The large magnetoresistance property of $La_{0.5}Sr_{0.5}CoO_{3-x}$ thin films prepared by pulsed laser deposition

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High-quality (001) thin film $La_{0.5}Sr_{0.5}CoO_{3-x}$ (LSCO) has been prepared on (001) $SrTiO_3$ substrates by pulsed laser deposition under different oxygen pressures with and without postannealing. *C*-axis expansion of the LSCO with reducing oxygen pressure was revealed. The electrical resistivity increased over five orders of magnitude when oxygen pressure varied from 1.0 mbar (plus postannealing) to 10^{-3} mbar. The negative magnetoresistance (*n*-MR) property as a function of temperature and oxygen pressure was investigated. Linear dependence of the *n*-MR ratio on magnetic field and temperature was found and significant effect of oxygen stoichiometry on the *n*-MR was demonstrated. The film prepared at 650 °C and 0.1 mbar oxygen shows a *n*-MR ratio of −16% at 81 K under a field of only 0.2 T. © *1998 American Institute of Physics.* [S0003-6951(98)01134-6]

Highly strontium-doped $LaCoO_\delta$ materials such as $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) exhibit quite high electrical and ionic conductivity and show promising applications as electrodes for fuel cells and nonvolatile Pb-based ferroelectric memories.[1–3] Recently, the critical combinatorial approach of this class of materials demonstrated a large negative magnetoresistance (*n*-MR) effect.[4,5] For example, the *n*-MR value of stoichiometric $Ln_xM_yCoO_3$ where Ln=La or Y and M=Ba, Sr, Ca, or Pb, at 60 K under a magnetic field of 10 T reaches up to 25%. The LSCO with different La:Sr ratios represents the most interesting material in addition to the $LnMMnO_3$ series as either new electrodes or magnetic sensor or recording media. The latter class of materials shows the attractive colossal magnetoresistance (MR) effect.[6] Conventionally it is proposed that an external magnetic field aligns the disordered local spins in the LSCO materials which are in transition toward the ferromagnetic state. Such an alignment may increase electron conduction through strong interaction between itinerant electron and local spins.[4,6] Note here that the electron-hopping process between neighboring Co^{+4} and Co^{+3} ions is realized by the O^{-2} anion between them. We therefore expect a strong effect of oxygen stoichiometry on the MR property of the LSCO materials.

A recently published study on the electrical property of LSCO thin films deposited on a $LaAlO_3$ substrate demonstrated a tremendous change of the film conductivity, depending on the postcooling treatment under different oxygen ambient.[7] This work presents updated evidence that oxygen vacancies determine the electrical and magnetic properties of LSCO to such a high extent that a deep understanding and good control of oxygen stoichiometry must be made in order to acquire a well-defined performance of the related devices. To our knowledge, there is no reported experiment on the MR property of thin film LSCO depending on oxygen stoichiometry. In this letter we report our systematic investigation of electrical and MR properties of oxygen-deficient LSCO thin films prepared by pulsed laser deposition (PLD). Our results indicate that the negative magnetoresistance (*n*-MR) effect can be greatly enhanced by depleting oxygen content in the films in spite of seriously damaged electrical conductivity.

The PLD experiment was performed by using a 248 nm KrF excimer laser of 5 Hz in frequency. The experimental apparatus and general performance were previously described.[8] A ceramic disk of stoichiometric LSCO was chosen as a target and (001) $SrTiO_3$ (STO) single crystals of $10\times10\times0.5$ mm^3 as substrates. The size of thin films was 10×5 mm^2. For all cases, the substrate temperature was 650 °C. The laser fluence of 2.0 J/cm^2 was chosen. A series of samples deposited and consequently cooled at oxygen pressures P_a from 10^{-3} to 1.0 mbar were fabricated. We also acquired several samples deposited at $P_a=1.0$ mbar plus postannealing at 650 °C and 1.0 atm oxygen for 10, 20, and 40 min. Therefore, it is expected that the oxygen content of the as-prepared samples differs from one to another. The thickness of thin films was ~1000 nm. The orientation and crystallinity of samples were checked by x-ray fine θ–2θ scan and ω scan. The film constitution was probed by x-ray photoelectron spectroscopy (XPS), although the oxygen content was hard to determine.

