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Textured $LaNiO_3$ Electrode Grown by Spin-Coating Technique

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Abstract. $LaNiO_3$ thin films were deposited by spin-coating technique on various substrates using metal naphthenates as starting materials. The highly oriented $LaNiO_3$ films with smooth and crack-free surfaces grown on $SrTiO_3$(100) and $LaAlO_3$(012) substrates were observed by X-ray diffraction θ–2θ scans, while the film on sapphire(0001) substrate showed polycrystalline structure. Resistivity vs. temperature curves of the textured $LaNiO_3$ films showed that the film possessed a good metallic character.

Keywords: $LaNiO_3$ thin film, spin-coating technique, metal naphthenates

1. Introduction

In recent years, conductive oxide layers such as $SrRuO_3$, IrO_2 and RuO_2, have been studied intensively. The $LaNiO_3$ (LNO), which is a perovskite-related Pauli paramagnetic and metallic oxide down to 0.4 K [1], has also attracted much attention in the past few years, as a conducting layer for applications in ferroelectric memories.

The primitive cell of LNO consists of two formula units and it is rhombohedral with lattice parameter $a = 0.5461$ nm and the rhombohedral angle of 60.41°, and pseudocubic 'a' of this oxide is 0.383 nm. Since most perovskite-type ferroelectric materials are of the same structure as LNO with a little lattice-mismatch, a better bonding between these ferroelectric materials and the LNO layer can be expected.

At present, most of textured LNO films have been prepared by physical process such as pulsed laser deposition (PLD) [2–4], and rf magnetron sputtering [5,6]. A wet chemical process provides a simple and versatile alternation for crystalline thin film preparation [7,8]. But so far as, very few works [9] have been reported on the successful preparation of epitaxial or textured LNO thin films by chemical process.

In this paper, we report on the fabrication of highly oriented conductive LNO thin films on various substrates by spin-coating technique.

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2. Experimental

The fabrication method of the LNO films was similar to that of $Pb(Zr,Ti)O_3$ films described in our previous paper [8]. Briefly, a homogeneous coating solution was prepared by mixing the constituent metal naphthenates of La and Ni (Nihon Kagaku Sangyo Co., Ltd. and Soekawa Rika Co., Ltd.) in toluene to achieve an appropriate viscosity for deposition of smooth films [concentration: 2.8(3) mg metal/ml coating solution]. Generally, metal naphthenate solutions are very stable, and there is no chemical reaction upon mixing or dilution in contrast to the case for metal alkoxide solutions, which are commonly used in sol-gel process. Molar ratio of the metals in solution was set as La:Ni = 1:1.

The cleaned $SrTiO_3$(100) (STO), $LaAlO_3$(012) (hexagonal index, h.i.) (LAO) and sapphire(0001) substrates were spin-coated with the precursor solution at 4000 rpm for 10 sec. After each coating, the film was dried at 110°C for 30 min and pyrolyzed at 500°C for 10 min in air. The process was repeated three times to prepare a thick layer of LNO. The films studied were typically 0.2 μm thick, confirmed by both the weight gaining and the observation of fractured cross section of the films with a scanning electron microscope (SEM), and final heat treatment was done in air at 750°C for 30 min.

Crystal structures for the LNO films were determined by X-ray diffraction (XRD) θ–2θ scans with CuKα radiation. Resistivity was measured by the four-point probe method.

3. Results and Discussion

Figures 1 and 2 show XRD θ–2θ scans for the LNO thin films on STO, LAO and sapphire substrates heat-treated at 750°C for 30 min in air, respectively. The (h00)/(00l) oriented LNO thin films were obtained and no evidence of misoriented peaks or metastable pyrochlore phase was observed for the films on STO and LAO, as shown in Fig. 1. On the other hand, the films prepared on sapphire(0001) substrate showed the (110) peak in addition to the (111) peak of LNO, as shown in Fig. 2.

From the above results, orientation of the films was found to depend strongly on the substrates used. STO has a cubic structure, the unit cell parameters being 0.3905 nm (ICDD File 35-734). LAO has a rhombohedral structure, however, interaxial angle is close to 60°. Thus, in this study, LAO is regarded as pseudocubic; LAO(012) (h.i.) corresponds to LAO(001) (pseudocubic indices). The unit cell parameter of LAO pseudocubic cell is 0.379 nm [10]. STO(100) and LAO(012) substrates gave highly oriented LNO films, while the film prepared on sapphire(0001) was polycrystalline. We assume that the differences of lattice mismatches between the film and the substrates provoked the differences of orientation of the films. The preferential growth behavior of the LNO/STO and the LNO/LAO can be easily understood by small lattice mismatch-values between the pseudocubic LNO film and the substrates used, i. e., 1.9% and 1.0(5)%, respectively.

