Epitaxial Strain and Superconductivity in $La_{2-x}Sr_xCuO_4$ Thin Films

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The report that T_c was doubled in underdoped $La_{2-x}Sr_xCuO_4$ films under *compressive* epitaxial strain has stirred great interest. We show that such films are extremely sensitive to oxygen intake, even at very low temperature, with startling consequences including colossal lattice expansion and a crossover from semiconductor to metallic behavior. We can bring T_c up to 40 K in La_2CuO_4 films on $SrTiO_3$ substrates—without *any* Sr doping and under *tensile* strain. On $LaSrAlO_4$ substrates, we reached $T_c = 51.5$ K, the highest so far in $La_{2-x}Sr_xCuO_4$.

Pressure dependence of the critical temperature (T_c) is a sensitive probe of the superconducting state. The effect of pressure on high-temperature superconductors (HTS) has been studied extensively [1–4]. In most HTS compounds it was found [5] that $\partial T_c/\partial p_a > 0$ and $\partial T_c/\partial p_c < 0$, where p_a and p_c denote the uniaxial pressure along the crystallographic a axis (parallel to the CuO_2 planes) and c axis (perpendicular to CuO_2 planes), respectively [6]. Hydrostatic pressure does not affect T_c much, because of compensation. In contrast, epitaxial strain is anticipated to have a substantial effect. For compressive strain, the in-plane lattice constant a shrinks, while the out-of-plane lattice constant c is expected to expand due to the Poisson effect. In this case, both terms add up, and one expects T_c to increase. Conversely, tensile epitaxial strain should reduce T_c.

In $SrTiO_3$ (STO), the substrate most frequently used for HTS thin film growth, the lattice constant is $a = 3.905$ Å. This is 3% larger than the in-plane lattice constant of bulk $La_{2-x}Sr_xCuO_4$ (LSCO), $a = 3.777$ Å, for optimal doping ($x = 0.15$). Hence, LSCO films are under tensile strain on STO and commonly have T_c lower than bulk samples. In contrast, $LaSrAlO_4$ (LSAO) has a 0.5% shorter constant, $a = 3.755$ Å. Indeed, LSCO thin films on LSAO tend to have T_c larger than bulk samples [7] with the record $T_c \approx 49$ K so far [8,9].

The statement that drew the most attention so far was that T_c can be doubled by epitaxial strain. Loquet *et al.* [9] found that $T_c = 49.1$ K in thin films of $La_{1.9}Sr_{0.1}CuO_4$ deposited on LSAO, almost twice higher than what is observed ($T_c = 25$ K) in the bulk compound with the same Sr doping level ($x = 0.10$). The claim was promptly endorsed by theorists: Chen *et al.* [10] studied a single CuO_2 layer using the *t-J* model with *d*-wave symmetry, assumed a 0.5% contraction of the a lattice parameter, and calculated $T_c = 49.1$ K, in an incredible agreement with the experiment. Extrapolating to other HTS compounds, speculations were even raised that near-room temperature could be reached in this way. For example, in $HgBa_2Ca_2Cu_3O_8$, $T_c = 134$ K at $p = 1$ bar and $T_c > 160$ K at $p = 310$ Kbar [11]; it would appear that all one needs is to deposit this material onto a suitable compressive substrate. Considering the impact this would have on superconductive electronics, this task was listed among the most important open problems in atomic-layer engineering of HTS materials [12].

However, these claims also drew some criticism. The 0.1% agreement between the theory and the experiment seems questionable, given the crudeness of the model (the weak-coupling BCS equation for T_c, a single CuO_2 layer, no interplane interactions). In fact, judging from the values of $\partial T_c/\partial p_a$ and $\partial T_c/\partial p_c$ in bulk LSCO, the enhancement of T_c should come for the most part from the *c*-axis expansion [13]. Moreover, Sato *et al.* [7,8] noticed that T_c was higher in films cooled down in a $O_2 : O_3$ mixture rather than in pure O_2 and speculated [13,14] that oxygen may be incorporated interstitially. Si *et al.* [15,16] made a similar observation. This is a salient point; if the T_c enhancement under study originated for the most part from inadvertent oxygen doping (in what otherwise would have been an underdoped sample), the promise to substantially elevate the maximum T_c in this way would subside.

In the present Letter, we attempt to resolve this controversy by a detailed study of the competing effects of epitaxial strain and oxygen incorporation. We deposited a large number (over 300) of LSCO films, on both STO and LSAO substrates, covering a range of doping levels (from $x = 0$ to $x = 0.35$) and film thickness (from 10 to 60 unit cells, i.e., from $d = 13$ nm to $d = 78$ nm). We annealed them in a controlled oxidation environment, spanning a very broad range (over 15 orders of magnitude) of equivalent oxygen partial pressure, and studied the effect on the crystal structure and transport properties.

