Thickness-induced insufficient oxygen reduction in La$_{2-x}$Ce$_x$CuO$_{4\pm\delta}$ thin films

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Abstract

A series of electron-doped cuprate La$_{2-x}$Ce$_x$CuO$_{4\pm\delta}$ thin films with different thicknesses have been fabricated and their annealing times are adjusted carefully to ensure the highest superconducting transition temperature. The transport measurements indicate that, with the increase of the film thickness (<100 nm), the residual resistivity increases and the Hall coefficient shifts in the negative direction. Furthermore, the x-ray diffraction data reveal that the c-axis lattice constant $c_0$ increases with the decrease of film thickness. These abnormal phenomena can be attributed to the insufficient oxygen reduction in the thin films. Considering the lattice mismatching in the $ab$ plane between the SrTiO$_3$ substrates and the films, the compressive stress from the substrates may be responsible for the more difficult reduction of oxygen in the thin films.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The electron-doped high-$T_c$ superconducting (SC) cuprates, e.g. (Ln,Ce)$_2$CuO$_{4+\delta}$ (Ln = La, Pr, Nd, Sm), have been extensively investigated since their discovery by Tokura et al in 1989 [1]. The hole-doped cuprates can exhibit superconductivity when introducing a sufficient concentration of hole carriers by either atom-substituting or oxygen doping in the insulating Ln$_2$CuO$_4$ host material. However, the superconductivity does not appear in the electron-doped cuprates until a metastable $T'$ phase is achieved by an extra annealing treatment of the as-grown samples. What happens during this annealing process is still controversial. Although oxygen reduction is widely considered as the crucial factor in this annealing process, it is hard to determine stoichiometrically because the amount of oxygen loss $\delta$ is always relatively small. The previous measurements of $\delta$ by either thermogravimetric analysis (TGA) [2–6] or iodometric titration analyses [7–9] cannot come to an agreement.

Many efforts have been made to clarify this puzzling issue. Based on the transport and the thermopower measurements, Jiang et al proclaimed that both the redundant and the indigent oxygen would induce more impurities and enhance the scattering [10–12]. The lack of oxygen can introduce a positive contribution and the excess oxygen always results in a negative contribution to the Hall coefficient, e.g. in Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO) thin films and single crystals as well as Pr$_{2-x}$Ce$_x$CuO$_4$ thin films [13, 14]. Riou and Richard et al studied the infrared transmission of the Pr$^{3+}$ crystal field in the Pr$_{2-x}$Ce$_x$CuO$_4$ single crystal and they pointed out that the oxygen in the CuO$_2$ plane is partially removed during the reduction [15, 16] instead of the apical ones. Using x-ray and neutron scattering methods, Kang et al have investigated the microscopic process of oxygen reduction in Pr$_{0.88}$La$_{0.12}$CeO$_4$ single crystals [17]. They suggested that both the repair of Cu deficiencies and the creation of oxygen vacancies can effectively reduce the disorder and provide itinerant carriers for superconductivity in the reduction treatment of the samples. Yamamoto et al [18] claimed that, if the reduction is not sufficient in the NCCO thin films, the excess oxygen will occupy the apical oxygen sites to compensate the Ce doping, while in the excessive reduction films, the oxygen deficiencies appear at regular oxygen sites in the CuO$_2$ plane. In our previous work, we have also found...
Table 1. $d$, $T_{c0}$, $T_{c}^{\text{onset}}$ and $t$ for various LCCO films. Here, $d$, $T_{c0}$, $T_{c}^{\text{onset}}$ and $t$ stand for the thickness, the transition temperature of zero resistance, the onset temperature of superconducting transition and the optimal annealing time for the sample with the designated thickness, respectively.

| Sample no. | $d$ (nm) | $T_{c0}$ (K) | $T_{c}^{\text{onset}}$ (K) | $t$ (min) |
|------------|----------|-------------|-----------------|--------|
| 1          | 17       | —           | —               | 12     |
| 2          | 33       | 21.5        | 26.5            | 20     |
| 3          | 67       | 26          | 27.5            | 23.1   |
| 4          | 100      | 26.5        | 28               | 26.8   |
| 5          | 150      | 26.5        | 28               | 35     |
| 6          | 200      | 27.3        | 28.5             | 39     |
| 7          | 600      | 27          | 28.5             | 70     |

that the extra annealing treatment can cause the Hall coefficient to shift in the positive direction in the dilute cobalt-doped La$_{2-x}$Ce$_x$CuO$_4$ thin films [19].

Recently, the significant influence of the lattice constant on oxygen reduction has been investigated by varying the doping concentration or substituting atoms with different radii [4, 5, 20–22]. It has been found that the decrease of the lattice constant $a_0$ in the $ab$ plane of the electron-doped cuprates can make the reduction of excess oxygen more difficult.

