Electron-doped superconductor $La_{2-x}Ce_xCuO_4$: Preparation of thin films and modified doping range for superconductivity

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We have investigated transport properties and a related electronic phase diagram of electron-doped $La_{2-x}Ce_xCuO_4$ (LCCO) thin films prepared by pulsed laser deposition. Using $BaTiO_3$ as a buffer layer, we could successfully extend the lower Ce composition limit for synthesis of a single-phase LCCO film down to $x=0.06$. Superconductivity in LCCO was found to occur within a Ce composition range $0.08 \leq x \leq 0.15$. The superconducting composition range is apparently shifted toward the lower Ce doping side, as compared with other electron-doped cuprate superconductors, such as $Nd_{2-x}Ce_xCuO_4$ (NCCO). In accord with this, the variations of the resistivity and the Hall effect as a function of Ce content x, are much larger than those of NCCO, tracking the shift of superconducting phase. Indeed, the transport properties of the LCCO films with the shifted optimum composition $x=0.11$ was found to be equivalent to those of the optimum NCCO ($x=0.15$). We discuss that this unusual phase diagram of LCCO originates from the reduction of the antiferromagnetic interaction as well as of the electron correlation strength.

I. INTRODUCTION

Electron-doped cuprate superconductors[1,2] in the $Ln_{2-x}Ce_xCuO_4$ (Ln=Nd, Pr, Sm, and Eu) family with the so-called T'-phase structure have been attracting considerable interest, because some properties are common to, but many are different from those of hole-doped cuprate superconductors. Among them, the most distinct feature is the phase diagram as a function of doping level; (i) a wide antiferromagnetic region,[3] (ii) a narrow Ce doping range for superconductivity, and (iii) absence of underdoped superconducting region.[2] The normal-state resistivity nearly proportional to T^2 is observed even at the composition with optimum T_C, which may suggest an *overdoped* character. Nevertheless, the superconducting order parameter of electron-doped cuprates has recently been confirmed to be of the same symmetry as those of hole-doped cuprates, namely $d_{x^2-y^2}$.[4-6] The resistivity measurements on $Pr_{2-x}Ce_xCuO_4$ (PCCO) films in high magnetic fields showed that the insulator-to-metal transition in the ground state occurs near the optimum doping level,[7] analogous to the hole-doped $La_{2-x}Sr_xCuO_4$ (LSCO).[8,9] This suggests that there is a glo-

bal electron–hole symmetry in doped Cu–O planes.[10]

Besides the above-mentioned similarities and dissimilarities between the electron- and hole-doping cases, the electron-doped cuprates, $Ln_{2-x}Ce_xCuO_4$, themselves exhibit an interesting variation of the physical properties with the change of Ln^{3+} ions. First, $Gd_{2-x}Ce_xCuO_4$ does not show superconductivity and the superconducting transition temperature T_C of the T'-phase superconductor increases with the increase of the ionic radius of Ln^{3+} ions.[11] Optical spectroscopy has proved that the antiferromagnetic interaction J and the charge transfer gap Δ decrease appreciably as the ionic radius of Ln^{3+} increases.[12,13] From these results, it is anticipated that the electronic parameters relevant to the superconductivity in the T'-phase cuprates strongly depend on the lattice parameters.

Among T'-$Ln_{2-x}Ce_xCuO_4$ systems, $La_{2-x}Ce_xCuO_4$ (LCCO) is unique, in that it is the only system which has larger Ln^{3+} ion than those of NCCO and PCCO. The T'-LCCO is known as a quasistable phase. The bulk samples have been prepared by using complicated synthetic process.[14,15] The single phase was formed only for a very narrow Ce composition range, $0.13 < x < 0.15$. The crystallin-