The films were synthesized in a unique multichamber combinatorial molecular beam epitaxy system, designed to enable atomic-layer engineering and optimization of complex oxide materials. The growth chamber contains 16 metal sources and a source of pure ozone. The deposition rates can be mapped using a scanning quartz-crystal oscillator, and they are controlled accurately in real time by a 16-channel atomic absorption spectroscopy system. Film growth is monitored by a reflection high-energy electron

diffraction (RHEED) system and several other state-of-the-art surface analysis tools [12].

Essentially every film was characterized in detail by RHEED, atomic-force microscopy (AFM), and x-ray diffraction (XRD). For this, we used a modified Staib Instrumente RH-35 RHEED system supplied with the k-Space Associates kSA-400 analysis software, a Digital Instruments NanoScope II apparatus consisting of a contact mode AFM and a scanning tunneling microscope, and a Philips 'Xpert Pro 4-circle x-ray diffractometer. Selected films were also characterized by Rutherford backscattering, at Charles Evans Associates in Mountain View, CA, and in Forschungszentrum Rossendorf, Dresden, Germany, for absolute calibration of deposition rates and to double-check the film stoichiometry.

The quality of the films was excellent overall, and we have selected a few dozen of the best for the present study. These films were essentially atomically smooth and perfect. The rms surface roughness as measured by AFM was 0.2–0.5 nm over an area of 2500 μm^2. Figure 1 is an image of a 78-nm-thick LSCO film on a LSAO substrate; a 10×10 μm^2 scan is shown to better see the terraces and one-unit-cell-tall steps that originate in a slight miscut of the substrate from the ideal (001) orientation. The XRD showed very high crystallinity and an absence of any secondary phases. The rocking curves showed FWHM of 0.1°, indicating that the crystalline coherence length was equal to the film thickness. The high quality of the films can be appreciated from finite-thickness oscillations, Fig. 2(a), and low-angle reflectance oscillations, Fig. 2(b), consistent with the anticipated film thickness and smoothness inferred from the AFM data.

We have postannealed these films in oxygen, varying the temperature T_a and the annealing time t_a. Here we focus on the effects of annealing at very low temperature, $T_a = 150$–200 °C, which were surprisingly large in some cases. The annealing time was typically $t_a = 10$–30 min, apparently long enough to reach the equilibrium, since repeated annealing produced no further change. In order to preserve

the equilibrium oxygen distribution, after annealing the samples were quenched down fast, within seconds, to room temperature, using liquid nitrogen for cooling. This is at least 2 orders of magnitude faster than the typical *in situ* cooling down process [7,8]. We also varied the oxidation power over a broad range, by annealing under high vacuum (with the oxygen partial pressure below 10^{-11} bars, in a high-pressure oxygen furnace up to $p = 200$ bars of O$_2$, and in an essentially pure ozone at $p = 10^{-4}$ bars, 10^{-3} bars, and 10^{-2} bars, respectively. We found that in this temperature range, 150–200 °C, the oxidation power of ozone at the lowest pressure used, $p = 10^{-4}$ bars, was significantly higher than that of O$_2$ even at the highest accessible pressure, $p = 200$ bars. This is worth emphasizing: at this low temperature, the oxidation power of ozone is higher than that of the molecular oxygen by a factor of more than 10^6. Altogether, we were able to tune the equivalent O$_2$ partial pressure from 10^{-11} bars to over 10^4 bars—a range of 15 orders of magnitude.

In nominally undoped or underdoped LSCO films, i.e., for $x < 0.15$, this postannealing process affected T_c and the film resistivity, ρ, in a dramatic way. For example, in La$_2$CuO$_{4+\delta}$ (LCO) films, by varying the postannealing
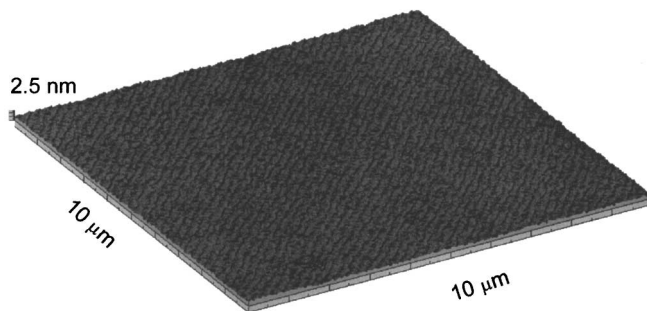

