# Oxygen content of $La_{1-x}Sr_xMnO_{3-y}$ thin films and its relation to electric-magnetic properties

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It is known that the electric and magnetic properties of typical double-exchange materials $La_{1-x}Sr_xMnO_{3-y}$ (LSMO) are strongly affected by oxygen nonstoichiometry $y$, as well as by divalent ion doping level $x$. In the present study, we fabricated LSMO ($x=0.4$) thin films on $SrTiO_3$ (STO) (001) and $LaAlO_3$ (LAO) (001) under various pressures of oxygen ambient $p_{O_2}$, and evaluated their oxygen content $3-y$ using non-Rutherford elastic resonance spectroscopy. The change of their electric and magnetic properties was also measured and discussed. It was revealed that the oxygen content $3-y$ does not increase monotonically as $p_{O_2}$ increases. Curie temperature $T_C$ and insulator-metal transition temperature $T_{IM}$ were correlated with $3-y$ for the films on STO. The film on LAO of a quite high $p_{O_2}$ showed ferromagnetism and a metallic conductivity, unlike the films of lower $p_{O_2}$'s. The ferromagnetism is attributed to $c/a$ axis ratio closer to that of the bulk. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2176323]

It has been clarified that $La_{1-x}Sr_xMnO_{3-y}$ (LSMO) ($0.175 \leqslant x \leqslant \sim 0.55$ and $y=0$) realizes a ferromagnetism and a huge negative magnetoresistance due to a double-exchange interaction mechanism. In the stoichiometric bulks (with no oxygen content deviation), Sr doping level $x$ equals to $Mn^{4+}$ ratio $z$, which drastically controls the electric and magnetic properties.[1,2] On the other hand, the lattice distortion ($c/a$ axis length ratio) caused by the mismatching between a LSMO film and a substrate also has been revealed to affect strikingly to its spin ordering (ferromagnetic or antiferromagnetic) and, therefore, to its electric conductivity, from the works on the thin films with various compressive/tensile in-plane strains being deposited on $LaAlO_3$ (LAO), $(LaAlO_3)_{0.3}-(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT), and $SrTiO_3$ (STO) substrates.[3]

Oxygen content is another important parameter which dramatically affects the physical properties of materials of strong electron correlation. For example, the critical temperature of a high-$T_C$ superconductor is quite sensitive to its oxygen content.[4] In the case of LSMO thin films, oxygen content may affect the electric magnetic properties in both ways through $Mn^{4+}$ and $c/a$ ratios. Considering that the chemical formula of this material including ionic valence can be written as $La_{1-x}{}^{3+}Sr_x{}^{2+}Mn_{1-z}{}^{3+}Mn_z{}^{4+}O_{3-y}{}^{2-}$, it is deduced that $Mn^{4+}$ ratio $z$ should satisfy a relation $z=x-2y$ due to the charge neutral condition. Therefore, a deviation of oxygen content from 3 is expected to cause a change of $z$ as if a shift of Sr doping level $x$ will do, and thus a change of physical properties. On the other hand, a change of oxygen content may also cause a change of lattice constant. Generally, deficiency of oxygen in a perovskite-type oxide $ABO_3$ will expand its unit cell volume, probably because the $B^{(+)}-O^{2-}-B^{(+)}$ bond with a Coulomb attractive force will be transformed into $B^{(+)}-B^{(+)}$ with a repulsive force. In the case of epitaxial thin films thinner than "critical thickness" the in-plane lattice constant is fixed to that of the substrate, and thus a change of unit cell volume of the film results in a change of the $c/a$ length ratio.

So it is obvious that the "oxygen nonstoichiometry" is a quite important parameter that is related to "spin," "charge," "orbit," and "lattice" in divalent ion-doped manganites. In the case of thin films, the electric and magnetic properties of LSMO are easily affected by changing the oxygen atmosphere during deposition or postannealing. It has been reported that thin films of $La_{1-x}Ca_xMnO_{3-y}$ ($x=0.3$) and LSMO ($x=0.15$ and 0.175), originally double-exchange ferromagnetic metals, show various electric behaviors from insulator to metal as its oxidation conditions are varied.[5,6]

It is an interesting question whether the influence that the oxygen content deviation of LSMO causes onto its electric-magnetic properties through the change of $Mn^{4+}$ ratio or through the lattice distortion. In order to solve the question, one has to measure the actual oxygen content of thin films. Non-Rutherford elastic resonance spectroscopy (NRERS) is one of very few techniques that enables the nondestructive evaluation of oxygen content in thin films. NRERS, using the same instruments as Rutherford backscattering (RBS), utilizes a nuclear reaction $^{16}O(\alpha,\alpha)^{16}O$ that occurs between an oxygen nucleus and a helium ion with certain incident energy (3.04 MeV in the present case). Since the oxygen signal obtained with this nuclear reaction is one order larger than that of RBS process, it is possible to detect the oxygen content even in thin films with high accuracy.[7]