ity, however, was not good enough to conduct the physical property measurements. Recently, Naito and Hepp[11] reported the successful preparation of single phase T'-LCCO thin films. The thin films were stabilized on $SrTiO_3$ (STO) substrates utilizing the epitaxial effects, and the single phase was obtained for a wide Ce composition range, $0.08<x<0.22$. As compared with $Nd_{2-x}Ce_xCuO_4$ (NCCO) and PCCO, they found superconductivity over a remarkably wide composition range of $x=0.08–0.2$. An optimum T_C of 30 K, that is the highest among T'-phase superconductors, was observed at $x=0.11$. LCCO has the largest in-plane Cu–O bond length d among the T'-phase cuprate superconductors, and the optimum T_C value fits with the empirical trend of T_C vs d. From the wide composition range for superconductivity, we anticipate that LCCO may show an *underdoped* superconductivity, absent for the hitherto known electron-doped superconductors, NCCO and PCCO. In the former study[11] on T'-LCCO films, however, the Ce content of $x>0.08$ was required for the stabilization of the T'-LCCO films on the STO substrates, and the films with $x\leqslant0.08$ contained a T-phase (La_2CuO_4 type) form as the secondary phase. Thus, the exact lower limit of the Ce composition which can produce the superconductivity was not identified.

In this study, we have investigated the transport properties of the single phase T'-LCCO thin films. Using $BaTiO_3$ (BTO) as a buffer layer, the single phase T'-LCCO thin films were successfully obtained with the extended Ce composition range from $x=0.06$ (an underdoped insulator) to 0.16 (an overdoped metal). The difference of the phase diagram for superconductivity as a function of x was clearly discerned between LCCO and NCCO, i.e., the shift of the superconducting region toward the low Ce doping level in LCCO as compared with the case of NCCO. Intimately linked with this, the Hall coefficient and the behavior of the normal-state resistivity in high magnetic field for the shifted optimum composition $x=0.11$ were almost equivalent to those for the optimum doped NCCO and PCCO ($x=0.15$). We argue the possible origin of the different x dependence of the electronic phase diagram and the transport properties in LCCO from those of the conventional electron-doped superconductors.

II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

We deposited the LCCO films on (100) $SrTiO_3$ (STO) substrates by a pulsed laser deposition (PLD) technique utilizing a KrF excimer laser as an exciting light source. This technique was completely different from a molecular beam epitaxy (MBE) technique employed in a previous study by Naito and Hepp.[11] In MBE, cation elements were thermally evaporated from their metal sources. In the case of the PLD, a ceramic compound is usually used as a target (an evaporation source), and the compositional ratio of cation atoms in a film coincides with that in a target. In the present study, therefore, we used the stoichiometric ceramics of BTO and LCCO as targets. The base pressure of our deposition chamber was usually below 5×10^{-9} Torr. At first, a 20-nm-thick BTO film was deposited as the buffer layer at a substrate temperature (T_S) of 820 °C in an oxygen pressure (P_{O_2}) of

1 mTorr. Subsequently, LCCO was deposited at $T_S=700–780$ °C in $P_{O_2}=300$ mTorr. Typical thickness of LCCO film was 100 nm. After the deposition, T_S was changed to 650 °C and the films were annealed in the P_{O_2} range between 1×10^{-7} Torr and 1×10^{-6} Torr for 15 min to remove excess apical oxygens. This P_{O_2} range was optimized so as to obtain the highest T_C and the lowest normal-state resistivity (see the following). Incidentally, we found no appreciable change in T_C and the resistivity when the annealing time was altered from 15 to 60 min at 650 °C, indicating that the 15-min annealing is sufficient to ensure enough oxygen diffusion.

The T'-phase crystal structure of the films was confirmed by x-ray diffraction (XRD). The composition of cation elements was analyzed using inductively coupled plasma spectroscopy (ICP). The Ce/La ratios agree reasonably with the prescribed ones of the targets for all the analyzed films, while the $Cu/(La+Ce)$ ratio was $\sim10\%$ larger than the ideal value. We scrutinized the surface of the films using a scanning electron microscope to find many particle-like precipitates on the surface. Micro-auger spectroscopy confirmed that the particles were CuO. Thus, it is likely that a certain amount of excess copper atoms detected by the ICP analysis corresponds to these CuO particles. We believe that these CuO particles on the film surface do not give rise to any serious influence on the transport and superconducting properties of the thin films. The temperature dependence of the resistivity was measured by a standard four-probe method. To measure the Hall coefficient, the films were patterned into the Hall bars with the channel width of 100 μm and the length of 1 mm.

