difference in the lattice parameters was observed between the films on LSAO and STO substrates. The values of a -axis and c -axis lengths for the film on LSAO were 3.750 and 13.280 Å, respectively, whereas those for the film on STO were 3.791 and 13.200 Å. The substrate dependence of the film structure can be roughly explained by the strain caused by the lattice mismatch between the films and the substrates. The values of a -axis length (a_0) for bulk samples of La₂CuO_{4+δ} (Ref. 26) are larger than that for LSAO and smaller than that for STO. Thus, the mismatch causes compressive stress in the films on LSAO and tensile stress in those on STO, and thereby the a -axis length decreases in the films on LSAO and increases in the films on STO. The expansion of the c -axis on LSAO and its compression on STO are correlated with the change in a_0 via the Poisson effect. It is likely that the strain in the films affects their T_c as in the case of the films with x around 0.15 cooled in O₂.

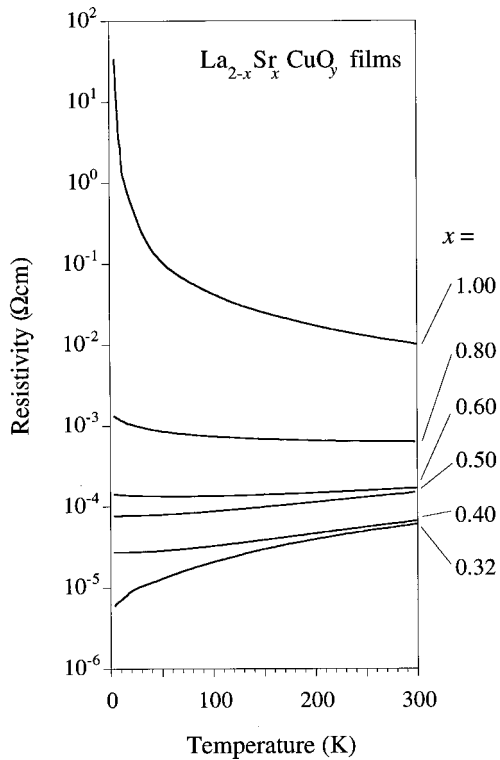


FIG. 9. Temperature dependences of the resistivity for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_y$ thin films on (001) LaSrAlO_4 substrates with $x = 0.32-1$. The thicknesses of the films are 4500 Å for $x = 0.32$, 520 Å for $x = 0.40, 0.60$, and 0.80, and 170 Å for $x = 0.50$ and 1.00.

For LSCO thin films with $x = 0.10$ grown with activated oxygen on LSAO substrates, Locquet *et al.* observed $T_c = 49$ K.⁵ Our films with $x = 0.10$ cooled in ozone on LSAO substrates show $T_c = 48$ K. The lattice constants for the ozone-cooled films were $a_0 = 3.756$ Å and $c_0 = 13.296$ Å, which are very close to those for their films. On the other hand, the temperature dependences of the resistivity of our films are different from that of their films. A clear change of slope was observed at 270 K for their films,⁵ but not for ours.

$$(3)x = 0.35-1.8.$$

The resistivity for the films on LSAO substrates in the compositional region $x = 0.32-1$ increases with increasing x in Fig. 9. This indicates the formation of oxygen deficiency in this compositional region as expected from the c -axis length in Fig. 1. The temperature dependences of the resistivity for the films with $x = 0.32-0.6$ are metallic and those for the films with $x > 0.6$ are semiconducting. The increase of the resistivity with x has been explained by the reduction of the carrier mobility and the cancellation of the hole doping with the increased oxygen vacancies.¹⁵

Figure 10 shows the temperature dependences of the resistivity for the films with $x = 1-1.6$ cooled in ozone on LSAO substrates. In this compositional region, the increase in x corresponds to Sr substitution for La in $\text{LaSrCuO}_{3.5+\delta}$, the compound with $x = 1$. The resistivity at low temperatures is three orders of magnitude reduced by the increase in x of 0.1, suggesting that the Sr substitution for La causes doping of holes into the CuO_2 planes with oxygen defects in