In this paper, electron-doped La$_{2-x}$Ce$_x$CuO$_4$ (LCCO) thin films with different thicknesses have been synthesized, and their annealing time were adjusted carefully to ensure the highest $T_c$ accordingly. Based on the transport measurement and the x-ray diffraction analysis, we have found that the decrease of the thickness may make it difficult to create the oxygen vacancies in the films during the annealing reduction.

2. Experiments

The optimally doped LCCO ($x = 0.105$) thin films with a thickness $d$ varying from 17 to 600 nm were fabricated on the (100)-oriented SrTiO$_3$ substrates by the dc magnetron sputtering method [23–25]. All the samples were annealed at 550 $^\circ$C in a vacuum lower than 10$^{-3}$ Pa, and the annealing time was adjusted to ensure the sharp SC transition and the highest $T_c$ accordingly. Based on the transport measurement and the x-ray diffraction analysis, we have found that the decrease of the thickness may make it difficult to create the oxygen vacancies in the films during the annealing reduction.

In order to investigate the effect of the film thickness on oxygen reduction, we study the transport properties of these LCCO films. Figure 2 shows the temperature dependence of the normalized resistance for the samples with different thicknesses. When the film thickness $d$ is larger than 100 nm, the curves are almost overlapping. This indicates that all the samples have quite similar temperature dependences. However, the ratio of the residual resistance (RRR), $T_{c0}$ and $T_{c}^{\text{onset}}$, decreases with the film thickness decreasing from 100 nm to 33 nm. If the sample is ultrathin, e.g. $d = 17$ nm, it becomes an insulator no matter how we adjust the annealing time. The dependence of the resistance and $T_c$ on the thickness can be attributed to the different influence of the substrate on the films. The thinner the film is, the more prominent
the influence of the substrate on the properties is when $d < 100$ nm. We propose that the influence of the substrate on the properties of the films can be worked out by the oxygen reduction during the annealing process. However, either the excess oxygen caused by insufficient reduction or the oxygen vacancies induced by the excessive reduction can act as impurities to enhance the scattering and suppress the superconductivity [11]. Since the Hall effect is an effective method to disclose the type of the carriers, we try to measure the Hall coefficient to clarify the controversy.

Figure 3 shows the Hall coefficient $R_H$ of the LCCO films with different thicknesses. We find that all the samples have an anomalous temperature dependence of $R_H$ with sign reversals. Since there are two kinds of carriers in electron-doped cuprates [11, 26], the Hall sign reversals versus the magnetic field and temperature can be attributed to competition between the hole-like and the electron-like carriers under the regime of the two-band model [27, 28]. Here, we will focus on the dependence of the Hall coefficient on the film thickness.

In figures 3(a) and (b) at $H = 2$ and $7$ T, the $R_H$ curves show quite a similar temperature dependence when $d \geq 100$ nm, respectively, while, in the case of $d = 67$ nm, the nonzero Hall resistance $R_H$ shows clear bias from those of $d \geq 100$ nm and shifts to the negative. As mentioned above [11–13, 19], the lack of oxygen will introduce a positive hole-like contribution to the Hall coefficient. Therefore, the enhancement of the negative $R_H$ of the thin films with $d = 67$ nm can be attributed to the excess oxygen due to the insufficient reduction process. Since the annealing time of the films with different thicknesses are adjusted to their optimal conditions to get the sharp transition and the highest $T_c$, we may conclude that it is almost impossible to get rid of all the excess oxygen in the thin films. The excess oxygen caused by insufficient reduction in the thin films not only enhances the impurity scattering but also results in the strong negative response of the Hall coefficient.

It is important to make clear that the mismatch effect between the substrate and the film originated from their different lattice constants in the $ab$ plane, which may lead to the difficult oxygen reduction in the ultrathin films as we have studied above. Figure 4 shows the $\theta–2\theta$ x-ray diffraction of the LCCO films with the thickness varying from 17 to 600 nm. All the films exhibit good $c$-axis orientation and the amplitude of the $(00l)$ peak increases monotonically with film thickness. We calculate the lattice constant $c_0$ along the $c$ axis and show its dependence on the film thickness in the inset of figure 4. We find that the lattice constant $c_0$ does not depend on the thickness when $d \geq 100$ nm, while if $d < 100$ nm, $c_0$ decreases with the increase in thickness, which can be understood as that the apical oxygen is easy to escape from the LCCO samples with the increase in film thickness [20]. We may notice that the bond-length mismatch or the internal stress due to the small rare-earth atom Ln$^{3+}$ substitution in the electron-doped Ln$_2$–Ce$_x$CuO$_4$ samples will cause it to be difficult for the oxygen reduction as reported in [5] and [21]. Since the lattice constants of $a_0$ are 3.905 and 4.010 Å for the SrTiO$_3$ crystal and the optimally doped LCCO
film, respectively, the mismatch effect between them will be very strong in the ultrathin LCCO films, e.g. \( d < 100 \text{ nm} \). Due to the compression stress from the SrTiO\(_3\) substrate, the lattice constant \( a_0 \) of the ultrathin films probably decreases, which may lead to it being more difficult for the oxygen reduction during the annealing process.

