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The colossal magnetoresistive La-Sr-Mn-O film by pulsed laser deposition

Fumiaki Mitsugi, Tomoaki Ikegami, Kenji Ebihara,
Jagdish Narayan* and Alexander M. Grishin**
Department of the Electrical and Computer Engineering, Kumamoto University, Kurokami, Kumamoto 860-8555, Japan
Fax: 81-96-342-3630, e-mail: mitsugi@st.eecs.kumamoto-u.ac.jp
*Department of the Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-7916, USA
Fax: 1-919-515-7642, e-mail: J_NARAYAN@NCSU.EDU
**Department of Condensed Matter Physics, Royal Institute of Technology, S-10044 Stockholm, Sweden
Fax: 46-8-790-6952, e-mail: grishin@cmp.kth.se

The colossal magnetoresistive $La_{0.8}Sr_{0.2}MnO_3$ (LSMO) films were grown on the MgO (100) single crystal substrates by KrF excimer pulsed laser deposition technique. The substrate temperature and oxygen pressure during deposition were changed in the range of 650-850℃ and 100-500 mTorr, respectively. The LSMO film deposited at 850℃, oxygen pressure of 500 mTorr and laser fluence of 2 J/cm^2 (5 Hz) showed the resistivity peak temperature of 330 K. The temperature coefficient of resistance (TCR) was about 3% at the room temperature. The x-ray diffraction measurement indicated the c-axis oriented LSMO (00*l*) peaks. The surface morphology observed by atomic force microscopy was very smooth with grain size of about 100 nm.
Key words: colossal magnetoresistance, LSMO, resistivity peak temperature, pulsed laser deposition

1. INTRODUCTION

Perovskite manganites of the $Re_{1-x}Ae_xMnO_3$ (Re: La, Nd, Pr or other rare earth elements; Ae: Ca, Sr, Ba or other alkaline earth elements) have the negative colossal magnetoresistance (CMR) effect. The CMR materials have potential for various device applications such as magnetic field sensor, hard disk read head and infrared bolometer sensor. The basic manganite of $ReMnO_3$ is an antiferromagnetic insulator. A substitution of the divalent Ae^{2+} for the trivalent Re^{3+} makes $Mn^{3+}(t^3_{2g}\,e_g^1)$ / $Mn^{4+}(t^3_{2g}e_g^0)$ mixed valence state. The electron hopping from Mn^{3+} to Mn^{4+} by a Mn-O-Mn path results in ferromagnetic ordering and metallic conductivity in accordance with the double-exchange (DE) interaction.[1] So, the Mn^{3+} / Mn^{4+} ratio and Mn-O-Mn bond length are the very important parameters. The transport property of the CMR material exhibits a transition from paramagnetic insulating state to ferromagnetic metallic state, and is characterized by the resistivity peak temperature (T_p) and Curie temperature (T_c), respectively. In most cases, the T_p is close to T_c. The sizes of the Re^{3+} ion and Ae^{2+} ion change the Mn-O-Mn bond length and have an effect on the transport property. It is necessary that the T_p (T_c) of CMR material is higher than room temperature to realize CMR application devices. The large radii of La^{3+} ion (1.15Å) and Sr^{2+} (1.13Å) ion shorten the Mn-O-Mn bond length, and that results in high T_p.[2]

In this paper, we investigated the structural and electric properties of the $La_{0.8}Sr_{0.2}MnO_3$ (LSMO) films deposited by KrF excimer laser deposition (PLD) method.