The single-phase T'-LCCO films were successfully synthesized down to $x=0.06$, which could not be obtained in the previous study.[11] Figure 1 (a) shows typical XRD patterns of the films. Even in the $x=0.06$ film, the XRD pattern exhibits (00l) peaks characteristic of the T' phase and not of the T-phase La_2CuO_4 (LCO). The lattice constant of c axis monotonically decreases from $x=0.06$ to 0.16, indicating the formation of solid solution [Fig. 1(b)]. Thus, the BTO buffer is considerably effective to stabilize the T' structure of LCCO, especially for lower Ce compositions. We suggest that the BTO ($a=3.99$ Å) buffer layer reduces the lattice mismatch between LCCO ($a=4.01$ Å) and STO ($a=3.905$ Å) and may restrain the nucleation of LCO phase ($a=3.81$ Å).

For the electron-doped superconductor, the removal of the excess oxygens at apical sites is essential to achieve superconductivity. It was reported that the superconductivity as well as the normal state properties strongly depend on the oxygen content.[16,17] To optimize the film quality, we annealed the films under various P_{O_2} conditions. Figure 2 exhibits the temperature dependence of the resistivity for the $x=0.15$ films annealed in various P_{O_2} from 1×10^{-7} to 1×10^{-3} Torr. The maximum T_C and the minimum resistivity at 300 K were simultaneously obtained in a P_{O_2} range between 5×10^{-7} Torr and 1×10^{-6} Torr. For other Ce contents, we confirmed that the optimum P_{O_2} range was quite

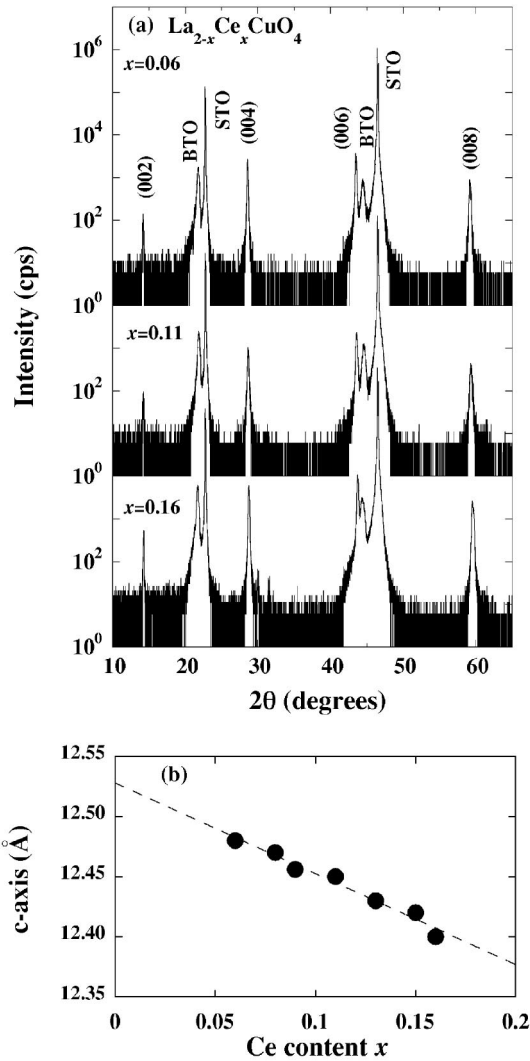FIG. 1. (a) X-ray diffraction patterns of $La_{2-x}Ce_xCuO_4$ films with $x=0.06$, 0.11, and 0.16. (b) c-axis lattice constant as a function of Ce content x.

similar, within the range between 1×10^{-7} and 1×10^{-6} Torr. In the following discussions on the doping dependence of the physical properties, all the results we present are those for the films that were *in situ* annealed under the optimum P_{O_2} condition.

