Controlling superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ by ozone and vacuum annealing

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Abstract In this study we performed a series of ozone and vacuum annealing experiments on epitaxial $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ thin films. The transition temperature after each annealing step has been measured by the mutual inductance technique. The relationship between the effective doping and the vacuum annealing time has been studied. Short-time ozone annealing at 470°C oxidizes an underdoped film all the way to the overdoped regime. The subsequent vacuum annealing at 350°C to 380°C slowly brings the sample across the optimal doping point back to the undoped, non-superconducting state. Several ozone and vacuum annealing cycles have been done on the same sample and the effects were found to be repeatable and reversible. Vacuum annealing of ozone-loaded LSCO films is a very controllable process, allowing one to tune the doping level of LSCO in small steps across the superconducting dome, which can be used for fundamental physics studies.

Keywords $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$; thin films; molecular beam epitaxy; ozone and vacuum annealing

1 Introduction

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ (LSCO) has been extensively studied as a prototype high temperature superconductor (HTS) due to its simple crystal structure. Its doping level can be tuned

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by varying either the strontium concentration or the oxygen content. Changing the strontium concentration requires fabricating a series of samples of different stoichiometry [1–3]. However, superconducting properties of cuprates are very sensitive to the details of sample preparation and to chemical impurities, and even small variations in the growth and post-annealing conditions from one to another synthesis experiment may introduce some uncertainty [4–6]. On the other hand, the oxygen content in a given sample can be easily tuned by just annealing the sample in oxygen or vacuum. The transition temperature (T_c) is significantly affected by subtle changes of oxygen stoichiometry and the effect of the oxygen content on the transport properties is very similar to that of strontium doping. By oxygen and vacuum annealing, a wide doping range — almost the entire superconducting dome — can be accessed in a single sample.

Oxygen annealing technique has been widely used in fabrication of high quality HTS cuprate samples. It usually requires annealing at a high temperature ($>400^\circ\text{C}$) or a high pressure for very long time [1, 7–9]. However, the homogeneity of the sample is not easy to control due to the complicated oxygen diffusion mechanism, which depends on the abundance and distribution of defects, mismatch-induced strain, etc. [10, 11]. The oxygen diffusion coefficient is very anisotropic; the oxygen diffusivity in ab plane is several orders of magnitude higher than that along the c axis [10, 11]. Moreover, annealing at high temperature for a long time may cause significant structural changes as well as chemical reactions induced by the depletion of one or the other of constituent elements, resulting in a broadened transition and/or increased normal state resistance [12]. In bulk samples, the long-time high-temperature annealing process can cause the superconducting volume to shrink, as indicated by a decrease in the ac susceptibility signal, even if the temperature of the onset of transition remains the same [7]. Annealing in a mixture of ozone and molecular oxygen (O_3/O_2) is a better option since it can be done at a lower temperature, and for a shorter time [2, 13–15]. However, using ozone annealing it is not easy to control the exact doping level, since the time it takes to fully oxidize a sample is too short.

In this work, we show that a short-time O_3/O_2 annealing can fully oxidize an underdoped LSCO thin film to the overdoped regime, and that subsequent low-temperature vacuum annealing slowly brings the film back to the non-superconducting state. Unlike the fast ozone annealing procedure, the vacuum annealing procedure at $350\text{--}380^\circ\text{C}$ takes more than 10 hours before the superconductivity is completely suppressed. Thus this is a more controllable procedure and we can tune the doping level across the superconducting dome in small steps. Very important, the film remains single-phase and very homogeneous at every point we reach, and it shows no degradation after several annealing cycles, indicating that this process is repeatable and reversible.