2. EXPERIMENT

Thin films of LSMO were prepared from stoichiometric target of $La_{0.8}Sr_{0.2}MnO_3$ by PLD technique on MgO (100) substrates. Figure 1 shows a schematic diagram of PLD method. The ambient oxygen gas was fed into the stainless steel chamber (ϕ=280 mm) after evacuating to base pressure of 10^{-6} Torr. The pressure of oxygen was adjusted by a mass flow controller. The MgO (100) substrate was heated by a flat plate heater (Neocera). KrF excimer laser beam (Lambda Physik LPX305icc, λ=248 nm, pulse duration=25 ns, maximum output=850 mJ/pulse) ablated the rotating ceramic target. The laser energy density and repetition rate were 2 J/cm^2 and 5 Hz, respectively. The deposition time was 10 min (3000 pulses). The distance from the target to MgO substrate was 40 mm. The substrate temperature (T_s) and oxygen pressure (P_{O2}) were varied in the range of 650-850 ℃ and 100-500 mTorr,

respectively.

The crystalline structure was examined using x-ray diffractometer (Rigaku RINT2000/PC) with CuKα radiation. The surface morphology of the film was observed by atomic force microscopy (Seiko Instruments Inc. SPI3800N). The film thickness was estimated by cross-sectional scanning electron microscopy (JEOL JSM-T200). The conventional four terminal resistance method (liquid nitrogen cryostat system) was used to measure the resistivity versus temperature (*R-T*) curves.

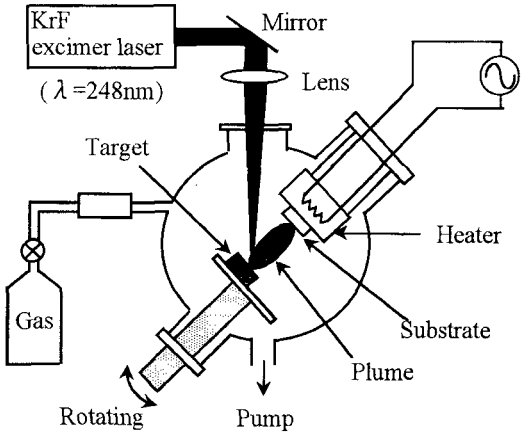

Fig.1 A schematic diagram of PLD method.

3. RESULTS AND DISCUSSION

Figure 2 shows the T_s (650-850℃) dependence of the *R-T* curves for the LSMO films deposited at P_{O2} of 100 mTorr. To measure the resistance of LSMO film, four Au electrodes were deposited by thermal evaporation method. Cross-sectional scanning electron microscopy images showed that the thickness of the film deposited 3000 pulses in P_{O2} of 100 mTorr is about 500 nm. T_s has no influence on the film thickness. T_p are 250 K, 257 K, 275 K and 285 K for the films deposited at 650℃, 700℃, 800℃ and 850℃, respectively. It is found that T_p increases with T_s and that resistivity tends to decrease with T_p (T_s).

Figure 3 shows the temperature coefficient of resistance (TCR) versus temperature curves for the above samples. TCR is defined as (dR / dt) / R which indicates the slope of *R-T* curve. The TCR of the film deposited at low T_s (650℃, 700℃) shows small value near the room temperature. The maximum TCR of the films deposited at 800℃ and 850℃ is about 2%. The TCR peak temperature tends to shift to the room temperature when T_s is increased.

Atomic force microscopy surface morphology of the film deposited at 850℃ was the smoothest (maximum roughness of 9nm) with the grain size of about 100 nm.

The x-ray diffraction measurement indicated only c-axis oriented (00*l*) peaks. Figure 4 shows the T_s dependence of the full width at the half maximum (FWHM) for the LSMO (002) peak. It is clear that the FWHM decreases with T_s. The narrow FWHM value of 1.00° was obtained for the film of T_p=285 K (T_s=850 K).

The c-axis lattice constant was calculated from the LSMO (002) peak (Figure 5). This result suggests that the increase of substrate temperature T_s enhances the oxidation of the film, which results in high degree crystallization, smooth surface morphology, large grain size and high T_p.