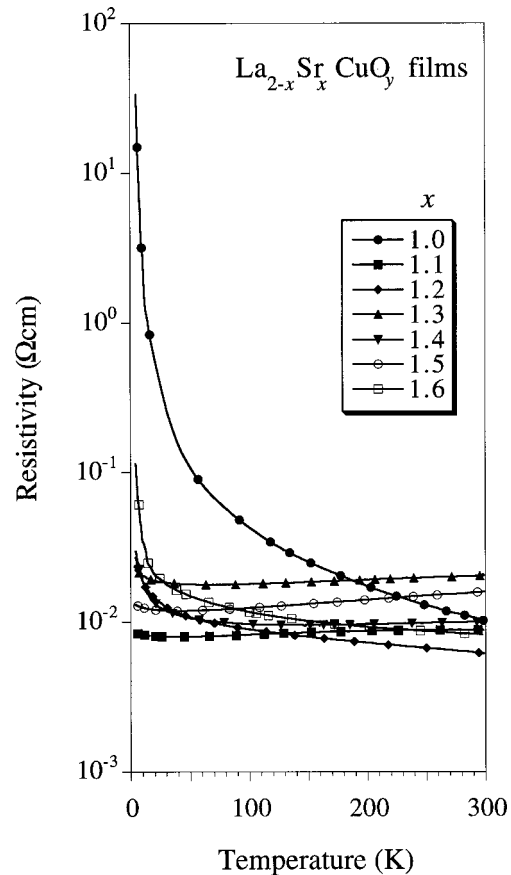


FIG. 10. Temperature dependences of the resistivity for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_y$ thin films on (001) LaSrAlO_4 substrates with $x = 1-1.6$ cooled in ozone. The thicknesses of the films are 170 Å for $x = 1.0, 1.2, 1.4, 1.6$, and 520 Å for $x = 1.1, 1.3$, and 1.5.

$\text{LaSrCuO}_{3.5+\delta}$. Except for temperatures lower than 50 K, the magnitude of the resistivity for the films with $x = 1.1-1.6$ concentrates in a narrow range between 2×10^{-2} and 6×10^{-3} Ω cm. The resistivity for the films does not show a systematic change with x . It may be, however, noteworthy that most of the films show metallic behavior except for $x = 1.2$ and 1.6. Furthermore, it should be noted that the resistivity for the films with $x = 1$ is higher than for the films with the adjacent compositions as shown in Figs. 9 and 10. Especially at the lowest temperature, the resistivity for the film with $x = 1$ is more than three orders of magnitude higher than for the films with $x = 0.8$ and 1.1.

These results of the resistivity measurements for the films with $x = 0.4-1.2$ described above show a qualitative agreement with those for the bulk polycrystalline samples annealed in oxygen,^{15,40} although the resistivity for the films is lower by one order of magnitude than for the bulk. The bulk samples showed metallic behavior with positive temperature coefficient of the resistivity for $x = 0.4-0.66$. The resistivity increased as x increased from 0.4 to 1, then decreased with increasing x from 1 to 1.2. These features agree with the results for the films in this study. On the other hand, the resistivity for the films are much different from that for the bulk samples quenched in air from 1200 °C.^{15,40} In the compositional region $x = 0.66-1.2$, the resistivity for the quenched bulk samples were higher than for the annealed

samples, and much more higher than for the thin films. The resistivity monotonically increases with x until $x=1.2$.

It has been reported^{15,40} that the quantity d in the oxygen composition $y=4-x/2+d$ is larger in the annealed samples than in the quenched samples for $x>0.4$.^{15,40} The annealed samples exhibited the same d value of about 0.11 in the composition range $x=0.33-1$ and an increase in d up to 0.33 for $x=1.2$. On the other hand, in the quenched samples, d gradually decreased with increasing x and vanished for x equal to and more than 1. From the comparison of the resistivity data, we expected that the oxygen compositions of the thin films with $x=0.4-1.2$ are close to those for the annealed ceramic samples. This is consistent with the comparison in the c -axis lengths discussed above. Moreover, the higher resistivity for the film with $x=1$ mentioned above also seems to be consistent with the abrupt change in d from 0.11 (for $x=0.33-1$) to 0.33 (for $x=1.2$) in the annealed polycrystalline samples.^{15,40}

For $x=1.3-1.6$, no transport data has been reported so far because of the formation of multiphase samples in the bulk synthesis.¹⁶ The resistivity data for films in this compositional region resemble those for the film with $x=1.1$ as mentioned above. Thus we expect that these films also have the oxygen composition of $4-x/2+d$ with d close to 0.33, i.e., the same d as for the annealed ceramic sample with $x=1.2$. This excess oxygen of d causes the hole doping into the system and makes the resistivity lower than for the films with $x=1$.

As shown in Fig. 11, it is remarkable that the films with $x=1.7$ show very high resistivity of 3 Ω cm at 300 K and 100 Ω cm at 100 K, which is much higher than that for other films. This composition is adjacent to the boundary between the K₂NiF₄-type phase and the Sr₂CuO₃-type phase as mentioned above. We speculate that the high resistivity may be explained by microscopic phase mixing due to a structural instability at this phase boundary, although no macroscopic phase separation is detected in the data for c_0 in Fig. 1.