2 Experiments

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ thin films were grown on LaSrAlO_4 substrates by means of an atomic-layer molecular beam epitaxy (ALL-MBE) technique [16]. The film structure was characterized in real time during growth by reflection high-energy electron diffraction (RHEED) and *ex situ* by atomic force microscopy (AFM) and x-ray

diffraction (XRD). The diamagnetic response as a function of temperature was measured by the two-coil mutual inductance technique. The film is placed between two coils and the real (reactive) part of the mutual inductance starts to drop when strong diamagnetic screening begins, indicating the formation of a complete supercurrent loop at T_c (zero resistance) [17]. At the same temperature, the imaginary (dissipative) part of the mutual inductance, $\text{Im}M(T)$, starts developing a peak as the superfluid density builds up, forming in the optical conductivity a δ -function at zero frequency. The sharpness of this peak is a measure of the film homogeneity; basically, T_c cannot vary across the sample by more than one half-width-at-half-maximum (HWHM) of this peak, lest we resolve two (or more) peaks.

A series of annealing processes were performed in a vacuum chamber with a base pressure 2×10^{-7} torr. The O_3/O_2 mixture has a pressure of 1.7 torr with 20% (weight per cent) ozone in it. Immediately after each annealing process, the two-coil mutual inductance was measured from room temperature down to the liquid helium temperature.

3 Results and Discussion

In what follows, we show the data for one $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ film with the Sr doping level of $x=0.08$ and the thickness $d = 50$ nm. After been kept in a dry box for extended time, the ‘aged’ film showed $T_c = 5$ K, see Fig. 1. Annealing in O_3/O_2 mixture at 470°C for 15 minutes brings T_c back to 26.6 K. This shows that ozone is very effective in oxidizing LSCO. However, from this T_c alone, one cannot tell whether the film is still underdoped or it has already been brought to the overdoped regime. A subsequent annealing in vacuum at 350°C for one hour did not affect T_c much. However, after annealing in vacuum at a higher temperature, 470°C , for just 15 minutes, the sample was not superconducting at all. This suggests that the superconductivity in LSCO is very sensitive to the temperature at which vacuum annealing is performed, and that there should be a threshold temperature, somewhere in the range between 350°C and 470°C , above which superconductivity is significantly suppressed even for a short-time annealing.

After the superconductivity has been fully suppressed by high-temperature vacuum annealing, we re-annealed it in O_3/O_2 mixture at 470°C for 15 minutes. In Fig. 2 we can see that the superconductivity has been fully recovered by ozone annealing. We then tried to anneal the same film in vacuum at 350°C for a longer time. After 8 hours of annealing in vacuum, the superconductivity did not disappear; on the contrary, T_c increased (from 25.8 K to 27.7 K). Since the oxygen is depleted during vacuum annealing, this increase of T_c indicates that we already brought the film to the overdoped regime by ozone annealing, and now by vacuum annealing we are bringing it back towards the optimal doping point. After additional 8 hours of annealing in vacuum at 350°C , we found that superconductivity is fully suppressed again. Apparently, depletion of interstitial oxygen out of LSCO by vacuum annealing at 350°C is a very slow process; the entire procedure takes more than 10 hours. The upside is that this makes it a very controllable process. In our ozone/vacuum annealing apparatus, the heating up or cooling down procedure takes only about 20 minutes, which is practically negligible compared to the vacuum annealing time. Thus we can perform vacuum annealing in relatively small steps, thus covering a wide range of doping levels.

In the inset of Fig. 2 we plot the imaginary part of mutual inductance measured immediately after the previous two vacuum annealing steps. The transition width, which defined as the half width at half maximum (HWHM), is only 0.25-0.37 K. This indicates that the sample remains single-phase and quite homogeneous after each annealing step.

In Fig. 3, we show another ozone- and vacuum-annealing cycle following the previous one. After annealing in O_3/O_2 mixture at 470°C for 20 minutes, the film is superconducting again with $T_c = 23.7$ K, and from previous experience we know that it is in the overdoped regime. From this point, we annealed the film in vacuum at 380°C, in a series of relatively short steps (1 or 2 hours). The mutual inductance was measured immediately after each vacuum annealing step. For the first three steps, T_c increases as shown in Fig. 3a. This indicates that the sample was moving from the overdoped regime towards the optimal doping point. In Fig. 3b, we show the subsequent steps, and one can see that T_c now decreases after each vacuum annealing step, which means the sample has passed the optimal doping point and now it is in the underdoped regime.