III. RESULTS AND DISCUSSION

Figure 3(a) shows the temperature dependence of resistivity for the films with various Ce contents. As expected, the magnitude of normal-state resistivity decreases with increasing Ce content. The low-temperature resistivity of the $x=0.06$ film tends to diverge with decreasing temperature, indicating an insulating ground state. With increasing x, the resistive drop associated with superconductivity is first observed at $x=0.08$. The transition for $x=0.08$, however, is rather broad and the residual sheet resistance per CuO_2 plane (~ 32 kΩ) is larger than the critical sheet resistance of $h/4e^2$ (≈ 6.45 kΩ), which may suggest a filamental nature
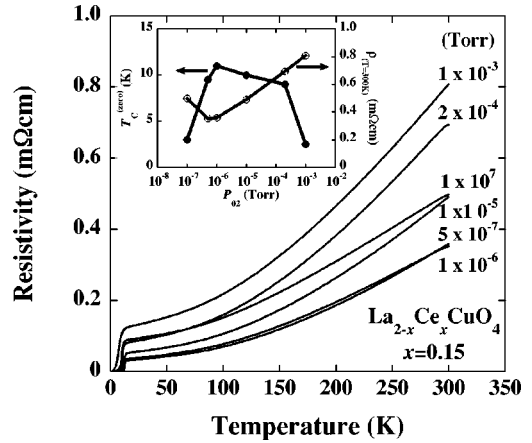

FIG. 2. Temperature dependence of resistivity for $La_{2-x}Ce_xCuO_4$ ($x=0.15$) films annealed in various oxygen pressure (P_{O_2}) at 650 °C. The inset shows P_{O_2} dependence of the zero resistance T_C ($T_C^{(zero)}$) and the resistivity (ρ) at $T=300$ K.

of superconductivity. Given the compositional inhomogeneity inherent in solid solution, the onset for the superconductivity in LCCO may be slightly larger than $x=0.08$. After a rather sharp rise of T_C with increasing x from 0.08, a maximum T_C is achieved for the $x=0.11$ films, where the onset and the zero resistance T_C are ~ 27 and 25 K, respectively. As x increases above 0.11, T_C eventually goes down. The $x=0.16$ film shows an incomplete resistance drop below $T \sim 3$ K. Because of the incomplete transition, we believe that the ground state of $x=0.16$ LCCO is a metallic but not-superconducting.[18] A superconducting-to-normal metal transition in overdoped region of LCCO, therefore, occurs between $x=0.15$ and 0.16.

Thus established phase diagram of LCCO as a function of Ce content x is demonstrated in Fig. 4. It is clear that the superconducting phase of LCCO occupies a distinctly different region from those of other electron-doped cuprate superconductors, such as NCCO and PCCO: The composition range for the superconductivity together with the optimum
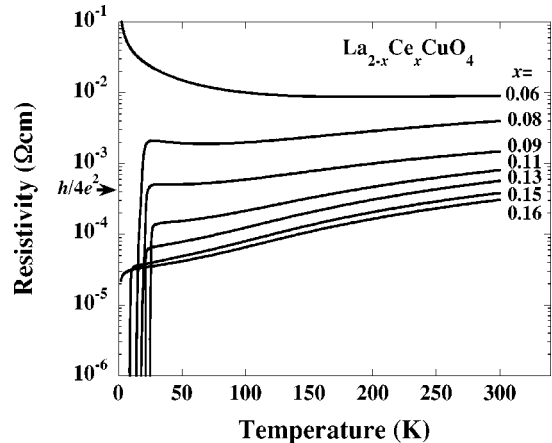