FIG. 1. AFM plot (3D) of a 78-nm-thick LSCO film on LSAO. It shows terraces, about 300 nm wide, between one-unit-cell-tall steps, as a consequence of a slight (0.1°) miscut of the LSAO substrate. The rms surface roughness of this film was 0.3 nm over the area of 2500 μm^2. Thinner films were even smoother.
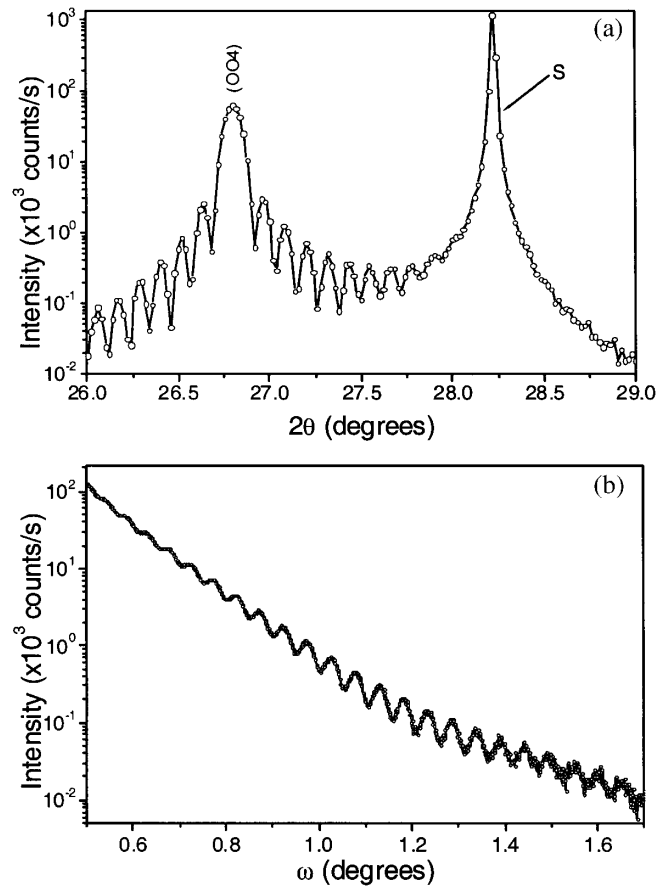

FIG. 2. X-ray data for the LSCO film shown in Fig. 1: (a) finite-thickness oscillations in the vicinity of the (004) reflection; (b) low-angle x-ray reflectance oscillations.

treatment it was possible to tune ρ_{ab} ($T = 300$ K) reversibly by a factor of 100—from less than 300 $\mu\Omega$ cm to more than 30 mΩ cm. Concomitantly, the temperature dependence $\rho_{ab}(T)$ changed from metalliclike to semiconductorlike. At low temperature the tuning range was therefore much broader, for example, at $T = 50$ K by a factor of more than 1000. The critical temperature also changed accordingly, from $T_c < 4$ K to $T_c = 40$ K on STO, and from $T_c < 4$ K to $T_c = 48$ K on LSAO. As an example, in Fig. 3(a) we show three $\rho(T)$ curves for a 20-unit-cell-(26-nm) thick LCO films on STO—as grown, annealed in vacuum, and annealed in ozone, respectively.

Low-temperature annealing in ozone affects profoundly the crystal lattice parameters, as well. The magnitude of the effect depends on the film thickness. In 40-unit-cell ($d = 52$ nm) thick LCO films, c can be varied by 0.04 Å, i.e., by 0.3%. However, the effect is much more dramatic in 10-unit-cell ($d = 13$ nm) thick films, the thinnest studied here, where we found the c lattice parameter to vary by as much as 0.3 Å, i.e., by more than 2%. This (reversible) c-axis expansion or contraction deserves to be called *colossal*. (For comparison, the thermal expansion in bulk LSCO amounts to less than 1% for $\Delta T = 1000$ K.)
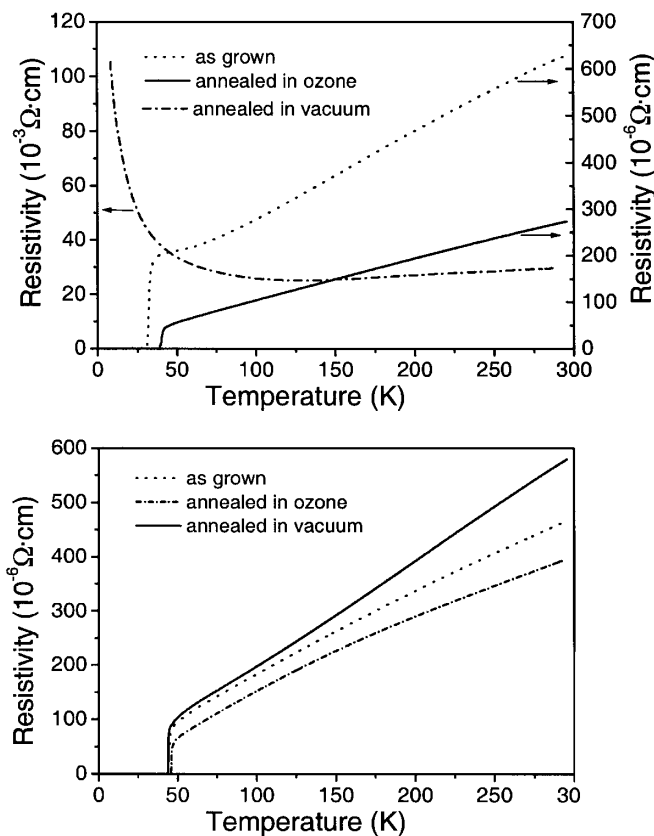
Indeed, it is tempting to ascribe this effect to oxygen intake, intercalation, and staging [17].

