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Time Effect in Chemical Oxidation of La$_2$CuO$_4$ Epitaxial Thin Films

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A series of LCO epitaxial thin films chemically oxidized by NaClO at 40 °C with different oxidation times ranging from 3 to 48 h have been prepared. The results demonstrate that, unlike powder samples, chemical oxidation of LCO thin films shows strong time effect. That is, resistances of the treated films exhibit initially semiconducting behavior and convert into superconducting behavior gradually with increasing oxidation time. With further increasing oxidation time, the resistances return to semiconducting behavior again. This effect was found to originate from the lanthanum deficiency in the topmost layer of the film that causes an insulating layer in the surface of the film, which seriously affects the superconductivity. The origin of lanthanum deficiency is also discussed.

Introduction

High-temperature superconductivity was first observed in the La$_2$CuO$_4$ (LCO) system, which has remained of central interest owing to its compositional and structural simplicity.[1] The material itself is a semiconductor and can be converted into a superconductor after accepting excess oxygen. The oxidation has usually been carried out by heat treatment under high oxygen pressure at elevated temperatures.[2−5] A French group[6−8] indicated that by using an electrochemical technique LCO can be oxidized in an aqueous base at or near room temperature. Rudolf et al.[9] and subsequently Takayama-Muromachi et al.[10,11] showed that superconductivity can be induced into LCO at room temperature by chemical oxidation utilizing proper oxidizers. Among the above oxidation methods, the chemical oxidation method is the simplest and most convenient in operation and thereby has been widely used to get oxygen over-stoichiometric in LCO-based materials.[12−21] Compared with the powder samples, LCO thin films are very difficult to be oxidized in an in situ deposition chamber, because their oxidations need a strong oxidizing environment provided by active oxygen, such as atomic oxygen[22] or ozone.[23] Hence, it is important to oxidize LCO films in an ex situ, postdeposition process. Locquet et al.[24,25] and Lees et al.[26,27] illustrated, respectively, that electrochemical oxidation and fluorination methodology could be used to controllably oxidize thin films of cuprate materials. Chemical oxidation was first extended to LCO films by Lees et al.[28] using an aqueous sodium bypobromite (NaBrO) solution. Recently,[29] we have successfully induced superconductivity in LCO films by chemical oxidation using sodium hypochlorite (NaClO) solution as the oxidizing agent. Systematic studies demonstrate that the oxidizing behavior of LCO epitaxial thin films differs dramatically from their bulk counterparts. It was found[19,20] that the content of excess oxygen in the chemical oxidized LCO powder sample increases with oxidation time, which versus the oxidation time obeys the law of second exponential decay. In LCO epitaxial thin films, however, one surprising feature is that there exists a critical oxidation time at which both conductivity

and superconductivity reach their optimum values, while over this time, conductivity comes back gradually to its semiconducting behavior as it does before oxidation, and superconductivity has been screened by this semiconducting behavior. In the present work we have discussed in details about this effect.

Results and Discussion

The epitaxial LCO films for use in the chemical oxidation process were fabricated by pulsed laser ablation deposition on LaAlO$_3$ (LAO) substrates. For details on sample preparation and experiments, see ref 29. Figure 1a shows a typical indexed X-ray-diffraction pattern from a parent LCO thin film. The sole presence of (00*l*) reflections in the pattern shows that the film consists of entirely *c*-axis-oriented grains. Figure 1b shows a rocking curve measured for the (004) reflection, with a full width at half-maximum equal to 0.28°. This narrow value reveals that the LCO film is well-oriented normal to the substrate surface. The visible splitting of the rocking curve is due to the twin boundary in the LAO substrate. The results of the two-point contact resistance at room temperature as a function of oxidation time are shown in Figure 2. With increasing oxidation time, the resistance decreases initially, passes through a minimum, and then increases for further oxidation time. This fact implies that there exists an optimum oxidation time, which is about 7 h, for chemical oxidation of LCO thin films. Figure 3 shows the temperature dependence of resistance (measured using four-point method) for samples oxidized at 40 °C with different oxidation intervals. The 3 h oxidized sample shows semiconducting behavior, evidencing that 3 h oxidation is too short to introduce enough excess oxygen into the film. When oxidation time is prolonged to 6, 12, and 18 h, the oxidized samples exhibit superconducting transitions all at about 32 K. This transition temperature is consistent with the previous reports[30,31] and is known as 32 K phase. Compared with the 6 h and 12 h oxidized samples, the superconducting transition of the 18 h oxidized sample occurs in an insulating background and becomes wider, indicating both conductivity and superconductivity inferior. The resistance of the 24 h oxidized sample comes back to semiconducting behavior again. Superconducting transition of this sample can only be seen as a hump around 32 K marked by an