A standard dc four-probe method for electrical measurement was used. Four pure silver pads of ϕ0.8 mm were deposited along the bisecting line over the film, with the inner two pads separating from 3.0 mm and the outer two from 6.0 mm symmetrically. For the *n*-MR measurement, the film surface was normal to the magnetic field *H* that varied linearly with time. The highest value of *H* was 0.2 T. The measurement was performed at a series of fixed temperatures.

The LSCO films prepared as described above are com-

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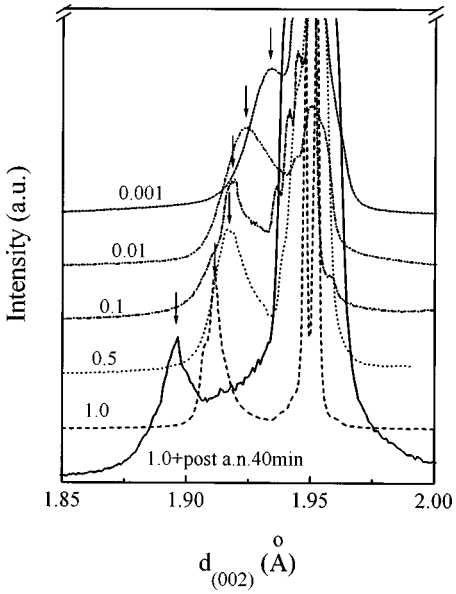

FIG. 1. Local XRD spectra for the LSCO thin films deposited on (001) STO substrates at 650 °C and different P_a (the values inserted in the figure, unit: mbar). Here ''+a.n.40 min'' means that the film was postannealed at 1.0 atm O_2 for 40 min, the same below.

pletely (001) oriented. The full width at half-maximum (FWHM) of the rocking curve for (002) LSCO reflection is only 0.5°–0.8°. Figure 1 presents the x-ray diffraction spectra of a series of samples prepared at different P_a. Figure 1 focuses on the local range around (002) reflections of LSCO and STO. Since the stoichiometric LSCO has a pseudocubic perovskite structure with lattice constant $c=0.382$ nm, a slight change of $d_{(002)}$ of LSCO was then expected, depending on the oxygen deficiency. It is shown that $d_{(002)}$ really shifted toward a larger value from the nominal one, 0.191 nm, as P_a decreased from 1.0 to 10^{-3} mbar. Expansion of the c axis is a well-known characteristic for the cubic-type perovskite structure with oxygen vacancies,[9,10] thus providing evidence of oxygen deficiency in the films. Note here that the sample prepared at 1.0 mbar plus postannealed at 1 atm oxygen for 40 min exhibited a $d_{(002)}$ slightly smaller than the nominal one, obviously due to the fact that the (001) plane of the LSCO was tensioned by the underlying STO substrate. The present results provide for the first time the data of LSCO correlating oxygen vacancies to the slight shift of $d_{(002)}$.

The XPS measurements revealed that the films showed quite good stoichiometry for La, Sr, and Co. For example, for a sample prepared at 0.2 mbar the evaluated atomic ratio of La:Sr:Co is 0.50:0.53:0.94, whereas the data counted from oxygen show big scattering, in spite of the changing tendency qualitatively consistent with P_a used. The thin film constitution may be represented by $La_{0.5}Sr_{0.5}CoO_{3-x}$.