Regarding the position the excess oxygen occupies in the lattice, Higgins [13] and Yamamoto [18] agree on the apical O(1) site in the CuO\(_2\) plane. Our previous studies [19] to the compression stress from the SrTiO\(_3\) substrate, the lattice may lead to it being more difficult for the oxygen reduction during the annealing process.

Here, we want to emphasize that the annealing process on the excessive reduction in the annealing process for the highest may lead to it being more difficult for the oxygen reduction during the annealing process.

\[ \text{O(1) site vacancies can be caused by} \]

\[ \text{The x-ray diffraction in the electron-doped LCCO thin films with} \]

\[ \text{the decrease of film thickness} \]

\[ \text{These nontrivial phenomena} \]

\[ \text{the difficulty of oxygen reduction in the thin films} \]

\[ \text{when} \]

\[ \text{the decrease of film thickness. These nontrivial phenomena enhance the difficulty of oxygen reduction in the thin films} \]

\[ \text{Acknowledgments} \]

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### References

[1] Tokura Y, Takagi T and Uchida S 1989 Nature \textbf{337} 345
[2] Wang E, Tarascon J-M, Greene L H, Hull G W and McKinney W R 1990 Phys. Rev. B \textbf{41} 6582
[3] Idemoto Y and Fueki K 1991 Japan. J. Appl. Phys. \textbf{30} 2471
[4] Kawashima T and Takayama-Muromachi E 1994 Physica C \textbf{219} 389
[5] Zhu Y T and Manthiram A 1994 Physica C \textbf{224} 256
[6] Serquis A, Prado F and Caneiro A 1999 Physica C \textbf{313} 271
[7] Suzuki K, Kishio K, Hasegawa T and Kitazawa K 1990 Physica C \textbf{166} 357
[8] Singh O G, Padalia B D, Prakash Om, Suba K, Narlikar A V and Gupta L C 1994 Physica C \textbf{219} 156
[9] Vlaeminck H, Groossens H H, Mouton R, Hoste S and Van Der Kelen G 1991 J. Mater. Chem. \textbf{1} 1863
[10] Jiang W, Peng J L, Li Z Y and Greene R L 1993 Phys. Rev. B \textbf{47} 8151
[11] Jiang W, Mao S N, Xi X X, Jiang X, Peng J L, Venkatesan T, Lobb C J and Greene R L 1994 Phys. Rev. Lett. \textbf{73} 1291
[12] Xu X Q, Mao S N, Jiang W, Peng J L and Greene R L 1996 Phys. Rev. B \textbf{53} 871
[13] Higgins J S, Dagan Y, Barr M C, Weaver B D and Greene R L 2000 Phys. Rev. B \textbf{73} 104510
[14] Gauthier J, Gagné S, Renaud J, Gosselin M-É, Fournier P and Richard P 2007 Phys. Rev. B \textbf{75} 024424
[15] Riou G, Richard P, Jandl S, Poirier M, Fournier P, Nekvasil V, Barilo S N and Kurnevich L A 2004 Phys. Rev. B \textbf{69} 024511
[16] Richard P, Riou G, Hetel I, Jandl S, Poirier M and Fournier P 2004 Phys. Rev. B \textbf{70} 064513
[17] Kang H J, Dai P C, Campbell B J, Chupas P J, Rosenkranz S, Lee P L, Huang Q Z, Li S L, Komiya S and Ando Y 2007 Nat. Mater. \textbf{6} 224
[18] Yamamoto H, Naito M and Sato H 1997 Phys. Rev. B \textbf{56} 2852
[19] Jin K et al 2006 Phys. Rev. B \textbf{74} 094518
[20] Matsumoto O, Utsuki A, Tsukada A, Yamamoto H, Manabe T and Naito M 2008 Int. Symp. on Superconductivity (arXiv:0811.1077v1)
[21] Zhu Y T and Manthiram A 1994 Phys. Rev. B \textbf{49} 6293
[22] Fujita K, Noda T, Kojima K M, Eisaki H and Uchida S 2005 Phys. Rev. Lett. \textbf{95} 097006
[23] Zhao L, Wu H, Miao J, Yang H, Zhang F C, Qiu X G and Zhao B R 2008 Phys. Rev. B \textbf{78} 174521
[24] Wu H et al 2006 Phys. Rev. B \textbf{73} 104512
[25] Jin K, Zhu B Y, Wu B X, Gao I J and Zhao B R 2008 Phys. Rev. B \textbf{78} 174521
[26] Armitage N P et al 2002 Phys. Rev. Lett. \textbf{88} 257001
[27] Jin K et al 2007 Phys. Rev. B \textbf{75} 214501
[28] Hurd C M 1972 The Hall Effect in Metals and Alloys (New York: Plenum)