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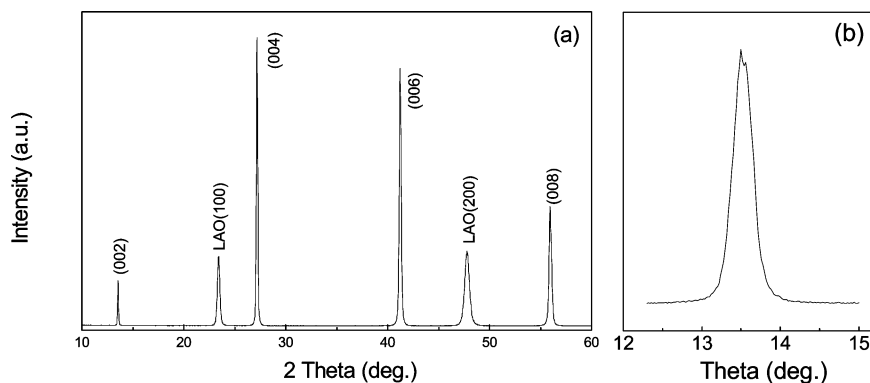
Figure 1. (a) Typical X-ray-diffraction pattern; (b) rocking curve measured for the (004) reflection for a parent LCO thin film.
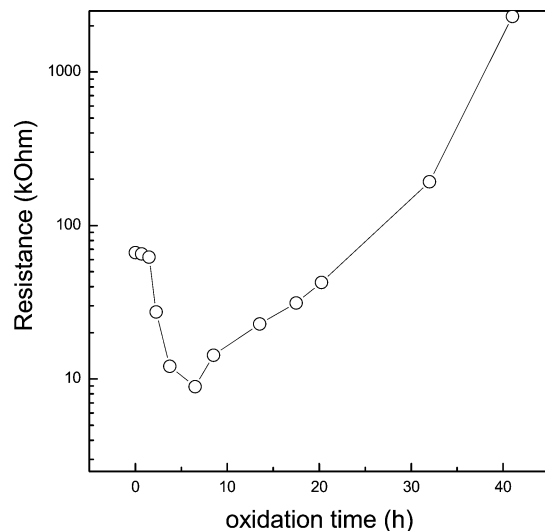

Figure 2. Time dependence of the two-point contact resistance measured at room temperature, shown in a half-logarithmic representation.

arrow. The resistance of the 48 h oxidized sample, however, is too large to be measurable reflecting an insulating feature of the sample. But the magnetic susceptibility measurement of the 48 h oxidized film shown in Figure 4 reveals a superconducting transition of about 21 K. The degeneracy of superconductivity is similar to that of the over-doped $La_{2-x}Sr_xCuO_4$ and will be discussed later. Here we refer to the 48 h oxidized film as the "over-oxidized" sample. Because the four-point method was performed by contacting the copper wires pressed onto the film surface, therefore, it gives the information of the topmost layer of the film. Magnetic measurement, however, gives the total information of the sample measured. Thus, we can come to the conclusion that an insulating layer is formed in the topmost of the film in "over-oxidized" sample, while the internal part of the film still remains superconducting state. This insulating layer was also observed in electrochemical oxidized LCO films by Daridon et al.[32] and in ozone oxidized films by Sato et al.[23] in an in situ deposition process.