FIG. 3. Temperature dependence of resistivity for $La_{2-x}Ce_xCuO_4$ films with $x=0.06-0.16$. The films used for the resistivity measurements were annealed under the optimum P_{O_2} condition (see the text) at 650°C.
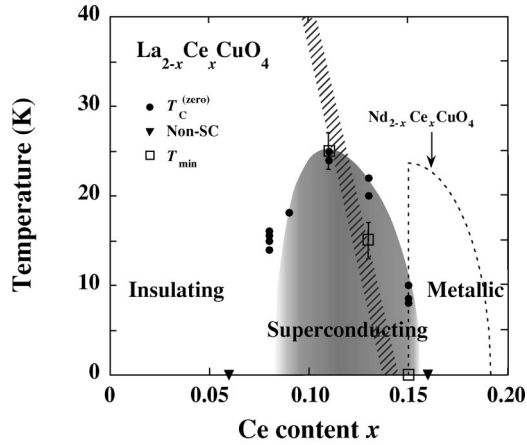
FIG. 4. Phase diagram determined from the resistivity data of $La_{2-x}Ce_xCuO_4$ films. The shaded area shows the superconducting region. The area surrounded by a dotted line shows the superconducting region of $Nd_{2-x}Ce_xCuO_4$ reported in Ref. 2. The squares and the hatched line represent the x dependence of insulator-to-metal crossover temperature observed in the temperature-dependent resistivity in magnetic fields.

FIG. 5. Temperature dependence of Hall coefficient of $La_{2-x}Ce_xCuO_4$ ($x=0.06–0.16$) and $Nd_{2-x}Ce_xCuO_4$ ($x=0.15$) films.

composition shifts significantly to lower Ce concentrations. The shift of the optimum composition was pointed out in a previous thin film study by Naito and Hepp.[11] Even in ceramic samples of NCCO, by partly substituting for Nd with La, a small but definite shift of the superconducting region with increasing d had been pointed out.[19–21] In these previous reports, it was discussed that the shift of the phase diagram might be due to the presence of excess electrons possibly generated by oxygen deficiencies at the tetrahedral sites in between the two La planes.

Another important feature seen in Fig. 4 is much narrower composition range for superconductivity than that reported by Naito and Hepp.[11] By comparing the phase diagram, we find that the width of the superconducting phase is as narrow as that of NCCO. This substantial difference from the previous work,[11] we believe, originates from the highly homogeneous distribution of dopant in the present films. Taking a look at the details of the LCCO phase diagram, the continuous increase of T_C in the underdoped side is clear, which at first glance seems to suggest the presence of the underdoped superconductivity. Considering the possible broadening of the phase boundary due to a compositional inhomogeneity, however, we cannot rule out at this stage the sudden appearance of superconductivity and the resultant absence of underdoped superconductivity as in the other electron-doped cuprates.[2] This issue should be tackled seriously in the future by further improving the homogeneity of samples.

In accord with the shift of the superconducting phase on the phase diagram, the x dependence of transport properties shows an appreciable change. In NCCO and PCCO, it is known that the normal state resistivity $\rho(T)$ shows a distinct T^2 behavior above the optimum composition of $x=0.15$. In the present LCCO system, $\rho(T)$ can be fitted with $\rho(T)=\rho_0+AT^2$ only above $x=0.11$. It should be emphasized that $x=0.11$ is the shifted *optimum* composition in the LCCO system. The composition range for T^2 resistivity in LCCO
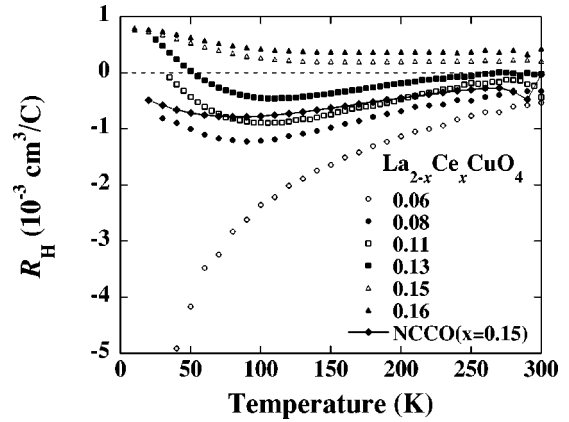
therefore tracks the superconducting phase.

