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Oxygen Stoichiometry Modification by O_2-Plasma Treatment in $La_{0.7}Ca_{0.3}MnO_{3-\delta}$

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Abstract

Oxygen-plasma effects of single crystal and thin film samples of $La_{0.7}Ca_{0.3}MnO_{3-\delta}$ have been studied. Our resistivity measurements indicate that oxygen plasma treatment gives rise to oxygen diffusion into bulk regions, which results in a decrease of Mn^{3+} concentration in oxygen nonstoichiometric $La_{0.7}Ca_{0.3}MnO_{3-\delta}$ and in the activation energies of Holstein's small polarons in the paramagnetic region.

1. Introduction

Perovskite manganites with mixed manganese valence, $La_xD_{1-x}MnO_{3-\delta}$, with D for a divalent metal, have attracted a great deal of attention due to the large negative "colossal" magnetoresistance (CMR) for $0.2 < x < 0.5$ [1~5]. In this composition range, the system shows the simultaneous appearance of metallic conduction and ferromagnetism at low temperatures while the end materials (x=0, 1) are insulating antiferromagnets. The underlying physics of this system has been traditionally explained in terms of the double exchange (DE) mechanism due to Zener [6-8]. Other effects such as lattice polarons due to the Jahn-Teller (JT) distortion [9], magnetic polarons, and electron localization [10] were also advanced as an additional physics.

Spin-phonon coupling has been considered in any theoretical understanding of the CMR. In the Jahn-Teller distortion formalism, a strong relationship between Mn^{3+} and legand oxygen ions in $La_{0.7}Ca_{0.3}MnO_{3-\delta}$ is intrinsically assumed [9]. Therefore, oxygen stoichiometry plays a very important role in the charge transport and magnetic properties. Thus, the feasibility of controlling oxygen content is one of the important issues in CMR investigations in view of the fundamental physics as well as the reproducible device fabrication [11]. Until now, the oxygen stoichiometry has been controlled by O_2 annealing at ambient pressure at very high temperatures. On the other hand, it will be shown in this work that oxygen-plasma treatment [12] can be a very effective low temperature process of controlling the oxygen stoichiometry in $La_{0.7}Ca_{0.3}MnO_{3-\delta}$.

2. Experiment

A $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) thin film with a thickness of 2000 Å was prepared by laser ablation on a (110) MgO substrate, and a single crystal sample was grown by the floating-zone method. The samples were oxygen-plasma treated with a RF power of 50 W for 2 hours at a pressure of 4.51 mTorr, and the substrate temperature was 200 °C. The resistivity was measured with the standard four-probe method, and dc magnetization was measured with a SQUID magnetometer (Quantum design Co., MPMS 5). The magnetic ordering temperature is conventionally defined to be the onset of the ferromagnetic magnetization, which gave the T_c of 250 K for thin film and 240 K for single crystal, in good agreement with the conductivity measurements.

3. Results and discussion

Fig. 1 shows the x-ray diffraction peaks before and after O_2 plasma treatment for the thin film sample. For relative intensities, the diffraction intensities were normalized

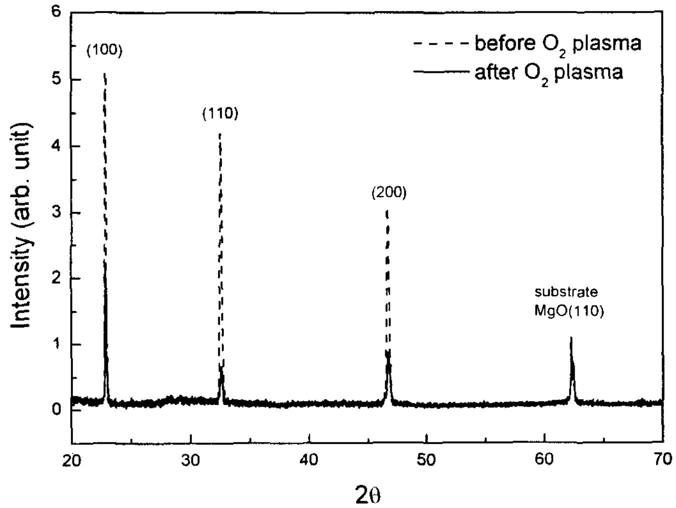

Fig. 1. The x-ray diffraction peaks before and after O_2 plasma treatment for thin film sample.

with the MgO (110) substrate peak. No shift of peak positions indicated the absence of macroscopic structural transformation caused by the oxygen plasma treatment. A likely explanation for the apparent decrease of the x-ray diffraction intensity after the O_2 plasma treatment is the plasma-induced surface etching effect.