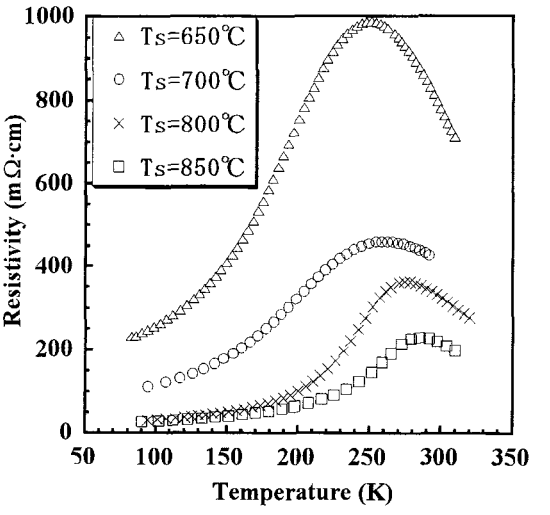

Fig.2 The substrate temperature (T_s) dependence of the resistivity versus temperature (*R-T*) curves for LSMO films (P_{O2}=100 mTorr, 500 nm).

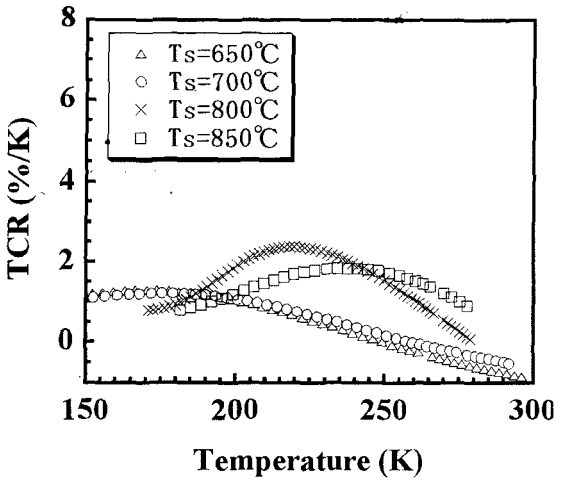

Fig.3 The substrate temperature (T_s) dependence of the temperature coefficient of resistance (TCR).

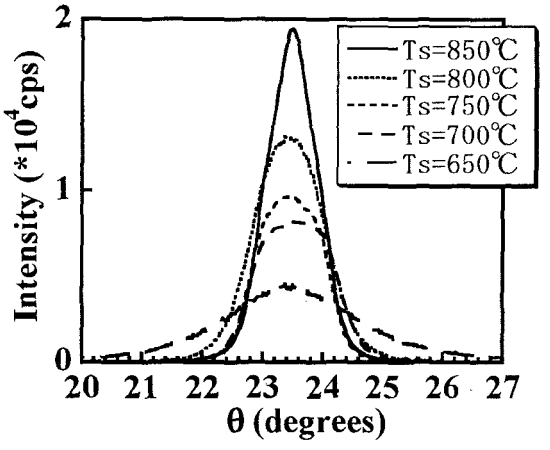

Fig.4 FWHM of the rocking curve for the LSMO films.

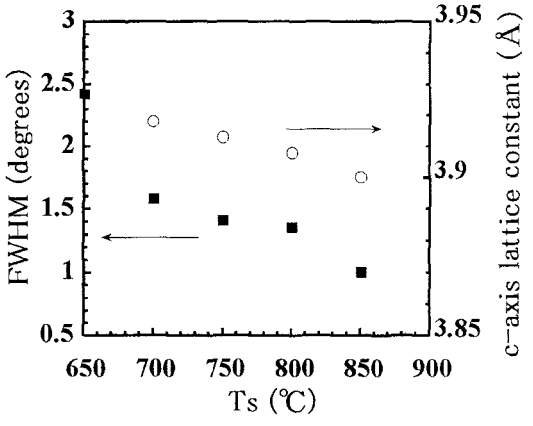

Fig.5 FWHM and c-axis lattice constant (calculated from LSMO(002) peak) of the LSMO films.

