

**In situ epitaxial growth of superconducting La-based bilayer cuprate thin films**I. Tsukada,\* Y. Nagao,<sup>†</sup> and Yoichi Ando<sup>†</sup>*Central Research Institute of Electric Power Industry, 2-11-1 Iwado-kita, Komae, Tokyo 201-8511, Japan*

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We investigate the epitaxial growth of bilayer cuprate  $\text{La}_2\text{CaCu}_2\text{O}_{6+\delta}$  using pure ozone as an oxidant, and find that even the crystal with parent composition without cation substitution can show metallic behavior with the aid of epitaxial-strain effect. The hole concentration is controlled simply by excess-oxygen doping, and the films grown under the optimum conditions exhibit superconductivity below 30 K. This is the first result on the superconductivity of bilayer  $\text{La}_2\text{CaCu}_2\text{O}_{6+\delta}$  induced purely by the excess oxygen.

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Epitaxial growth technique is quite useful for the study of high- $T_c$  superconductors, because one can easily modify lattice parameters by choosing an appropriate substrate. In particular,  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO) thin films can have higher  $T_c$  than bulk crystals by adding in-plane compressive strain.<sup>1,2</sup> On the contrary to such a monolayer cuprate as LSCO, few results have been reported on the role of epitaxial strain in bilayer cuprates  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (YBCO) or  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  (BSCCO) so far, probably because no remarkable improvement of superconducting properties has been found in these compounds; Cu-O chain layers in YBCO or cleavable Bi-O layers in BSCCO may relax rapidly the lattice mismatch from the substrate in the initial growth stage. However, since bilayer cuprates show in general higher  $T_c$  than monolayer ones, it would be fascinating if a remarkable  $T_c$  enhancement is induced by the epitaxial strain.  $\text{La}_{2-x}(\text{Sr,Ca})_{1+x}\text{Cu}_2\text{O}_{6+\delta}$  (La2126) is a good bilayer compound for the study of epitaxial growth, because this compound has a simpler crystal structure than YBCO and BSCCO. A few results on thin-film growth of La2126 on  $\text{SrTiO}_3$  (100) have been reported,<sup>3,4</sup> but unfortunately superconducting films have never been obtained. As is widely known, La2126-type structure can be rather easily obtained by a conventional solid-state reaction method,<sup>5,6</sup> although postannealing under the high-pressure oxygen of 10–400 atm is indispensable to induce superconductivity.<sup>7,8</sup> The results of Refs. 3 and 4 imply that their oxidation techniques were not efficient enough to oxidize the films as high-pressure oxygen does. Thus, one needs to develop a special technique to oxidize samples. One of the good candidates for oxidizing gas is pure ozone, because its handling techniques have been well established for more than a decade,<sup>9,10</sup> and have recently been applied to synthesize new superconductors such as  $\text{Ba}_2\text{CuO}_{4-\delta}$  and  $\text{Sr}_2\text{CuO}_{4-\delta}$ .<sup>11,12</sup> It has been reported that chemical activity of ozone is higher than that of molecular oxygen at GPa pressure,<sup>13</sup> although the lifetime of ozone at high temperatures is quite short (e.g.,  $\sim 10^0$  s at 200 °C, and  $\sim 10^{-3}$  s at 500 °C).<sup>14</sup> In this paper we report a successful growth of superconducting La2126 thin films using pure ozone. In order to see the sole effect of oxidation by ozone, we concentrate on the parent composition,  $\text{La}_2\text{CaCu}_2\text{O}_6$  (LCCO), in this report. A more-detailed account of the results for Sr and Ca substituted compounds will be described elsewhere.