In Fig. 4 (top panel), we plot T_c vs. annealing time, and it shows a dome-like phase diagram. An effective hole-doping level, p , can be determined using the empirical parabolic relation $T_c/T_{c,max} = 1 - 82.6(p - 0.16)^2$ [18], which has been verified for several HTS cuprates [19]. Using this calculated effective doping, we can then plot the hole density as a function of annealing time, see the bottom panel in Fig. 4. The hole doping appears to decrease linearly with the annealing time, from the overdoped to the deeply underdoped regime. Note, however, there are actually two different oxygen depletion mechanisms. One involves the ‘extra’ (interstitial) oxygen atoms, which are responsible for additional holes compared to the nominal doping of $x=0.08$, driving the film into the overdoped and near-optimal doped regime. These interstitial oxygen atoms have relatively low binding energy and are depleted first during vacuum annealing, resulting in an almost linear decrease of the effective doping level. However, once the interstitial oxygen has already been totally depleted and we have reached $p = x = 0.08$, additional vacuum annealing may cause formation of oxygen vacancies in the CuO_2 layers. Thus, we expect that in the deeply underdoped regime, when $p \leq 0.08$, the doping vs. annealing time curve may deviate down from the linear relationship. We hope to explore this in future detailed measurements in the deeply underdoped regime.

While as we have shown, we can control the vacuum annealing process reasonably well, in our present experimental setup, we cannot precisely control ozone annealing. We have experimented with the short ozone annealing times, nominally 10-20 minutes, but note that the heating up time is also about 20 minutes. Namely, the sample has to be heated up in ozone, in order to avoid any damage caused by high-temperature vacuum annealing. So the actual ozone annealing time may be about 20-30 minutes, so there is not too much room for us to control the annealing time. On the other hand, as seen from Fig. 2 and Fig. 3, apparently it makes no difference whether we anneal in ozone for 15 minutes or 20 minutes; the sample has already been brought to the overdoped regime and saturated. Hence, the well-controllable process that we have developed consists of a short annealing in ozone at a relatively high temperature (470°C), followed by a sequence of annealing cycles in

vacuum, at low temperature (350-380°C). Note that the sample did not show any degradation after three ozone and multiple vacuum annealing cycles, indicating that the process is repeatable and reversible.

From the fact that just several hours of vacuum annealing at relatively low temperature one can profoundly change the hole density and superconducting properties of LSCO films, one could get an impression that LSCO is volatile. Nevertheless, our LSCO films are actually quite robust and resilient as long as they are not heated above the threshold temperature. Annealing at 350°C in vacuum for one hour did not change the transition temperature at all. We have observed T_c unchanged in LSCO films after being kept in a dry box for several years. Thus, we can use the vacuum-annealed LSCO films just like strontium-doped ones, for a study of the fundamental physics across the superconducting dome, with the great advantage of using one and the same sample.

4 Conclusions

Annealing in O_3/O_2 mixture for 15 minutes at 470°C fully oxidizes an underdoped LSCO thin film all the way to the overdoped regime. The subsequent annealing in vacuum at 350°C or 380°C for more than 10 hours slowly brings the film back to the non-superconducting state. During vacuum annealing, the effective doping level changes linearly with time, as the interstitial oxygen atoms are being depleted and the oxygen vacancies generated. This turns out to be a very controllable process to tune the effective doping in LSCO in small steps across the superconducting dome. The films show no degradation after multiple ozone- and vacuum-annealing cycles, indicating that the method is a repeatable and reversible. It can be used to study the fundamental physics of HTS across almost the entire superconducting dome in a single sample.