The electrical resistivity ρ as a function of temperature is presented in Fig. 2 for all samples. The sample postannealed for 40 min showed metal-conductive character whereas the others exhibited semiconducting property. The metal-insulator transition was sensitive to the deposition parameters, although the resistivity was well defined. What is surprising is that four to six orders of magnitude in ρ were covered either at $P_a=1.0$ mbar with postannealing for 40 min at 1.0 atm or directly at $P_a=10^{-3}$ mbar. In addition,

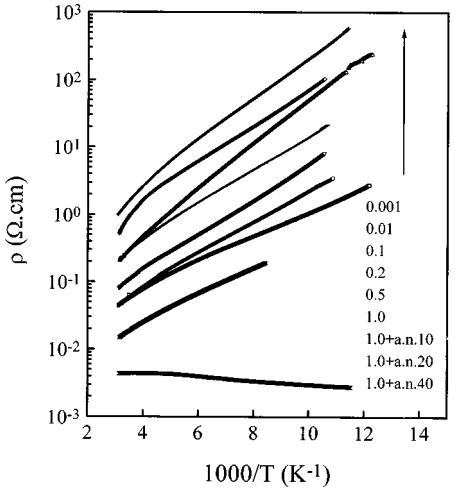

FIG. 2. $\rho(T)$ for thin film LSCO prepared at different pressures of oxygen. The values of oxygen pressure (mbar) are inserted in the figure.

good liner correlation between ρ and $1/T$ was established. The present data look similar to those acquired by Madhukar *et al.*[7] and an excellent explanation based on a defect model and change in the oxidation state of Co ions was given there.[7]

The *n*-MR property in these oxygen deficient LSCO thin films was greatly improved in spite of remarkable damage in the conductivity. Figure 3 presents the measured data at 81 K for the sample deposited at $P_a=0.1$ mbar, where $\sigma(H)$ is the relative MR ratio, $[\rho(H)-\rho(H=0)]/\rho(H)$. When H changed linearly between 0 and 0.2 T, a linear but opposite response of ρ was observed. The data are well reproducible. Although ρ was as high as 250 Ω cm, an *n*-MR value of -16% was already recorded at $H=0.2$ T. This value is much higher than the data previously reported for $LnMCoO_{\delta}$, for instance,

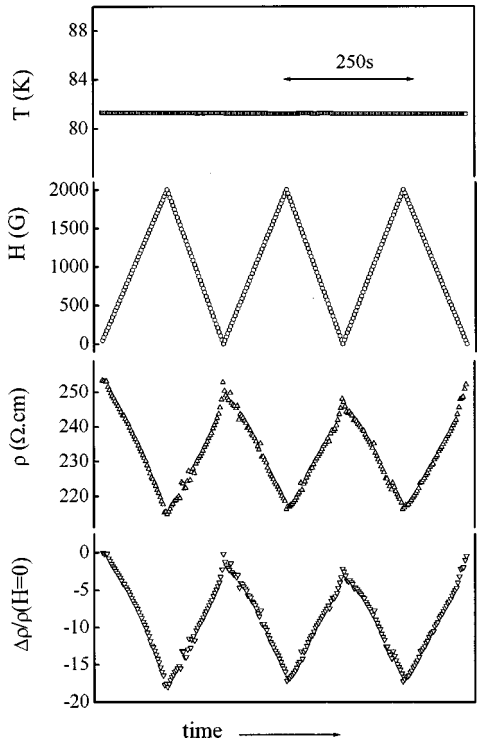

FIG. 3. T, H, ρ, and σ plotted against time, for sample prepared at $P_a=0.1$ mbar.

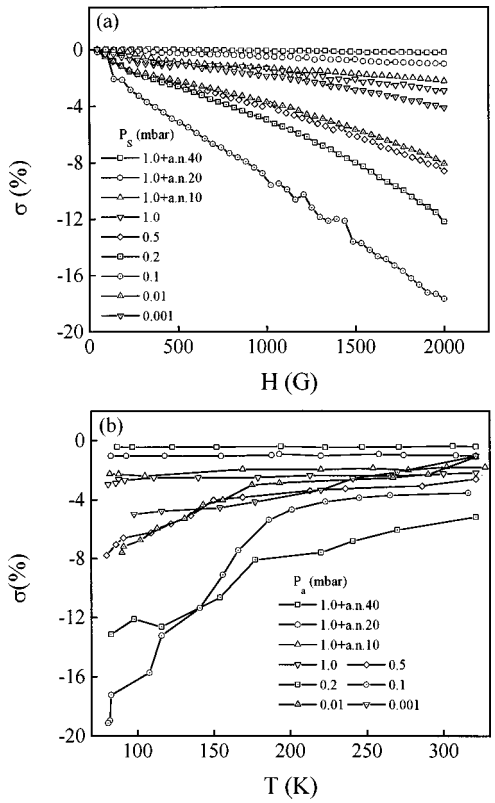

FIG. 4. (a) $\sigma(H)$ at $T\approx 85$ K and (b) $\sigma(T)$ at $H=0.2$ T for the thin films prepared at different values of P_a with and without postannealing. The data represent averaging of four measurements and there appears an error bar of $\pm(5$–$10)\%$.