All the films were prepared by pulsed laser deposition (PLD). A nonsuperconducting polycrystalline target with the nominal composition of La:Ca:Cu = 2:1:2 was prepared by a

conventional solid-state reaction method. The target was ablated by KrF excimer laser ( $\lambda = 248$  nm) under pure ozone. It should be noted that we can access higher gas-pressure regime in a PLD chamber than in a conventional molecular-beam epitaxy (MBE) chamber. The ozone pressure for the present experiment was set to 15 mPa, which is higher by one order of magnitude than the typical pressure in MBE experiments. To control the oxygen contents, we change the temperature at which ozone is turned off ( $T_{\text{O}_3}$ ) during the cooling-down process. The substrate temperature during the growth is kept at 800 °C for all the films shown in this paper. The resistivity and Hall-coefficient measurements are done for samples mechanically patterned in a six-terminal shape in order not to add any heat-treatment process that might change the oxygen contents of the sample.

First, we tried to determine what substrate is suitable for LCCO thin films. Figure 1(a) shows the x-ray ( $\text{CuK}\alpha$ ) diffraction of LCCO films grown on  $\text{LaAlO}_3$  (100),<sup>15</sup>  $(\text{LaAlO}_3)_{0.3}(\text{SrAl}_{0.5}\text{Ta}_{0.5}\text{O}_3)_{0.7}$  (100), and  $\text{SrTiO}_3$  (100). (We will call them LAO, LSAT, and STO, respectively.) These films are fully oxidized with  $T_{\text{O}_3} = 65$  °C. The films grown on LAO and LSAT show highly  $c$ -axis oriented structure of La2126 phase. Both films are free from an impurity phase such as  $(\text{La,Ca})_2\text{CuO}_4$ ; the 002 peak of  $(\text{La,Ca})_2\text{CuO}_4$  is expected to show up at  $13.5^\circ < 2\theta < 14^\circ$ ,<sup>1</sup> which is completely absent in the films grown on LSAT and LAO. In contrast, the film grown on STO shows weaker diffraction intensities and includes  $(\text{La,Ca})_2\text{CuO}_4$  as an impurity phase (indicated by \*), which indicates that the lattice misfit is too large in this case, and the thermodynamically stable  $(\text{La,Ca})_2\text{CuO}_4$  may show up. Thus, the STO substrate, which was used in the previous experiments,<sup>3,4</sup> is considered to be inappropriate for the growth of LCCO thin films. The  $c$ -axis length of the film on LAO is estimated to be  $\approx 19.65$  Å, which is longer than that of the film on LSAT (19.62 Å). These results can be explained as the result of lattice mismatch: the misfit of LCCO is positive to LAO ( $\approx 1.20\%$ ) and negative to LSAT ( $\approx -0.89\%$ ). In this situation, it is expected that the LCCO film feels a compressive strain on LAO, while it feels a tensile one on LSAT; consequently, the film on LAO has longer  $c$ -axis length than that on LSAT. Our results are consistent with this picture, and therefore, we conclude that the epitaxial-strain effect works in LCCO films on LAO and LSAT. It should be noted that the  $c$ -axis lengths of both films are larger than that reported for polycrystalline