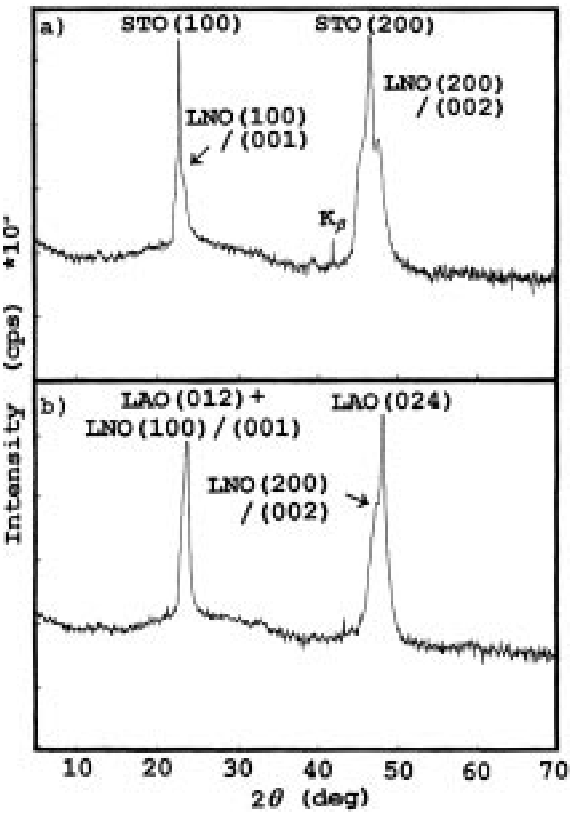

Fig. 1. XRD θ–2θ scans of LNO films on STO (a) and LAO (b) substrates heat-treated at 750°C.

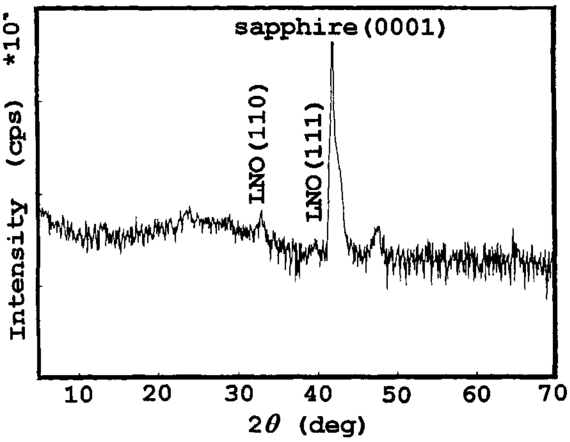

Fig. 2. XRD θ–2θ scans of LNO films on sapphire substrate heat-treated at 750°C.

Sapphire is a rhombohedral structure with lattice parameters of $a = 0.4759$ nm and $c = 1.2991$ nm. Therefore, on sapphire, too large lattice misfit-value ($\sim 19.5\%$) along a-axis should be considered to make textured growth of LNO difficult in this work.

Using the STO and LAO peaks as an internal calibration standard, the lattice constants $d_\perp$ of highly oriented LNO films perpendicular to the substrate surface in Fig. 1 were determined to be 0.382(7) nm and 0.384(5) nm, respectively. The lattice constants of these films are close to the value of bulk crystal.

Resistivity versus temperature measurements was carried out using four-point probe method for the highly oriented LNO films on STO and LAO substrates. Figure 3 shows a plot of resistivity according to the temperature for the LNO films heat-treated at 750°C. The temperature dependence

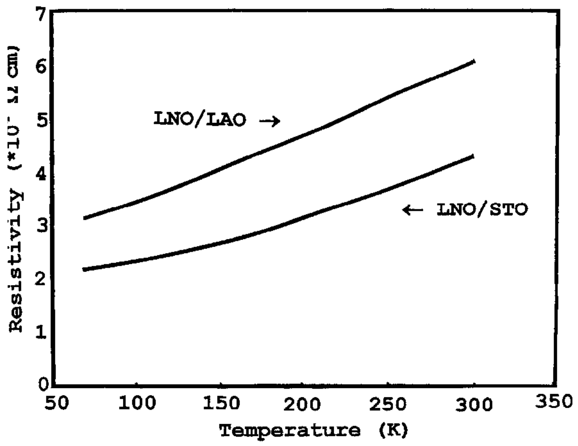

Fig. 3. Resistivity vs. temperature for LNO films on STO and LAO heat-treated at 750°C.

exhibits good metallic behavior, which is important for electrode application. The $\rho_{300\,K}/\rho_{100\,k}$ of LNO on STO and LAO was about 1.83 and 1.73, respectively, and these values are comparable to those of LNO films by physical dry method [2,3]. The resistivity at room temperature for the LNO/STO and the LNO/LAO is $4.2 \times 10^{-4} \Omega \cdot$ cm and $6.04 \times 10^{-4} \Omega \cdot$ cm, respectively.

Figure 4 shows SEM photograph of a free surface of the highly oriented LNO film on STO substrate heat-treated at 750°C. Generally, in the chemical solution method, the pores and cracks easily recognized in the product films. On the contrary, the surface of film prepared was very smooth and no texture was observed as shown in Fig. 4. It should be noted that we have successfully prepared crack-free and conductive LNO films with high orientation by simple and low-cost chemical solution method.

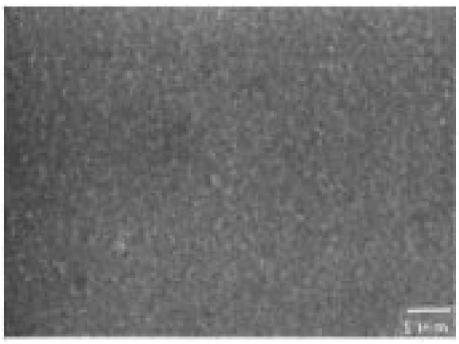

Fig. 4. SEM surface morphology of LNO film on STO heat-treated at 750°C.

4. Summary

LNO films were deposited by spin-coating technique on various substrates using metal naphthenates as starting materials. The highly oriented LNO films with smooth and crack-free surfaces grown on STO and LAO substrates were observed by XRD θ–2θ scans, while the film on sapphire showed polycrystalline structure. The resistivity vs. temperature curves of the textured LNO films showed that the LNO film possessed good metallic character.

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