

# Epitaxial growth of ferromagnetic $\text{La}_2\text{NiMnO}_6$ with ordered double-perovskite structure

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Epitaxial thin films of ordered double-perovskite  $\text{La}_2\text{NiMnO}_6$  were deposited on  $\text{SrTiO}_3$ ,  $(\text{LaAlO}_3)_{0.3}-(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ , and  $\text{LaAlO}_3$  substrates by a pulsed-laser deposition method. A rock-salt-type ordering for  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  ions was confirmed through structural and magnetic measurements. Despite the difference in heteroepitaxial constraints on the crystal structure, the magnetic properties of the films were quite similar to each other and also to those of bulk  $\text{La}_2\text{NiMnO}_6$ . © 2006 American Institute of Physics. [DOI: 10.1063/1.2226997]

Magnetic semiconductors have recently attracted a great deal of attention for possible applications in spintronics devices, such as magnetodielectric capacitors<sup>1,2</sup> and spin filtering tunnel junctions.<sup>3,4</sup>  $\text{La}_2\text{NiMnO}_6$  (LNMO) is a ferromagnetic semiconductor and one of the most promising materials for spintronics devices. A bulk sample of LNMO is usually synthesized by a solid state reaction and crystallizes in an ordered double-perovskite with a pseudocubic structure, in which  $\text{NiO}_6$  and  $\text{MnO}_6$  octahedra are ordered in a rock-salt configuration.<sup>5–8</sup> Although most transition-metal oxides are antiferromagnets due to superexchange interactions between magnetic ions, LNMO is a ferromagnet and its magnetic properties can well be explained by Kanamori-Goodenough rules. The ordered arrangement of the  $\text{NiO}_6$  and  $\text{MnO}_6$  octahedra gives rise to  $180^\circ$  ferromagnetic interactions between  $\text{Ni}^{2+}$  ( $d^8, S=1$ ) and  $\text{Mn}^{4+}$  ( $d^3, S=3/2$ ) ions.

A great advantage of device applications for LNMO is that the material demonstrates ferromagnetic ordering near room temperature (ferromagnetic transition temperature,  $T_C=280$  K). This is in sharp contrast to many other ferromagnetic semiconducting oxides that exhibit ferromagnetic ordering at very low temperature [e.g.,  $\text{SeCuO}_3$  ( $T_C=25$  K),<sup>9</sup>  $\text{EuO}$  ( $T_C=77$  K),<sup>10</sup> and  $\text{BiMnO}_3$  ( $T_C=100$  K) (Ref. 1)]. In addition, recent findings on magnetocapacitance and magnetoresistance in this material have improved possibilities for device applications.<sup>11</sup> It is necessary to fabricate LNMO in thin film form to use it for spintronics devices.<sup>12</sup> We succeeded in preparing double-perovskite LNMO thin films epitaxially grown on different substrates by pulsed-laser deposition (PLD). We report on the growth conditions for these films in this letter and discuss their structural and magnetic properties.

LNMO films were deposited with a PLD system. A stoichiometric LNMO prepared with a standard solid state reaction was used for the target.  $\text{SrTiO}_3$  (STO),  $(\text{LaAlO}_3)_{0.3}-(\text{Sr}_2\text{AlTaO}_6)_{0.7}$  (LSAT), and  $\text{LaAlO}_3$  (LAO)

with a cubic (001) surface were used as substrates. The distance between the LNMO target and substrate was 4.5 cm. The respective cubic lattice constants of these substrates are 3.905, 3.868, and 3.789 Å. The total thicknesses of the deposited films were 600 Å. Their crystal structures were evaluated by reflection high energy electron diffraction (RHEED) and x-ray diffraction (XRD) using  $\text{Cu } K\alpha$  radiation. Their magnetic properties were investigated by measuring dc magnetization with a superconducting quantum interference device (SQUID) magnetometer.