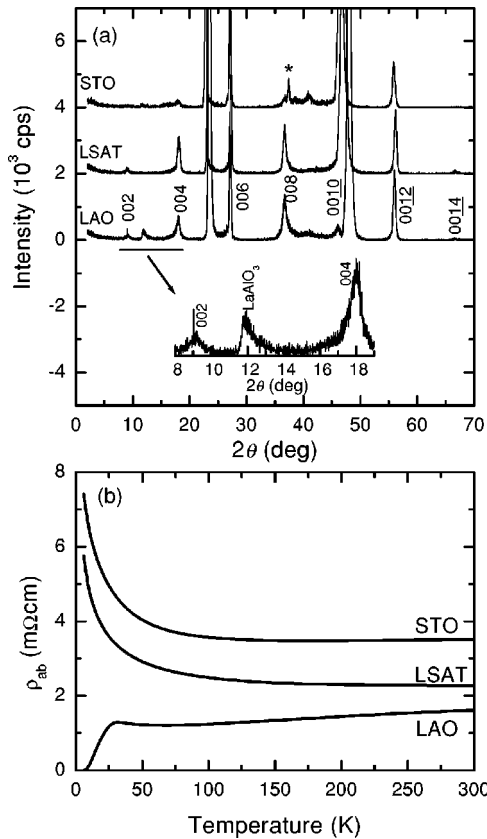


FIG. 1. (a) X-ray diffractions of  $\text{La}_2\text{CaCu}_2\text{O}_{6+\delta}$  thin films grown on  $\text{LaAlO}_3$  (100), LSAT (100), and  $\text{SrTiO}_3$  (100); the diffraction peak from  $(\text{La,Ca})_2\text{CuO}_4$  impurity phase is indicated by \*. Expanded diffraction pattern in the range  $8^\circ < 2\theta < 18^\circ$  is also shown for the film grown on  $\text{LaAlO}_3$ . (b) Temperature dependences of the resistivity of the corresponding films.

sample  $\text{La}_2\text{CaCu}_2\text{O}_{6.037}$ ,  $19.5169 \text{ \AA}$ , that were prepared under 1 atm oxygen.<sup>16</sup> This deviation is probably due to the difference in the amount of excess oxygen, and suggests that the ozone annealing is really effective in giving large amount of excess oxygen.

The substrate dependence appears also in the temperature dependence of the in-plane resistivity  $\rho_{ab}(T)$  as shown in Fig. 1(b). The film on STO shows semiconducting behavior as is easily expected from its poor crystallization suggested from the x-ray diffraction. What is interesting is that the films on LSAT and LAO exhibit contrasting behavior; the former shows semiconducting behavior down to 2.5 K, while the latter keeps metallic behavior and exhibits superconductivity below  $\approx 30$  K. The room-temperature resistivity of the superconducting sample (2 m $\Omega$  cm) is lower than that reported for single crystals.<sup>20</sup> However, we could not reduce the resistivity below 1 m $\Omega$  cm as other typical superconducting cuprates, which might be due to oxygen inhomogeneity in the sample. The observed substrate dependence is probably due to the directions of strain as was observed in LSCO thin films;<sup>1,2</sup> the compressive strain is helpful in enhancing metallic behavior while the tensile strain gives the opposite effect. However, it is not so simple to understand from a microscopic viewpoint that similar epitaxial-strain effects are observed both in monolayer LSCO and in bilayer LCCO: In

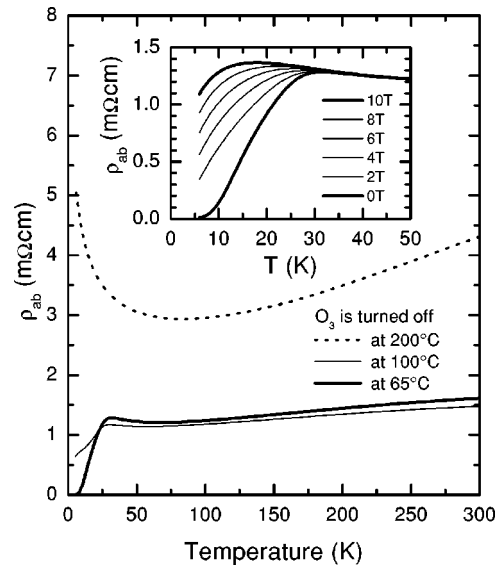


FIG. 2. Temperature dependences of the resistivity of  $\text{La}_2\text{CaCu}_2\text{O}_{6+\delta}$  thin films prepared at different  $T_{\text{O}_3}$ . The film prepared with  $T_{\text{O}_3} = 200^\circ\text{C}$  shows an insulating behavior, while those prepared with  $T_{\text{O}_3} = 100^\circ\text{C}$  and  $65^\circ\text{C}$  show superconductivity below  $\approx 30$  K.

LSCO, the characteristic tilting of the  $\text{CuO}_6$  octahedra, which is believed to dominate  $T_c$ , can be controlled by the epitaxial strain. On the other hand, such a characteristic structure is absent in LCCO, and we need further studies on structural analysis.