Figure 6 shows the P_{O2} (100-500 mTorr) dependence of the *R-T* curves for the LSMO films (T_s=850℃, 3000 pulses). The high ambient pressure suppressed the plasma plume and reduced film thickness. Thickness of the sample deposited in 100 mTorr oxygen was 500 nm as mentioned above. Both films deposited in P_{O2} of 300 and 500 mTorr have thickness of about 200 nm. It is found that the resistivity is largely decreased and T_p rises over the room temperature by increasing P_{O2}. The sample of 500 mTorr oxygen has T_p of 330 K and very low resistivity of 20 mΩ · cm. TCR of this film is about 3% (at 280 K) near the room temperature (Figure 7). This value is the typical result of LSMO film.[2] It is desirable that the temperature at the TCR maximum point is close to room temperature.

The c-axis lattice constants were 3.90Å, 3.89Å and 3.88Å for the LSMO films of 100 mTorr, 300 mTorr and 500 mTorr, respectively. It is shown that as for the preparation of oxide LSMO film, the oxygen content is a key parameter similar to the fabrication of oxide superconductor and ferroelectrics.

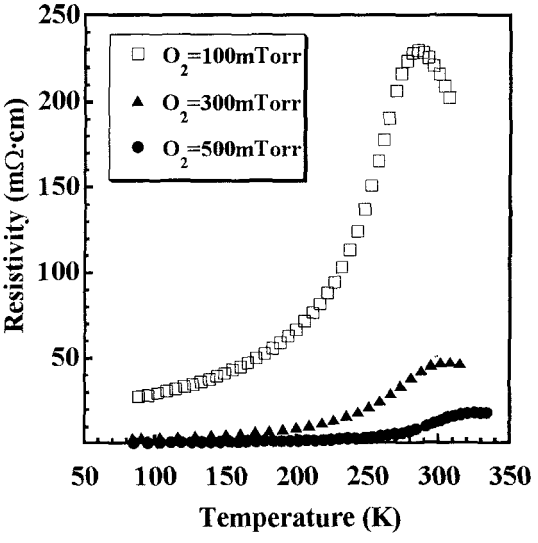

Fig.6 Oxygen pressure (P_{O2}) dependence of the resistivity versus temperature (*R-T*) curves for LSMO films (T_s=850℃).

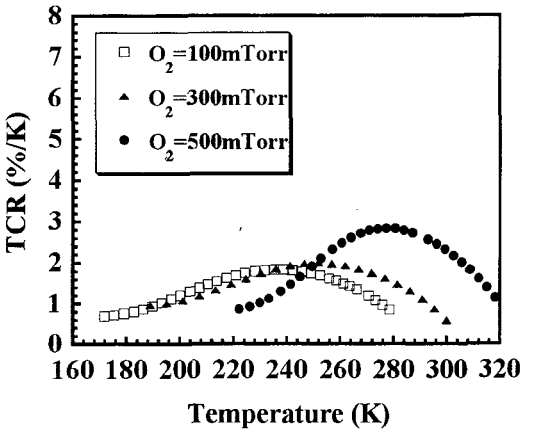

Fig.7 Oxygen pressure (P_{O2}) dependence of the temperature coefficient of resistance (TCR).

4. CONCLUSION

We prepared the colossal magnetoresistive LSMO films on MgO (100) substrate changing the deposition conditions of T_s and P_{O2}. The surface morphology was smoothed with increasing T_s. The maximum roughness of the film prepared at 850℃ in 100 mTorr was below 10 nm. This surface condition was caused by high degree crystallization (narrow rocking curve). It was found that high deposition temperature and high oxygen pressure tend to decrease the resistivity, increase T_p and shorten c-axis lattice constant. The LSMO film deposited at 850℃ in 500 mTorr oxygen has T_p of 330 K, TCR of 3% (at room temperature) and c-axis lattice constant of 3.88Å. It suggests that the oxygen content in the film increases with increasing T_s and P_{O2}, which results in excellent structural and electric properties.

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