References

1. H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida, Y. Tokura, *Phys. Rev. B* **40**, 2254 (1989)
2. H. Sato, A. Tsukada, M. Naito, A. Matsuda, *Phys. Rev. B* **61**, 12447 (2000)
3. Y. Ando, S. Komiya, K. Segawa, S. Ono, Y. Kurita, *Phys. Rev. Lett.* **93**, 267001 (2004)
4. H. L. Kao, J. Kwo, R. M. Fleming, M. Hong, J. P. Mannaerts, *Appl. Phys. Lett.* **59**, 2748 (1991)
5. M. Z. Cieplak, M. Berkowski, S. Guha, E. Cheng, A. S. Vagelos, D. J. Rabinowitz, B. Wu, I. E. Trofimov, P. Lindenfild, *Appl. Phys. Lett.* **65**, 3383 (1994)
6. S. Sanna, S. Agrestini, K. Zheng, R. D. Renzi, N. L. Saini, *Europhys. Lett.* **86**, 67007 (2009)
7. J. M. Tarascon, L. H. Greene, W. R. Mckinnon, G. W. Hull, T. H. Geballe, *Science* **235**, 1373 (1987)
8. I. E. Trofimov, L. A. Johnson, K. V. Ramanujachary, S. Guha, M. G. Harrison, M. Greenblatt, M. Z. Cieplak, P. Lindenfild, *Appl. Phys. Lett.* **65**, 2481 (1994)
9. M. Zu, Y. Zhang, H. Wen, *Supercond. Sci. Tech.* **20**, 676 (2007)
10. E. J. Opila, H. L. Tuller, B. J. Wuensch, J. Maier, *J. Amer. Ceramic Soc.* **76**, 2363 (1993)
11. J. L. Routbort, S. J. Rothman, *J. Appl. Phys.* **76**, 5615 (1994)
12. A. Edelstein, S. Qadri, R. Holtz, P. Broussard, J. Claassen, T. Francavilla, D. Gubser, P. Lubitz, E. Skelton, S. Wolf, *J. Crystal Growth* **85**, 619 (1987)
13. W. Si, H. C. Li, X. X. Xi, *Appl. Phys. Lett.* **74**, 2839 (1999)
14. W. Si, X. X. Xi, *Appl. Phys. Lett.* **78**, 240 (2001)
15. I. Bozovic, G. Logvenov, I. Belca, B. Narimbetov, I. Sveklo, *Phys. Rev. Lett.* **89**, 107001 (2002)

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16. I. Bozovic, IEEE Trans. Appl. Supercond. **11**, 2686 (2001)
 17. A. T. Fiory, A. F. Hebard, P. M. Mankiewich, R. E. Howard, Appl. Phys. Lett. **52**, 2165 (1988)
 18. M. R. Presland, J. L. Tallon, R. G. Buckley, R. S. Liu, N. E. Flower, Physica C: Supercond. **176**, 95 (1991)
 19. J. L. Tallon, C. Bernhard, H. Shaked, R. L. Hitterman, J. D. Jorgensen, Phys. Rev. B **51**, 12911 (1995)

Fig. 1 The real part of mutual inductance measured as a function of temperature after a series of annealing procedures in sequence: 0, aged for several years in a dry box at room temperature; 1, annealed in O_3/O_2 at 470°C for 15 minutes; 2, annealed in vacuum at 350°C for 60 minutes; 3, annealed in vacuum at 470°C for 15 minutes.

Fig. 2 (Main panel) The real (reactive) part of mutual inductance measured after the film was annealed again: 1, in O_3/O_2 mixture at 470°C for 15 minutes; 2, in vacuum at 350°C for 8 hours; 3, in vacuum at 350°C for another 8 hours. (Inset) The imaginary (dissipative) part of mutual inductance. The steps number 1 and 2 refer to the same steps as in the main panel. The arrows indicate the full width at half maximum of the peaks; T_c in the film must be uniform to better than one-half of that value, or else we would have resolved double (or multiple) peaks.

Fig. 3 The real part of the mutual inductance measured after a series of annealing procedures in sequence: 1, in O_3/O_2 mixture at 470°C for 20 minutes; 2, in vacuum at 380°C for 1 hours; 3-7, in vacuum at 380°C for 2 hours each.

Fig. 4 (Top panel) T_c from the curves in Fig. 3 as a function of the vacuum annealing time. (Bottom panel) The effective doping level (p = number of holes per LSCO formula unit) as a function of the vacuum annealing time.