We first examined the optimum conditions for growing the ordered double-perovskite LNMO films on STO substrates. We deposited LNMO at temperatures between 650 and 900 °C under oxygen pressure of 100 mTorr, and confirmed that the single crystal perovskite structure stabilized between 750 and 800 °C. We thus fixed the growth temperature at 770 °C in the present experiments. The film deposited at this temperature exhibited (001) sharp Bragg peaks for the simple cubic perovskite structure, as can be seen from the XRD pattern in Fig. 1(a). The results of the  $\phi$  scan of the in-plane (200) reflection in Fig. 1(b) clearly demonstrate epitaxial growth of the LNMO film. We also found that the ordering of  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  ions of LNMO films was strongly affected by the oxygen pressure during the deposition. Figure

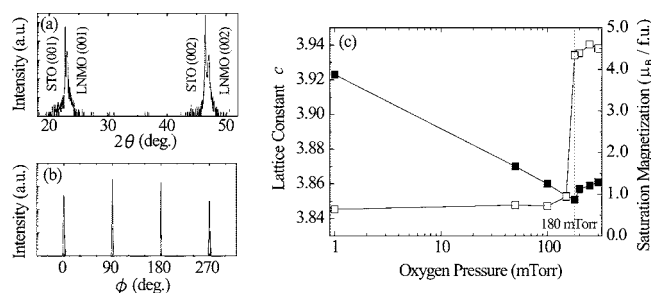


FIG. 1. (a)  $2\theta$ - $\theta$  x-ray diffraction pattern and (b)  $\phi$  scan of in-plane (200) reflections of the heteroepitaxial LNMO/STO(001) film. (c) Out-of-plane lattice constant  $c$  (■) and saturation magnetization in a magnetic field of 10 kOe at 5 K (□) of LNMO films deposited on STO substrates under various oxygen pressures at 770 °C.

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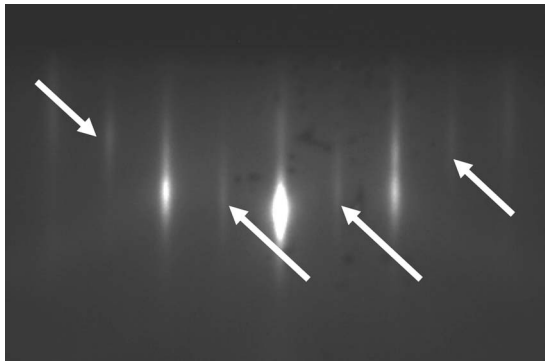


FIG. 2. RHEED pattern of the LNMO thin film on the STO substrate with a (110) beam incidence. The arrows indicate twofold superstructure peaks.

1(c) shows out-of-plane lattice constant  $c$  and saturation magnetization at 5 K for the LNMO films deposited at 770 °C under various oxygen pressures. Although all the samples had well-crystallized perovskite structures, the out-of-plane lattice constant  $c$  of the films changed significantly with oxygen pressure. It seems that the change in lattice constant is related to the ordering of  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  ions and that high oxygen pressure stabilizes this ordering in the structure. Indeed, the magnetic moments of the samples synthesized under oxygen pressures above 180 mTorr drastically increased and reached the value observed in bulk samples, which have a rock-salt-type ordering.<sup>8</sup> We thus concluded that an oxygen pressure over 180 mTorr is necessary to synthesize the ordered double-perovskite LNMO film.

It is noted that the LNMO film crystallized in the double-perovskite structure with the optimum condition, in which  $\text{NiO}_6$  and  $\text{MnO}_6$  octahedra were ordered in a rock-salt configuration. The RHEED patterns with the (110) and  $(1\bar{1}0)$  beam incidences for the film on the STO substrate revealed streaks from a twofold superstructure (Fig. 2), while the pattern with the (100) beam incidence had no superstructure streaks, which clearly indicates a  $\sqrt{2}a \times \sqrt{2}a$  superstructure. This  $\sqrt{2}a \times \sqrt{2}a$  superstructure originates from the rock-salt-type ordering of  $B$  site ions in the double-perovskite structure.<sup>13</sup> Indeed, we could not observe such clear superstructure streaks in RHEED patterns with the (110) beam incidence for samples deposited below an oxygen pressure of 180 mTorr, which had a small degree of magnetization, as shown in Fig. 1.