According to the above results, we chose the LAO substrate for further study, in which we tried to control the amount of extra oxygen. Figure 2 shows the  $T_{\text{O}_3}$  dependence of  $\rho_{ab}(T)$ . If we turn off ozone at  $T_{\text{O}_3} = 200^\circ\text{C}$ , which is typical for the growth of LSCO films with ozone as an oxidant, superconductivity does not appear.  $\rho_{ab}(T)$  exhibits metallic behavior down to  $\approx 80$  K, but resistivity upturn appears in the lower-temperature region. This temperature dependence is similar to that reported for  $\text{La}_{2-x}\text{Ca}_{1+x}\text{Cu}_2\text{O}_{8+\delta}$  ceramic samples annealed under 1–2 atm oxygen,<sup>8,17</sup> but is more metallic than that of the as-grown bulk crystals of  $\text{La}_{1.90}\text{Ca}_{1.10}\text{Cu}_2\text{O}_6$ .<sup>20</sup> By decreasing  $T_{\text{O}_3}$  to  $100^\circ\text{C}$ ,  $\rho_{ab}(T)$  decreases significantly and superconductivity shows up; the room-temperature resistivity decreases roughly by three times, and the resistivity drop appears around 30 K. However, this film does not show zero resistivity above 2.5 K, which suggests that the superconducting regions are segmented. Only after reducing  $T_{\text{O}_3}$  to  $65^\circ\text{C}$ , we could obtain zero resistivity at  $\approx 5$  K. We emphasize that this is an important result to observe zero resistivity in LCCO. Although Fuertes *et al.*<sup>16</sup> have reported a slight decrease of ac magnetic susceptibility below 45 K for ceramic LCCO, they observed neither metallic nor superconducting behavior in resistivity measurements, and bulk superconductivity was not confirmed. In order to confirm the presence of bulk superconductivity, we have applied magnetic field along the  $c$  axis (inset of Fig. 2), and have observed a typical  $T_c$  suppression by the magnetic field. Super-

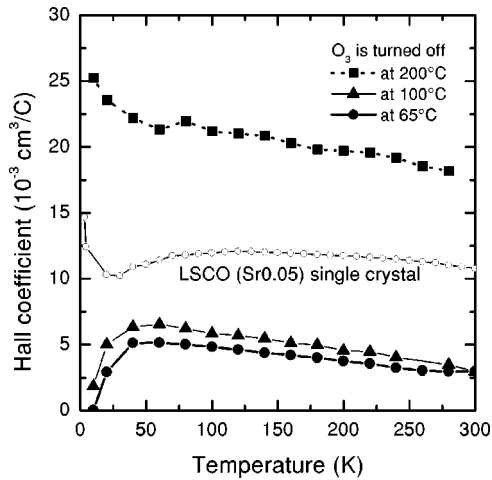


FIG. 3. Temperature dependences of the Hall coefficient of  $\text{La}_2\text{CaCu}_2\text{O}_{6+\delta}$  films. The Hall coefficient of the insulating film prepared at  $T_{\text{O}_3} = 200^\circ\text{C}$  exceeds  $1 \times 10^{-2} \text{ cm}^3/\text{C}$  at room temperature, while those of superconducting films are  $\approx 3 \times 10^{-3} \text{ cm}^3/\text{C}$  at room temperature. The data of single crystal  $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$  are taken from Ref. 18; this gives an approximate boundary of the carrier concentration between insulating and superconducting phases for LSCO.

conductivity remains even at  $H = 10 \text{ T}$ , which may reject the possibility of filamentary superconductivity. It should be noted that the difference between the films prepared at  $T_{\text{O}_3} = 65^\circ\text{C}$  and  $100^\circ\text{C}$  is found only in zero-resistivity temperature, while the magnitude of the normal-state resistivity and the  $T_c$  onset are almost unchanged. Therefore, decreasing  $T_{\text{O}_3}$  from  $100^\circ\text{C}$  to  $65^\circ\text{C}$  does not seem to change the carrier density drastically. One possibility is that by lowering  $T_{\text{O}_3}$  the distribution of extra oxygen becomes more homogeneous, but this should be confirmed experimentally.