Figure 5 shows the temperature dependence of Hall coefficient R_H for the LCCO films. The R_H for the film with $x \leqslant 0.11$ (optimum doping) has a negative sign, confirming the dominant electron contribution in the lightly doped region. As x increases, the R_H systematically increases and eventually changes its sign from negative to positive. As a function of temperature, the superconducting films with $x \geqslant 0.11$ show the characteristic upturn in R_H at low temperatures, and the sign changes from negative to positive with decreasing temperature. The positive R_H at low temperatures was observed commonly in the *superconducting* NCCO single crystals and films with $x \geqslant 0.15$,[7,16,17,22–26] and discussed in terms of a two-band model and an anomalous inelastic scattering of hole-like carriers.[22] As far as the gross feature is concerned, therefore, the variation of the doping dependence of $R_H(T)$ in LCCO is quite analogous to those of NCCO. However, it is clear that the variation in LCCO is much larger than that in NCCO. Indeed, the $R_H(T)$'s of the optimally doped LCCO ($x=0.11$) and NCCO ($x=0.15$) films are quite close to each other both in magnitude and temperature dependence. This result again suggests that the variation of transport properties as a function of x is essentially scaled by the location of the superconducting dome and/or the optimum-T_C composition.

Another x-dependent quantity of interest is the location of an insulator-to-metal transition for the ground state ($T=0$ K), which has been frequently discussed in connection with the quantum critical point.[27] Ando and co-workers[8,9] have investigated the low-temperature normal-state resistivity of hole-doped LSCO with the use of high magnetic fields to suppress the superconductivity. They found that in hole-doped LSCO the IM transition for the ground state occurs near the optimum doping level ($x=0.16$), i.e., inside the superconducting region. A similar behavior in the IM transition has also been observed in the electron-doped PCCO, suggesting the electron–hole doping symmetry of the CuO_2 planes for the ground states.[7]

We found that the IM transition point at $T=0$ K in LCCO shifts to the lower x side and positions within the superconducting region. Figures 6(a) and (b) display the resistivity at 0, 8, and 15 T as a function of temperature for the
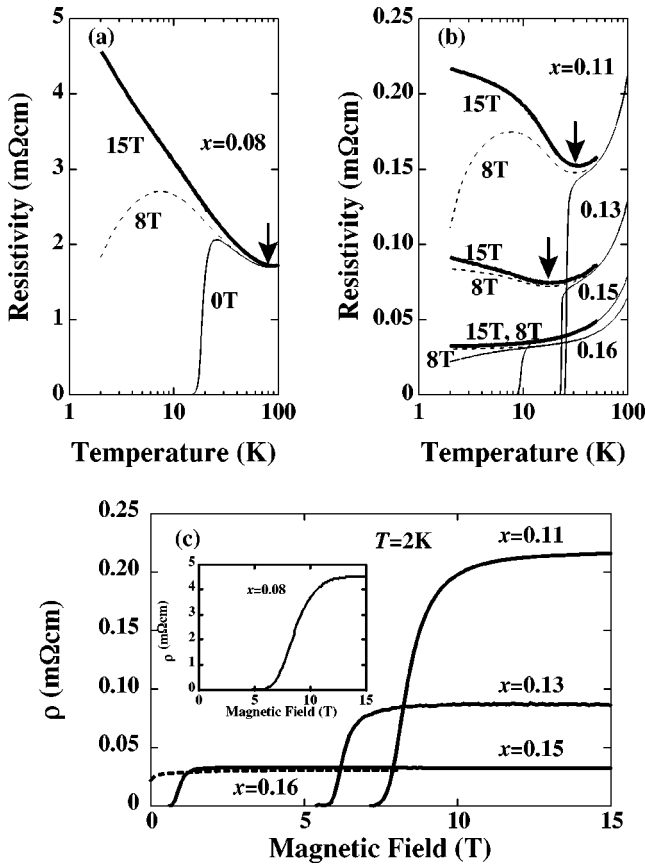
FIG. 6. Resistivity as a logarithmic function of temperature ($\log T$) for the films in magnetic fields of 0 T (thin lines), 8 T (dashed lines), and 15 T (thick lines); (a) $x=0.08$ and (b) $x=0.11$, 0.13, 0.15, and 0.16. Arrows indicate the resistivity minimum which represents the insulator-to-metal crossover. (c) Magnetic field dependence of the resistivity at $T=2$ K for the films with $x=0.08$ (inset), 0.11, 0.13, 0.15, and 0.16 (dashed line).