To get further information of the topmost surface layer during chemical oxidation, experiments with scanning Auger spectroscopy (PHI-610/SAM; the scanned spot area was 1×1 mm^2; the accelerating voltage and current of the primary electron beam were 3 kV and 25 mA) have been performed on LCO films treated with various oxidation times. For clarity, only the results of the 3, 12, and 24 h oxidized samples are shown in Figure 5. The inset shows the Auger depth profiles, from which some features can be extracted. First of all, the ratio of La:Cu is not 2:1, because the atomic Auger sensitivities of La and Cu are
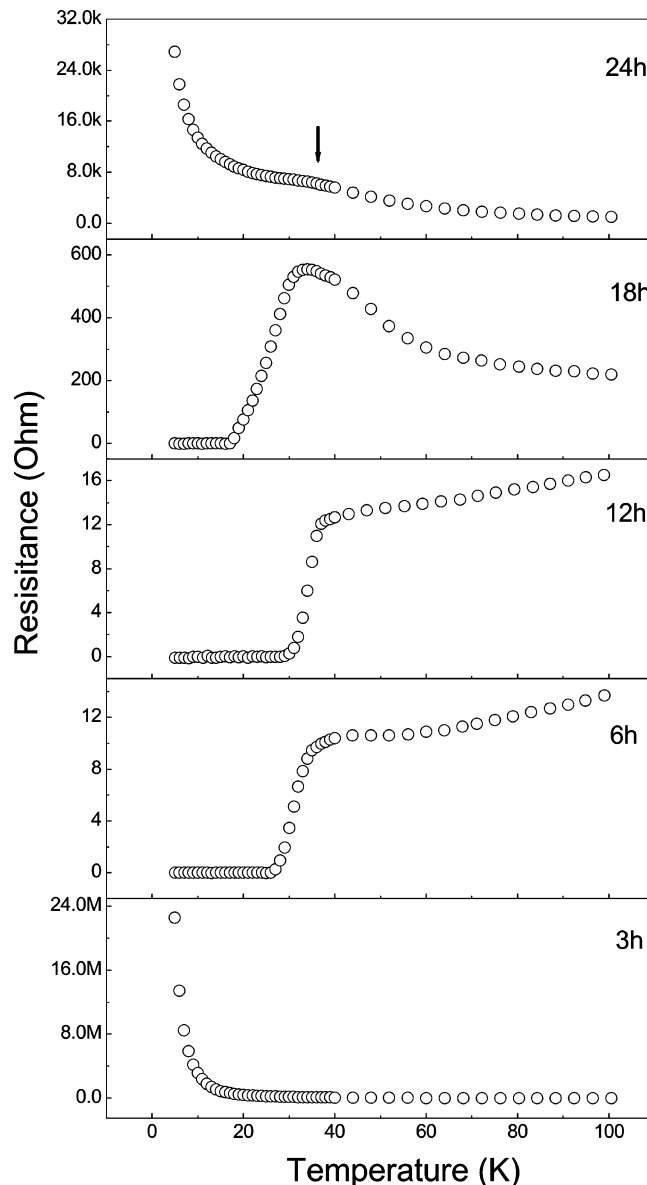

Figure 3. Temperature dependence of resistance (four-point method) for epitaxial LCO films treated with various oxidation intervals showing in each figures.