Finally, we applied the activation-type model $\rho = A \exp(E/k_0T)$ and the variable range hopping (VRH) model $\rho = A \exp[(Q/k_0T)^{1/(n+1)}]$, where n is the dimension number, in order to fit the resistivity data for the films with $x=1-1.8$, excluding those with metallic behavior ($d\rho/dT > 0$). Although not conclusive, the VRH models with $n=2$ or 3 showed a fairly good fitting for all of the data.

$$(4)x=1.8-2.$$

In the compositional region $x=1.8-2$, it is suggested by the change in the c -axis length that the films have the Sr₂CuO₃-type structure with one-dimensional CuO chains. So we had better start from $x=2$. As seen in Fig. 11, the resistivity at 300 K for the film with $x=2$ is about 10^{-1} Ω cm in the semiconducting region, suggesting the holes are induced by excess oxygen to the CuO chains to some extent, but the number of holes is insufficient for metallic transport. A nonmetallic behavior in the temperature dependence of the resistivity was also reported for strongly oxidized bulk samples of Sr₂CuO_{3+ δ} , while the measurements of the magnetic susceptibility and the Seebeck coefficient

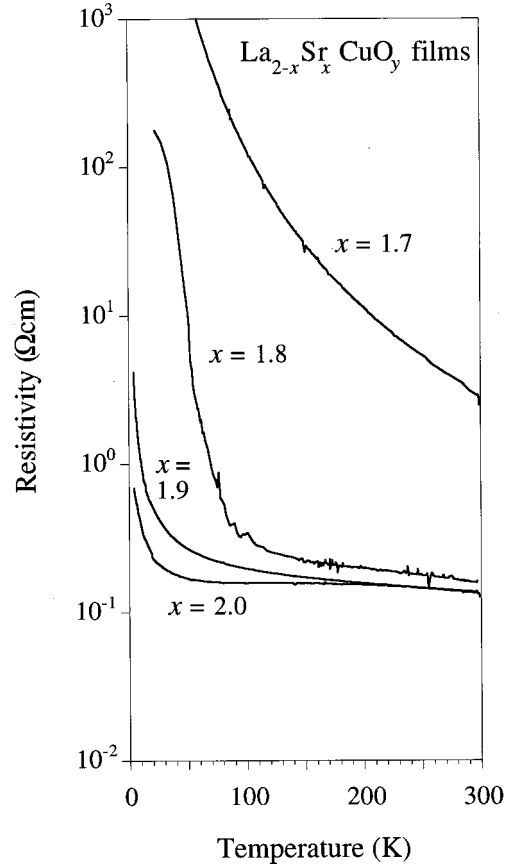


FIG. 11. Temperature dependences of the resistivity for La_{2-x}Sr_xCuO_y thin films with $x=1.7-2$ cooled in ozone. The films with $x<2$ were grown on (001) LaSrAlO₄ substrates. The film with $x=2$ was grown on a (100) SrTiO₃ substrate. The thicknesses of the films are 520 \AA for $x=1.7-1.9$, 170 \AA for $x=1.8$, and 300 \AA for $x=2.0$.

indicated the metallic nature of the compound.¹⁹ Decreasing x from 2 causes substitution of divalent Sr ions by trivalent La ions, resulting in the reduction of the number of holes and gradual increases in the resistivity to $x=1.8$, as shown in Fig. 11. The resistivity data for this composition range were also compared with the activation-type model and the VRH models with $n=1-3$. Although not conclusive again, the VRH model with $n=1$ showed good fitting.

Several films with $x=1.8-1.9$ were also cooled in oxygen in an attempt at electron doping of the CuO chains in Sr₂CuO₃ by the cation substitution without excess oxygen. However, those films appeared to decompose. The resistivity for these films was too high to be measured by our experimental setup, indicating that the attempt for electron doping was unsuccessful.

IV. SUMMARY

In summary, we obtained single-phase (001)-oriented thin films of LSCO for the entire compositional region $x=0-2$, including $x=1.3-2$, where multiphase formation has been reported for bulk samples. Based on the results of x-ray diffraction and the resistivity measurements for the films, we discussed the following points. (1) Because of the strain effect, T_c for the films on LSAO substrates is higher than for

the bulk samples. The observed correlation between T_c and c_0 suggests that the expansion in the c -axis direction is essential for the enhanced T_c in the films. We also found that a higher T_c is accompanied by a lower $\rho(0\text{ K})$, which is suggested to indicate the reduced local spin fluctuation. (2) The strain in the films seems to suppress the “1/8 anomaly.” (3) For $x < 0.15$, the cooling in ozone is effective in introducing excess oxygen into the films and results T_c higher than 40 K regardless of x . (4) For $x = 0.4 - 1.7$, the films have the K_2NiF_4 -type crystal structure with oxygen defects in the

CuO_2 planes. (5) In the compositional region $x = 1.8 - 2$, the films have the Sr_2CuO_3 -type structure with one-dimensional CuO chains, in which the number of holes is insufficient for metallic transport.

The present work suggests that thin-film technique is useful to increase T_c in HTSC and to search for superconductivity in materials difficult to be synthesized by bulk technique. Additionally, the T_c correlations with c_0 and $\rho(0\text{ K})$ observed in this study are clues to find out the key factors of T_c in HTSC.

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