$\sigma(0.2\ \mathrm{T})\sim -1.0\%$ and $\sigma(H=10\ \mathrm{T})\sim -25\%$. And indeed, it is the highest value achieved to date.[4] Our data demonstrated the significant effect of oxygen vacancies on the MR property of LSCO materials.

Looking at the value of σ at $T=85$ K for samples deposited at different conditions, we found significant effect of P_a on the *n*-MR property, as shown in Fig. 4(a). $\sigma\sim -1.0\%$ was detected for the sample deposited at higher pressure plus postannealing at 1.0 atm O_2, quite close to the data reported earlier.[4] As P_a decreased down to 0.5, 0.2, and 0.1 mbar without postannealing, σ was greatly improved up to -8%, -12%, and -17% at $H=0.2$ T, respectively. Upon further lowering of P_a to 0.01 and 0.001 mbar, σ recovered once more toward lower absolute values. Nevertheless, $\sigma\sim -4.0\%$ at $H=0.2$ T, still much higher than that reported previously,[4] was measured even at $P_a=0.001$ mbar, although ρ increased up to $\sim 700\ \Omega$ cm. In Fig. 4(b) are plotted the data at $H=0.2$ T against T over a range from 320 to 77 K. In spite of considerable scattering, the gradual growth of σ with decreasing T was clearly established. For those samples that were prepared at lower pressure of oxygen but showed higher $|\sigma|$, such a growth was remarkable. Those samples after postannealing exhibited very weak temperature dependence of σ.[4] According to the ''double-exchange'' model,[4,6] the MR effect may be observed only during a transition toward the ferromagnetic state. At room temperature that may be comparable to or less than the Curie point, a low $|\sigma|$ is reasonable because the system may not be in the well-defined ferromagnetic state. However, it is unclear whether such a mechanism is the sole origin of the MR effect for present case.

An acceptable explanation for the effect of oxygen vacancies on the MR property looks to be complicated. For the effect of oxygen vacancies on the conductivity, we may use the model proposed by Madhukar *et al.*[7] to interpret the experimental results. On the other hand, the role of oxygen vacancies in the MR effect is still unclear. For some oxides like LSCO, the interaction between magnetic field and local electrons leads to local spin-ordering of these electrons during a ferromagnetic transition. This ordering improves the electron conductivity. For the samples where there is high number of holes, the scattering effect may be strong as the magnetic field is applied, which compensates for the effect of local ordering. For the large MR effect at a mediate number of oxygen vacancies, it is argued that the local ordering of electrons become dominant as the number of holes decreases drastically. At this point, we wonder how the electron hopping between Co^{3+} and Co^{4+} is affected by the oxygen vacancies. More oxygen vacancies may trap more holes, so that fewer electrons are free to interact with the magnetic field. Nevertheless, this argument is just speculation before experimental evidence is presented, for instance, magnetization data for the different samples.

As a summary, we have demonstrated large *n*-MR effect in LSCO ($La_{0.5}Sr_{0.5}CoO_{3-x}$) thin films prepared on (001) STO substrates under reduced oxygen pressures. A maximal value of -16% in the *n*-MR ratio was recorded around liquid nitrogen temperature under $H=0.2$ T for the sample deposited at 650 °C and 0.1 mbar oxygen. The thin films exhibited expansion along *c* axis with decreasing oxygen pressure. The conductivity of the thin film LSCO was seriously damaged due to the incorporated oxygen vacancies. The *n*-MR effect shows remarkable dependence on temperature and the oxygen stoichiometry in the film.

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