The evaluation of oxygen content in thin films would also give us the answers to some other questions. What is the relation between oxidation conditions (for example, ambient $O_2$ pressure during deposition, $p_{O_2}$) and the actual oxygen content? What is the best deposition condition in the viewpoint of oxygen incorporation into the films? The latter ques-

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tion arose because there are many reports on fabrication of LSMO films with a pulsed laser deposition (PLD) technique, with quite different values of the oxygen pressure (0.1–300 mTorr).[3,8]

In the present study, we evaluated oxygen content deviation $y$ of LSMO ($x=0.4$) thin films fabricated in various $p_{O_2}$'s on (STO) (001) and (LAO) (001) substrates, using NRERS. The electric and magnetic properties of these films were also measured, and oxygen nonstoichiometry effect on the physical properties of LSMO is discussed, considering $Mn^{4+}$ ratio and $c/a$ ratio.

The LSMO films were deposited using a pulsed laser deposition technique (KrF excimer laser; Lambda Physik Co., Compex 102) on STO (001) and LAO (001) substrates with a stoichiometric LSMO ($x=0.4$) ceramic target. The deposition conditions are 2 J/cm$^2$ of laser fluence, 4 Hz of repetition rate, 750 °C of substrate temperature, 0.3–300 mTorr of ambient $O_2$ pressure $p_{O_2}$. The samples were annealed for 30 min in the same temperature and ambient as during deposition, and then cooled down rapidly. RBS simulation revealed the number of deposited atoms to be $(320-400)\times10^{15}$ at./cm$^2$, which is converted to the thickness of 38–50 nm, supposing the unit cell volume of the bulk.

The orientation and out-of-plane lattice constant ($c$-axis length) of the films were examined by performing $2\theta$-$\omega$ scans using x-ray diffractometer (XRD) system (Philips Co., Cu $K\alpha$ line), resulting in the $c$-axis orientation for all the films. The crystallinity of each film was indicated by full width half maximum (FWHM) of LSMO (002) peak from an $\omega$ scan rocking curve.

Temperature dependence of magnetization ($M$-$T$) of each film was measured with a superconducting quantum interference device (SQUID) system (Quantum Design Co.), under a magnetic field $H=0.2$ T. Temperature dependence of resistivity ($\rho$-$T$) was measured under 0 and 5 T of magnetic field using a physical properties measurement system (PPMS) (Quantum Design Co.).

NRERS measurements were performed in a RBS system (Nissin High-Voltage Co., NT-1700H) using a He ion beam with incident energy of 3.04 MeV, accumulation charge of 5 $\mu$C, and scattering angle of 170°. The measurement configuration of each sample was carefully chosen to avoid channeling. Figure 1 shows the typical RBS/NRERS data of a LSMO ($x=0.4$) film deposited in 0.3 mTorr of $O_2$ on an STO substrate. The procedure to evaluate the oxygen content is as follows. (1) Draw a straight base line which fits the raw data for substrate metal elements (390–570 channels). (2) Integrate the signals of the oxygen resonance peak (357–390 channels) subtracted by the base line. Here we set the starting channel of integration region as the midpoint of the rising slope, because the bottom part of the slope may include the information from the substrate.

Figure 2 shows the $\rho$-$T$ and $M$-$T$ of LSMO films deposited on STO substrates. All the films on STO are metallic at the temperature below insulator-metal (IM) transition temperature $T_{IM}$, which is the same property as a LSMO ($x=0.4$) bulk. There is a rough trend that $T_{IM}$ and Curie temperature $T_C$, which are close to each other, decrease as $p_{O_2}$

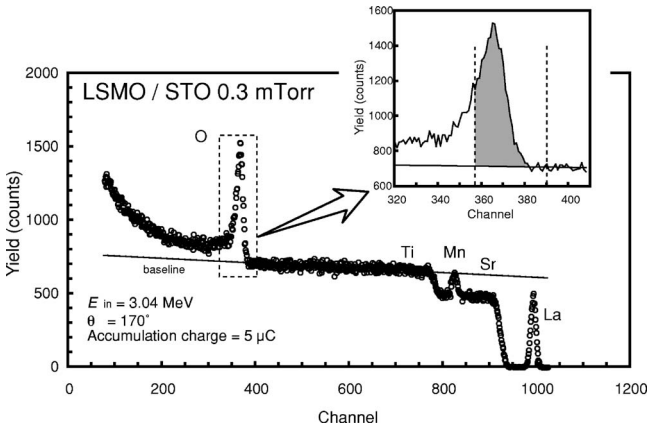


FIG. 1. RBS/NRERS data of a LSMO ($x=0.4$) film deposited in 0.3 mTorr of $O_2$ on a STO substrate, and the procedure to evaluate the oxygen content.

decreases. However, we note that $T_C$ ($\sim T_{IM}$) is lower in the film of $p_{O_2}=3$ mTorr than that of 0.3 mTorr. The reduced $T_C$ and $T_{IM}$ are reproducible and not accidental.