LCCO films with $x=0.08-0.16$. Magnetic field was applied parallel to the c axis of the films (normal to the surface of the films). Figure 6 (c) demonstrates that the superconductivity can be suppressed in a magnetic field of 15 T. For $x\lesssim0.13$, the temperature dependence of the resistivity in a magnetic field exhibits a crossover from metallic ($d\rho/dT<0$) to non-metallic ($d\rho/dT>0$) at a finite temperature ($T_{\min}$), as indicated by arrows in Figs. 6(a) and (b). The film with $x\geqslant0.15$ exhibits a metallic behavior down to 2 K in the magnetic field, and hence the ground state is metallic. This indicates that an IM transition in the ground state of LCCO occurs at a composition between $x=0.13$ and 0.15, which is inside the superconducting region. These behaviors can be summarized as an IM crossover line in the phase diagram (Fig. 4), which is a trace of $T_{\min}$ as a function of x. Clearly, the IM crossover line extrapolates to a composition between $x=0.13$ and 0.15 at $T=0$ limit.

Ando, Boebinger, and co-workers[8,9] have reported that in an underdoped and superconducting LSCO, both in-plane resistivity ρ_{ab} and out-of-plane resistivity ρ_c in high magnetic fields exhibit a logarithmic divergence ($\rho\propto\ln T$) at low temperatures. In the present study, as shown in Fig. 6(a), the

in-plane resistivity of $x=0.08$ under 15 T shows a logarithmic divergence as $T\rightarrow0$, analogous to LSCO.[28] In contrast to the $x=0.08$ film, the in-plane resistivity of $x=0.11$ and 0.13 under 15 T deviates from the logarithmic dependence and seems to have a finite value in the $T\rightarrow0$ limit, which may suggest a mixture of an insulator and a metal. In this sense, the actual IM transition may occur even at lower composition than $x=0.13$, which therefore is closer to the optimum doping. Incidentally, Boebinger et al.[9] showed that k_Fl ($=hc_0/\rho e^2$, where k_F, l, and c_0 are the Fermi wave number, the mean free path, and distance between CuO_2 plane, respectively) at the IM transition is estimated to be as large as 13 from the sheet resistance per CuO_2 plane. In the present study, the k_Fl value is estimated to be about 17 from the resistivity for the $x=0.13$ film at 2 K, which is close to that observed at the field induced IM transition of LSCO.[9]

Establishing the remarkable shift of the superconducting phase in the phase diagram of LCCO, we now discuss a possible origin of the shift. One possibility we have to consider first may be an inhomogeneity of the films. Since the T'-LCCO is a quasistable phase and barely stabilized in the form of a thin film, a phase separation into quasistable T'-LCCO and stable T-LCO might have occurred in our films. If this were the case, the phase separation would make the actual Ce content of LCCO phase larger than the Ce content determined by ICP analysis. Suppose the actual Ce content of LCCO phase in the $x=0.11$ film were 0.15, that is the optimum Ce content for NCCO, the volume fraction of LCO would be about 0.27. However, any appreciable peak assigned to the T-LCO phase was not detected in the XRD of the present LCCO films, which clearly excludes the possibility of the phase separation as the major origin of the shift of the optimum x.