The change of carrier concentration is confirmed more directly by a Hall-effect measurement, where we found the results being consistent with the behavior of  $\rho_{ab}(T)$ . Figure 3 shows the temperature dependence of the Hall coefficient  $R_H$  of the films shown in Fig. 2. The film prepared at  $T_{\text{O}_3} = 200^\circ\text{C}$  seems to have insufficient amount of holes;  $R_H$  exceeds  $1 \times 10^{-2} \text{ cm}^3/\text{C}$ . This value is typical for LSCO with  $x = 0.05$ , which is nonsuperconducting.<sup>18</sup> Once we decrease  $T_{\text{O}_3}$  to  $100^\circ\text{C}$ ,  $R_H$  remarkably decreases to the order of  $10^{-3} \text{ cm}^3/\text{C}$ . The films prepared at  $T_{\text{O}_3} = 100^\circ\text{C}$  and  $65^\circ\text{C}$  have almost the same  $R_H \approx 3 \times 10^{-3} \text{ cm}^3/\text{C}$  at room temperatures, and no remarkable difference is found between them down to 20 K. This is consistent with the resistivity data. The rapid decrease at  $T < 40 \text{ K}$  is due to the superconducting transition.

We can roughly evaluate the strength of oxidation by comparing the measured  $R_H$  with reported values. Nishikawa *et al.*<sup>19</sup> reported the Hall coefficient for a polycrystalline  $\text{La}_2\text{CaCu}_2\text{O}_6$  sample annealed under 20 atm oxygen. They reported  $R_H \approx 7 \times 10^{-3} \text{ cm}^3/\text{C}$  at room temperature, which is higher than that of our films prepared at  $T_{\text{O}_3} \leq 100^\circ\text{C}$ . This implies that the ozone annealing down to  $100^\circ\text{C}$  or lower is more effective than the annealing in 20 atm oxygen.

Now let us discuss the role of excess oxygen on hole doping. The first report on superconductivity in La2126 gave us an impression that the Sr substitution of La was indispensable for superconductivity,<sup>7</sup> and more detailed systematic studies on  $\text{La}_{2-x}\text{Ca}_{1+x}\text{Cu}_2\text{O}_{6+\delta}$  also demonstrated that  $T_c$  increased with increasing  $x$  when annealed under 10–20 atm oxygen.<sup>8</sup> In the latter case, however,  $T_c$  and the magnitude of resistivity seem to approach certain saturation values upon increasing the annealing pressure to 400 atm, which implies that the obvious  $x$  dependences are diminished when the excess oxygen is fully added. Similar results were obtained for single crystals annealed in 400 atm oxygen.<sup>20</sup> Therefore, we had better conclude that the Ca or Sr concentration is not a good measure of hole density, but rather a complicated combination of alkaline-earth substitution and high-pressure annealing determine  $T_c$  and the transport properties in La2126 compounds.<sup>21</sup> This consideration was supported by a Hall-effect measurement;<sup>19</sup> it was reported that  $R_H \approx 7 \times 10^{-3} \text{ cm}^3/\text{C}$  for pure  $\text{La}_2\text{CaCu}_2\text{O}_6$  was suppressed only to  $R_H \approx 4.5 \times 10^{-3} \text{ cm}^3/\text{C}$  for  $\text{La}_{1.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_6$ . This change is far smaller than that expected from the Ca concentration by using the simple formula  $R_H = 1/(ne)$ , where  $n$  and  $e$  are hole density and electric charge, respectively. It is likely that a non-negligible number of holes doped by Ca substitution is compensated by a decrease of excess oxygen, and the measured Hall coefficient becomes far larger than that expected from the Ca concentration.