In contrast, the effect of low-temperature annealing was much smaller or absent in optimally doped and overdoped LSCO films, i.e., for $x \geq 0.15$. This behavior is illustrated in Fig. 3(b), where we show three $\rho(T)$ curves for an LSCO film with $x = 0.15$—as grown, annealed in vacuum, and annealed in ozone, respectively [18]. The striking difference in oxygen sensitivity between the nominally undoped and optimally doped cases is apparent if one contrasts Fig. 3(a) with Fig. 3(b). This finding is in line with observations by Sato et al. [13,14] and Si [15,16] that their films with smaller x were more sensitive to the cooldown regime, as well as with the earlier studies on bulk LCO [19].

In the context of discussion of the role of epitaxial strain, we emphasize that we have achieved $T_c = 40$ K in LCO films on STO substrates, Fig. 3(a). This is *higher* than what is observed ($T_c = 36$ K) in optimally Sr-doped bulk LSCO [20,21]. Note that these films were under *tensile* strain, and there was no Sr doping whatsoever. In this case, the observed high-temperature superconductivity can be ascribed only to the incorporation of additional oxygen.

We have observed, in qualitative agreement with Refs. [7–9] and [13–16], that the lattice parameters c and a showed some dependence on the substrate. For example, we found the c-axis lattice constant to be consistently somewhat longer in LCO on LSAO (typically $c = 13.29$ Å, for the highest T_c) than on STO ($c = 13.17$–13.26 Å). However, the "colossal expansion" of ultrathin LCO films exposed to ozone is about 3 times bigger on STO than on LSAO. T_c also depends on the substrate, insofar that its maximum value is somewhat higher in films on LSAO. In Fig. 4, we show the $\rho(T)$ curve for a composite film consisting of a 15-unit-cell thick layer of LSCO with $x = 0.15$, covered with a 5-unit-cell layer of LCO, as grown, on a LSAO substrate. It shows zero resistance at $T_c = 51.5$ K, the highest value reported

FIG. 3.   Temperature dependence of resistivity of (a) LCO film, and (b) LSCO film; as grown, annealed at 200 °C in vacuum, and annealed at 200 °C in ozone, respectively.
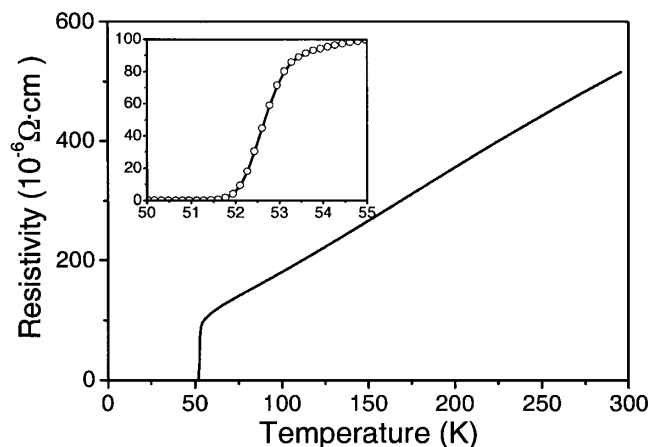

FIG. 4.   Temperature dependence of resistivity of a film consisting of a 20-nm-thick layer of LSCO covered with a 6.5-nm-thick layer of LCO, on a LSAO substrate.

so far in LSCO. However, the difference between the maximum T_c that we observed in films on tensile STO substrates ($T_c = 40$ K), and on compressive LSAO substrates ($T_c = 51.5$ K), is still relatively small and secondary as compared to the primary effect of oxygen content variation.

In conclusion, we have studied a large number of single-crystal LSCO thin films under both compressive and tensile epitaxial strain. We see no evidence that T_c can be doubled by compressive epitaxial strain alone. We have seen only a moderate ($< 30\%$) enhancement, with the record $T_c = 51.5$ K so far. On the contrary, we have strong evidence that extra oxygen can be incorporated easily in nominally undoped or underdoped LSCO films, even at very low temperature, and that this affects dramatically both the crystal structure and T_c. This great sensitivity to oxygen content is the primary cause of the observed huge variations of T_c in such films.

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