Figure 3 shows the $\rho$-$T$ and $M$-$T$ of LSMO films deposited on LAO substrates. Obviously, the LSMO films on LAO for $p_{O_2}\leqslant 30$ mTorr are insulating and antiferromagnetic, while that for $p_{O_2}=300$ mTorr shows metallic and ferromagnetic behaviors. It has been reported that LSMO ($0.3\leqslant x\leqslant 0.5$) films on LAO substrates become $C$-type antiferromagnetic, due to the compressive strain that occurs between LSMO ($a=3.873$ Å for bulk) and LAO ($a=3.792$ Å).[3] The present results of LSMO ($x=0.4$) films on STO and LAO agree with the results in Ref. 3, except the ferromagnetic metallic behavior of LSMO on LAO deposited under high oxygen pressure ($p_{O_2}=300$ mTorr).

Figure 4 shows various film properties such as $c$-axis length (a), FWHM of LSMO (002) peak (b), $T_C$, $T_{IM}$, and the

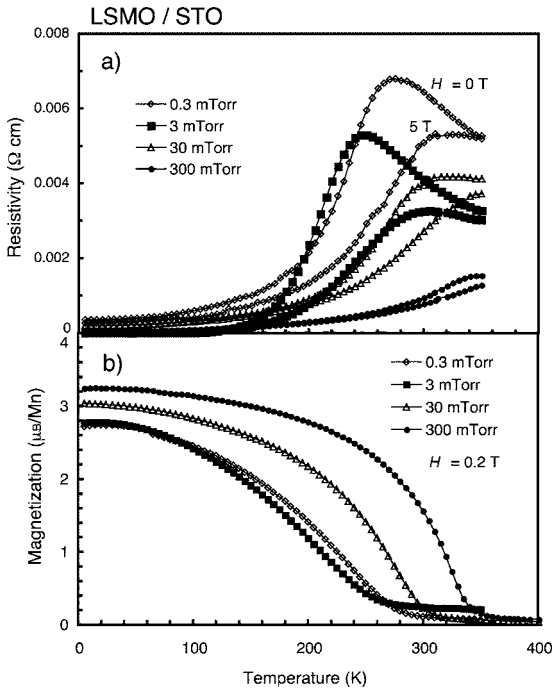


FIG. 2. Temperature dependence of resistivity in 0 and 5 T magnetic field (a) and magnetization (b) of LSMO ($x=0.4$) films deposited on STO substrates.

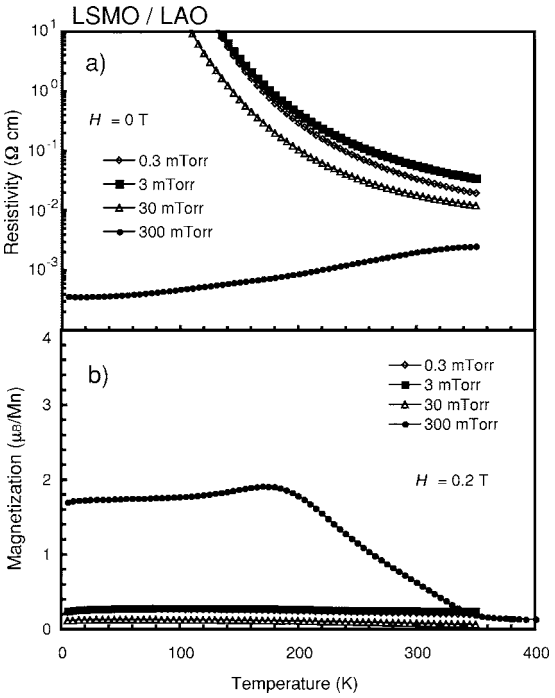


FIG. 3. Temperature dependence of resistivity in zero field (a) and magnetization (b) of LSMO ($x$=0.4) films deposited on LAO substrates.