In the present case, the hole density is simply dominated by the amount of excess oxygen, which will be useful to establish a hole-density vs  $T_c$  phase diagram for La2126. As is suggested by Fig. 3, we can use the Hall coefficient as a measure of hole concentration, even though the exact amount of excess oxygen remains unknown. In that sense, our results are similar to those reported for  $\text{La}_{1.89}\text{Ca}_{1.11}\text{Cu}_2\text{O}_{6+\delta}$  single crystals,<sup>22</sup> where the authors investigated in detail the annealing pressure dependence of the resistivity and the Hall coefficient. Our advantage over the bulk crystals is the absence of cation substitution that might introduce crystallographic disorder. If we compare the Hall coefficient at room temperature between  $\text{La}_{1.89}\text{Ca}_{1.11}\text{Cu}_2\text{O}_{6+\delta}$  single crystals<sup>22</sup> and our films, the hole concentration of our films prepared with  $T_{\text{O}_3} = 65^\circ\text{C}$  is almost the same as that of the single crystals annealed at 300 atm oxygen. This indicates that the ozone annealing in the vacuum chamber is comparable to the high-pressure oxygen of 100 atm order. For bulk samples, 400 atm might be the highest oxygen annealing pressure by hot isostatic pressure, but this pressure seems to be still insufficient to obtain the optimally doped samples. On the other hand, the ozone pressure for this study is set to 15 mPa, but this is not the upper limit. It is technically possible to increase the ozone pressure higher than 15 mPa, which seems to be the only way to obtain not only to the optimally doped but also to the overdoped samples of La2126 compounds.

Finally, we briefly mention where the excess oxygen goes. It was confirmed for  $\text{La}_{1.82}\text{Ca}_{1.18}\text{Cu}_2\text{O}_{6+\delta}$  (annealed at 400 atm oxygen) by neutron diffraction<sup>23</sup> that the excess oxygen is located between two neighboring  $\text{CuO}_2$  planes. Thus, it is

natural to expect that the excess oxygen is located at this position in our films also. However, we cannot believe that all of the excess oxygen occupy this position. According to Ref. 23, the  $c$ -axis length of the sample with excess oxygen is longer only by  $\approx 0.005$  Å than that of the sample without excess oxygen. In contrast, our LCCO films have far longer  $c$ -axis length regardless of substrates compared to the bulk LCCO samples;<sup>16</sup> even the  $c$ -axis length of the film on LSAT, which feels an in-plane tensile strain, is longer by  $\approx 0.11$  Å than that of the bulk samples. Thus, it is difficult to attribute the observed remarkable elongation of the  $c$  axis only to the oxygen between the neighboring  $\text{CuO}_2$  planes. It is rather likely that the excess oxygen goes also into the interstitial sites at  $\text{La}_2\text{O}_2$  blocks such as in  $\text{La}_2\text{CuO}_{4+\delta}$ ; the elongation of the  $c$ -axis length by 0.04–0.06 Å was reported for  $\text{La}_2\text{CuO}_{4+\delta}$ ,<sup>24</sup> which suggests that the remarkable elongation of the  $c$ -axis length in the present case is due to the same mechanism.

In any case, the ozone-annealed LCCO parent compound provides a unique opportunity for the study of bilayer cuprates, where the carrier concentration can be widely controlled without cation substitution. It was discussed that the cation substitution introduces “quenched” disorder while the

oxygen intercalation gives “annealed” disorder,<sup>25</sup> and the latter seems to give much benign influence on the structure of  $\text{CuO}_2$  planes. Such a situation has never been realized in bilayer YBCO, because the change in oxygen contents is always accompanied by the change in transport properties of Cu-O chain layer, and thus, one cannot purely observe the response of  $\text{CuO}_2$  bilayers. We can tune the transport properties of the LCCO films in a wide range from insulator to superconductor, which provides a more ideal situation than the extensively studied YBCO.

In summary, we have succeeded in growing superconducting  $\text{La}_2\text{CaCu}_2\text{O}_{6+\delta}$  thin films by choosing an appropriate substrate and by performing a strong oxidation using pure ozone. As was reported for monolayer cuprate films, the slight compressive strain along the in-plane direction is found to be helpful to make  $\text{La}_2\text{CaCu}_2\text{O}_{6+\delta}$  metallic. The low-temperature ozone annealing is found to be comparable to or more effective than high-pressure oxygen annealing. Our next step is to extend target compounds to multilayer cuprates where the combination of epitaxial strain and the strong oxidation will become more important to obtain higher  $T_c$ .

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