Concerning oxygen deficiencies which possibly generate excess electron carriers, we believe that it is not a primal origin of the shift. In the present study, the films were annealed under the optimized P_{O_2} conditions ($1\times10^{-7}-1\times10^{-6}$ Torr) at 650 °C. From the oxygen nonstoichiometry studies on $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$,[29] the oxygen vacancies of the present films annealed at the above P_{O_2} condition can be estimated to be at least $\delta\sim0.03$. Previous reports on $Nd_{1-x-y}La_yCe_xCuO_4$ ceramics[19–21] suggested that the amount of the oxygen deficiencies increases with increasing the average size of Ln^{3+} ion for a constant annealing condition. Therefore, the estimate of oxygen vacancies, $\delta\sim0.03$, likely provides the lower limit. The oxygen vacancies with $\delta\sim0.03$ can provide 0.06 electrons to this system. Considering that this is the lower limit, at first glance, the oxygen vacancies would have accounted for the observed shift. If the oxygen vacancies were indeed the origin of the shift, the variation of the annealing condition ($P_{O_2}=1\times10^{-7}-1\times10^{-3}$ Torr, as shown in Fig. 2) and a resultant change of oxygen content ($\delta\sim0.03-0.015$, respectively) in this study would lead to an appreciable shift of the superconducting region upon changing the annealing condition. However, we found that the location of the optimum Ce doping level ($x=0.11$) *does not depend* on the annealing conditions, though the maximum T_C value systematically changes with varia-

tion of the annealing condition.

A more plausible origin of such a difference in the electronic phase diagram among the T'-phase compounds may be the critical dependence of the antiferromagnetic exchange interaction J and the charge transfer (CT) gap Δ on the change of lattice constants. Concerning the undoped (parent) T'-phase compounds, it was reported that J estimated from the two-magnon Raman spectra for a series of T'-Ln_2CuO_4 (Ln=Gd, Eu, Sm, Nd, and Pr) decreases with increasing the ionic radius of Ln^{3+}, i.e., increasing an in-plane Cu–O bond length d.[12] The Δ of this system as determined by the optical conductivity spectra decreases with increasing d.[12,13] The same trend was observed also in the pressure effect on Δ for T'-phase Eu_2CuO_4.[30] The variation of the correlation gap Δ in the parent insulator should reflect the electron correlation strength and dominate the critical doping level for the Mott transition, as demonstrated for the filling-control Mott transition in $LnTiO_3$.[31] From the empirical trends, it is estimated that J and Δ of T'-phase La_2CuO_4, which has never been synthesized but is considered as the parent compound of LCCO, would be smaller by $\sim 5\%$ and $\sim 9\%$, respectively, than those of Nd_2CuO_4. It is to be noted that the critical doping level for the occurrence of the Mott transition, or equivalently the appearance of superconductivity in the present case, is governed by the competition between the antiferromagnetic and superconductive phases. Then, because of the smallest J of T'-La_2CuO_4 in the T'-phase system, the antiferromagnetic region of LCCO as a function of Ce doping should become narrower in the doping level, as compared with the case of NCCO. Furthermore, the decrease of Δ is the cause of the decrease in the critical doping level for the filling-control Mott transition. Thus, the above two effects may lead to the shift of the superconducting region to the lower Ce side. This scenario seems to be closely linked with the facts that $Gd_{2-x}Ce_xCuO_4$ with the smallest d among the T'-phase cuprates shows no superconductivity and that the optimum T_C of T'-phase cuprates increases with increasing the ionic radius of Ln^{3+}.[11]

IV. SUMMARY

We have successfully synthesized thin films of single phase T'-structure $La_{2-x}Ce_xCuO_4$ (LCCO) ($x=0.06$–0.16) on $SrTiO_3$ substrates, using $BaTiO_3$ as the buffer layer. Superconductivity appears in the Ce composition range of $0.08 \leq x \leq 0.15$, and the film with $x=0.11$ has the optimum $T_C^{(\text{zero})}$ well above 25 K. The resistivity measurements under high magnetic fields have revealed that an insulator-to-metal transition in the normal state at $T=0$ for LCCO occurs near the optimum doping, analogous to the cases of hole-doped $La_{2-x}Sr_xCuO_4$ (LSCO) and electron-doped $Pr_{2-x}Ce_xCuO_4$ (PCCO) but with the different optimum doping level x. The overall phase diagram of LCCO is qualitatively similar to those of $Nd_{2-x}Ce_xCuO_4$ (NCCO) and PCCO, but the superconducting region is shifted toward the low Ce doping side. The modified electronic phase diagram of LCCO is likely ascribed to the reduction of the antiferromagnetic interaction as well as of the electron correlation strength due to the elongated in-plane Cu–O bond length in this compound.

ACKNOWLEDGMENTS

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