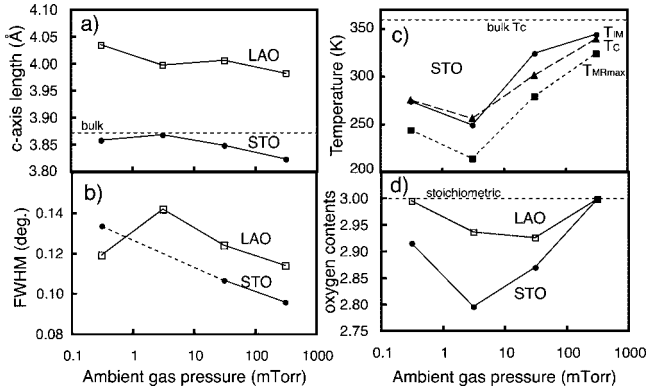


FIG. 4. $C$-axis length (a), full width half maximum of LSMO (002) peaks in $\omega$ rocking curves (b), $T_C$, $T_{IM}$, and the temperature where magnetoresistance becomes maximum ($T_{MR\ max}$) (c), and oxygen contents (d) for the LSMO ($x$=0.4) films deposited on STO and LAO substrates plotted vs $p_{O_2}$. Oxygen content in the LSMO films of $p_{O_2}$=300 mTorr is assumed to be 3. The FWHM datum for the film of $p_{O_2}$=30 mTorr on STO is lacking because the peak of the film overlapped that of the substrate.

temperature where magnetoresistance becomes maximum ($T_{MR\ max}$) (c), and oxygen contents (d) plotted versus $p_{O_2}$. Here we assumed the oxygen content in the LSMO films at $p_{O_2}$=300 mTorr to be 3. Since we could not prepare a reliable standard sample for evaluation of the oxygen content, the absolute value of oxygen contents is not obtained. It is the subject for a future study.

Note that the oxygen content of the film for $p_{O_2}$ =3 mTorr is less than that for 0.3 mTorr, for both STO and LAO. Here it was revealed that the oxygen content of thin films does not always increase monotonically as $p_{O_2}$ increases. This result implies that there exists a pressure in which the film easily/hardly incorporate oxygen. In comparison to the FWHM of the films on LAO, one can see a tendency that the films with narrower XRD peak contain more oxygen. It suggests that a film incorporates oxygen under a good condition for epitaxial film growth, even if the oxygen ambient pressure is as low as 0.3 mTorr.

There was a correlation between oxygen content and $T_C$ ($\sim T_{IM}$) for the films on STO. The lowest $T_C$ of the film for $p_{O_2}$=3 mTorr can be explained with the largest oxygen deficiency. For the LSMO films on STO with the oxygen contents quite low ($p_{O_2}$ of 3 and 30 mTorr), one may expect that the $Mn^{4+}$ ratio $z$ may be less than 0.175, and that their electric property would be insulating according to the $x$-$T$ phase diagram.[1] Actually, however, all the films on STO show IM transition. It suggests that not only $Mn^{4+}$ ratio but also the effect of lattice distortion should be taken into account.

In many cases, oxygen deficiency of a perovskite-type oxide causes an expansion of the unit cell volume. On the other hand, $Mn^{4+}$ ratio also should be changed by the change of oxygen content, according to the relation $z=x-2y$. One can suppose that the deficiency of oxygen content from 3 would cause the nominal $x$ decrease, but would cause $c/a$ ratio increase. Considering the plot of $c/a$ ratio versus $x$ [Fig. 3(a) in Ref. 3] and adopting $z$ instead of $x$, oxygen deficiency would shift the point along the borderline between $C$-type antiferromagnet and ferromagnet in the case of a LSMO film on a LAO susbstrate. This may be the reason why no drastic change between antiferromagnetic and ferromagnetic states occurred. As an exception, LSMO on LAO ($p_{O_2}$ =300 mTorr) showed ferromagnetic metallic properties, in spite of the similar oxygen content and similar FWHM to the film of $p_{O_2}$=0.3 mTorr. It is considered that $c/a$ ratio of 300 mTorr film is smaller than that of 0.3 mTorr film and slightly closer to that of the bulk ($c/a$=1.0), which allows the film to form ferromagnetic (FM) domains. A broad ferromagnetic transition of this film suggests the existence of domains with inhomogeneous magnetic properties. These results imply that the unit cell volume of the films may differ for different fabrication conditions, even if their oxygen content coincides.

In conclusion, we compared the oxygen contents and electric-magnetic properties of LSMO ($x$=0.4) thin films deposited on STO (001) and LAO (001) substrates under various oxygen ambient pressures. It was clarified that oxygen content does not always increase monotonically as the fabrication ambient pressure increases. The condition to produce a high-quality epitaxial film is suggested to be equal to the condition that oxygen atoms are incorporated into the film effectively.

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