different. Second, the 24 h oxidized sample shows a decrease of lanthanum signal at the surface of the film. Meanwhile, the surface Cu-rich signal can also be clearly seen in this figure. Third, with increasing oxidation time, the thicknesses of the oxidized films become thinner as indicated by the rapid changes of the La or O compositions. The main panel of Figure 5 shows
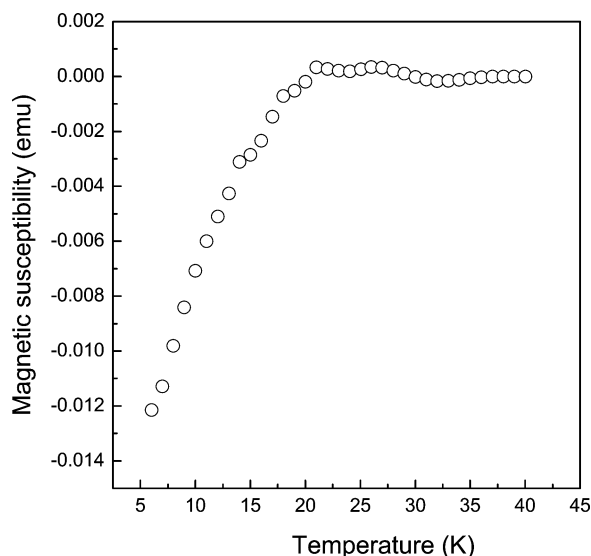
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Figure 4. Magnetic susceptibility vs temperature for the 48 h oxidized film.
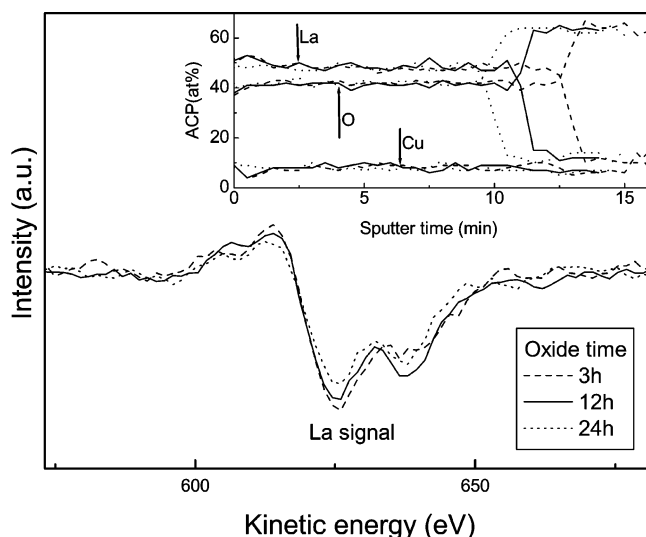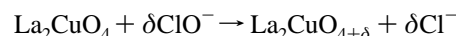

Figure 5. Differential Auger intensities obtained on the surface for LCO films with oxidation times of 3, 12, and 24 h. These intensities have been normalized with the oxygen peaks at 511 eV of each sample. The inset shows the Auger depth profiles of these films.

the results of the differential Auger intensities measured on the topmost surface of the treated films. These intensities have been normalized with the oxygen peaks at 511 eV (not shown here) of each sample. It is visible that the relative intensity of the La signal, namely, La concentration, decreases with increasing oxidation time. Therefore, it may be deduced that, during the chemical oxidation process, lanthanum deficiency in the surface results in an insulating layer of the film, and thus affects the observed superconductivity measured by the four-point method. The thickness of the insulating layer estimated from the Auger depth profile (the inset of Figure 5) is about 40 nm and much larger than that of the ozone oxidized film[23] which was less than 5 nm.

It was reported that alkali hypochlorites are able to react with LCO.[9] The aforementioned third feature is also strong indicative of the reaction between the oxidizing agent and the surface of the film. Thus, one possible origin of the lanthanum deficiency is that it might dissolve into the solution due to the formation of lanthanum chlorite and/or lanthanum hydroxide. On the other hand, the two-step insertion mechanism[22] may be a possible

process of the oxygen doping. That is, first, oxygen is transported into the surface of the film, via the following chemical reactions:

$$La_2CuO_4 + 2\delta OH^- \rightarrow La_2CuO_{4+\delta} + \delta H_2O + 2e^-$$

$$La_2CuO_4 + \delta ClO^- \rightarrow La_2CuO_{4+\delta} + \delta Cl^-$$

Second, oxygen diffuses into the internal part of the film through various defects as oxidation channels;[33] hence, the content of excess oxygen decreases with the depth. This underlies the fact that the superconductivity of the "over-oxidized" film is inferior.