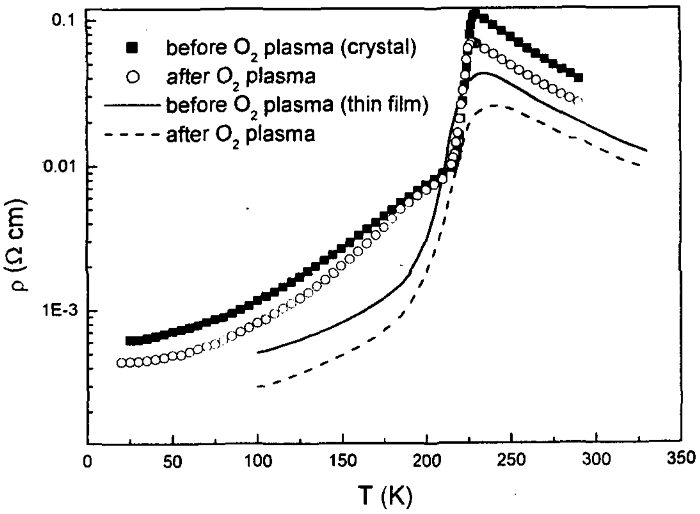

Fig. 2. The temperature dependence of the resistivity for the single crystal and thin film samples.

The temperature dependence of the resistivity for the single crystal and thin film samples are shown in Fig. 2. In both samples, it is noticed that the resistivity has decreased after the O_2-plasma treatment, which indicates that oxygen has diffused into the bulk regions. Effects within bulk regions must be sensitively reflected in the charge transport mechanism. Figure 3 displays plot of the resistivities above T_c as a function of reciprocal temperature. While the charge transport phenomena in the paramagnetic region is still controversial [11, 13, 14], we may obtain the activation energies using the Holstein's small polaron model [11, 13]. In that model, the temperature dependence of the resistivity above T_c is described by

$$\rho(T) = A\ T \exp\left(E_{hop}/k_B T\right), \qquad (1)$$

where E_{hop} is the polaron binding energy. The results of the fits according to Eq. (1) are shown in Table 1, which indicates that significant decreases in the activation energies have taken place in both samples after the plasma treatment.

As is well known, the Jahn-Teller distorted Mn^{3+} concentration is strongly correlated

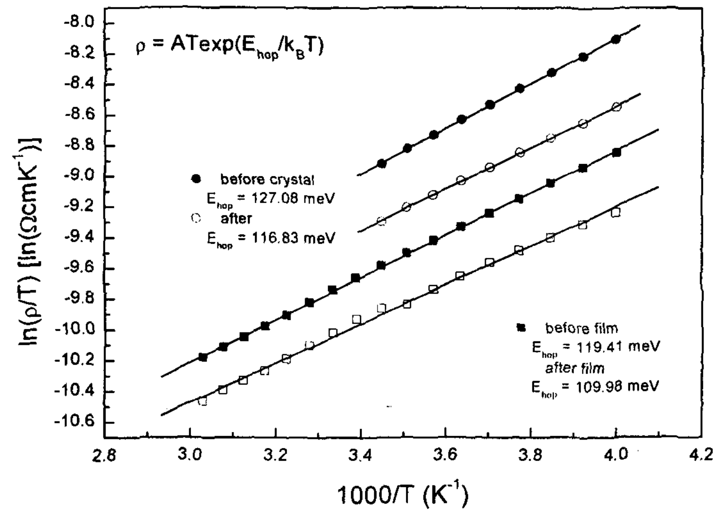

Fig. 3. The resistivities above T_c as a function of reciprocal temperature.

with the oxygen content. Thus the change in the Mn^{3+} concentration will also affect the Mn^{4+} concentration and the charge transport mechanism via an electron-lattice coupling. Using Teresa et al.'s work [11] and results, we were able to obtain the Mn^{3+} concentration. In Table 1, decreases in the Mn^{3+} concentration are observed after the plasma-treatment in both samples.

Table 1. The activation energies and Mn^{3+} concentrations before and after the O_2-plasma treatment.

Sample type	Before O_2 plasma		After O_2 plasma	
	E_{hop} (meV)	Mn^{3+} (%)	E_{hop} (meV)	Mn^{3+} (%)
Single crystal	127	83	117	80
Thin films	119	80	109	77

In summary, oxygen-plasma treatment was shown to be an effective low-temperature method of oxygen stoichiometry in the LCMO structure. The resistivity decreased after the plasma treatment, and decreases in the polaron activation energy and the Mn^{3+} concentration were also observed in the single crystal and thin film samples.

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