We deposited LNMO films on LSAT and LAO substrates under the same conditions to grow ferromagnetic films on STO substrates (oxygen pressures of 300 mTorr) to evaluate the effect of heteroepitaxial constraint on the magnetism of the thin films. Figures 3(a)–3(c) are logarithmic intensity mappings in the reciprocal space around the (103) reflection of the simple perovskite structure for the LNMO thin films deposited on STO, LSAT, and LAO substrates, respectively. The in-plane lattice constants of the films on STO and LSAT match those of substrates, confirming coherent epitaxial growth of the films. In contrast, the peak position of the LNMO (103) reflection has slightly shifted from that of the LAO substrate along the  $Q_{100}$  axis, as can be seen from Fig. 3(c). In addition, the full width at half maximum of the peak of the LNMO film on LAO is apparently broader than those of the films on STO and LSAT. Since the lattice parameter  $a$  of pseudocubic bulk LNMO is about 3.88 Å,<sup>8</sup> which is close to the lattice parameters of STO and LSAT, epitaxial LNMO

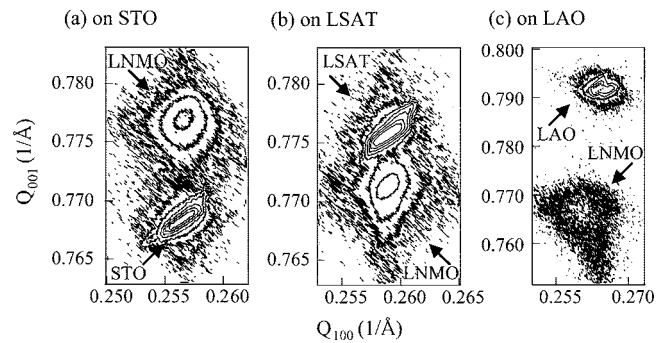


FIG. 3. Logarithmic intensity mappings around the LNMO (103) peak in reciprocal space for LNMO films grown on (a) STO, (b) LSAT, and (c) LAO substrates.

thin films are coherently grown on these substrates. Although the LNMO films are also grown epitaxially on the LAO substrates, the 2.5% lattice mismatch between the films and the substrates causes relaxation in the LNMO structure.

The LNMO films on all the substrates exhibited ferromagnetic behavior at low temperature. Figure 4 plots the dependence of saturation magnetization on temperature measured under an applied magnetic field of 10 kOe parallel to the plane. The saturation magnetization ( $M_S$ ) at low temperature of the films deposited on STO and LSAT substrates was about  $4.6\mu_B/\text{f.u.}$ , which is close to the expected spin-only value of  $5\mu_B$  for ferromagnetic ordering of  $\text{Ni}^{2+}$  ( $S=1$ ) and  $\text{Mn}^{4+}$  ( $S=3/2$ ) ions. The value of  $M_S$  at 10 K of the film on LAO was slightly smaller (about  $4.0\mu_B$ ) than that of the films on STO and LSAT. This may be due to the presence of non-magnetic regions near the defects in the crystal structure caused by lattice mismatch. These large observed  $M_S$  values clearly indicate that the Kanamori-Goodenough ferromagnetic interaction between  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  spins is dominant in these films. We also note that the ferromagnetic transition temperature of all three films was 280 K despite the slight changes in structure. These values for saturation magnetization and ferromagnetic transition temperature are comparable to those of bulk samples reported by Dass *et al.*<sup>8</sup> The heteroepitaxial constraints on the structure did not drastically affect the magnetic properties of the LNMO films.

In summary, epitaxial thin films of ferromagnetic LNMO with an ordered double-perovskite structure were deposited

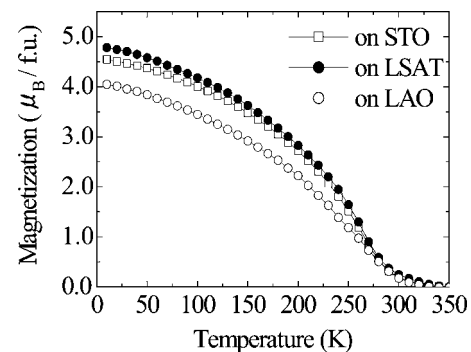


FIG. 4. Dependence of magnetization on temperature measured under an applied field of 10 kOe for LNMO films deposited on STO, LSAT, and LAO substrates.

on STO, LSAT, and LAO substrates. We found that the ordering of  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  ions was strongly affected by the oxygen pressure during the deposition and that an oxygen pressure over 180 mTorr was necessary to stabilize the ordered double-perovskite structure. Ferromagnetic behavior was confirmed for LNMO films deposited on all the substrates, and the magnetic properties we observed were comparable to those of bulk LNMO. The ferromagnetic properties of these films can well be explained by the Kanamori-Goodenough rule. We should be able to fabricate spintronics devices with these ferromagnetic thin films.

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