The topmost layer with lanthanum deficiency acts as a protect layer which limits the interior part of the film for further reaction with the agent. This is not a limitation in powder samples since the randomly oriented crystallites cannot form a cover layer on the surface, thereby allowing the chemical reaction and oxygen diffusion. So time effect does not exist in oxidized powder samples.

It is quite natural to expect that time effect and the optimal oxidation conditions depend strongly on film thickness and quality, because the competition between La loss and oxidation, namely, the competition between semiconducting behavior and superconducting behavior will vary significantly with film thickness. To check on this point, we have fabricated LCO films with thickness varying from 50 to 250 nm and chemically oxidized for 12 h. Figure 6 shows the resistance vs temperature curves for the oxidized films with different thicknesses. The film with thickness of 250 nm exhibits superconductivity at about 32 K, whereas the film with 150 nm thicknesses shows complete semiconducting behavior. The resistances of the oxidized 100 nm and 50 nm thick films are too large to be measurable. These results prove the presence of competition between semiconducting behavior and superconducting behavior during the oxidation process. For obtaining optimal superconductivity in the LCO film, the chemical oxidation time must be long enough to achieve the best oxidation status, which inevitably introduces semiconducting behavior in the topmost layer of the film. Hence, the film must be thick enough to compensate the electrical property degradation.

On the other hand, the significant deference in chemical oxidation behavior between LCO powder samples and epitaxial thin films implies that grain alignment, namely, the film quality, has a marked effect on this behavior. Indeed, time effect does not appear in c-axis textured LCO thin films prepared by NaClO oxidation. These results will be reported elsewhere.[34]

Conclusion

In conclusion, superconductivity has been introduced into epitaxial LCO thin films through the process of postdeposition chemical oxidation using a NaClO solution. The systematical change in superconductivity of the oxidized films suggests that there exists an optimum oxidation time at which superconductivity reaches an optimum value, whereas beyond this time, superconductivity becomes inferior. This time effect was found to be caused by the chemical reaction between the topmost layer of the film and the agent solution which results in an insulating layer due to the lanthanum deficiency in the topmost layer of the film that seriously affects the superconductivity.

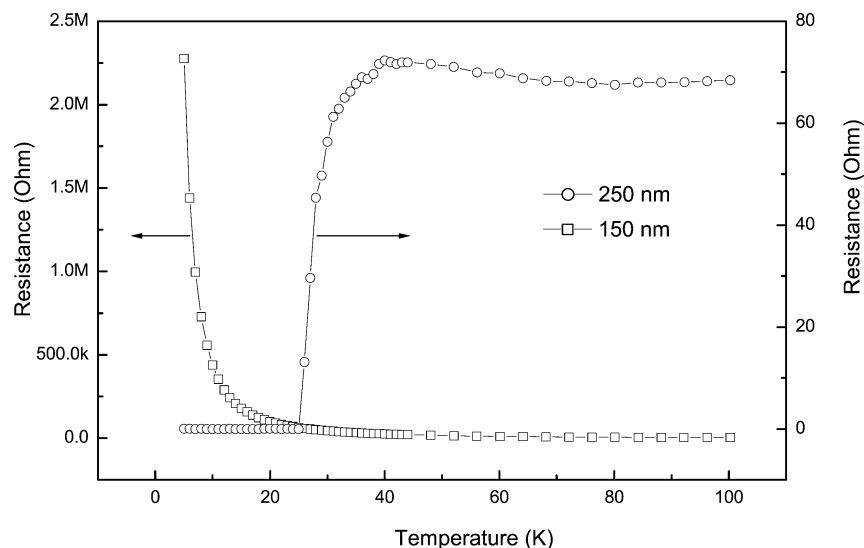**11000** *J. Phys. Chem. B, Vol. 108, No. 30, 2004*

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Figure 6. Temperature dependence of resistance for the oxidized LCO films with different thicknesses. The oxidations were performed at 40 °C for 12 h.

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