The Korean Journal of Ceramics, **4** [3] 231 - 234 (1998)

Effect of Substrates on Structural and Electrical Properties of Chemical Solution Derived $LaNiO_3$ thin Films

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(Received July 1, 1998)

$LaNiO_3$ thin films were fabricated on various substrates by spin-coating technique using metal naphthenates as starting materials. Highly-oriented $LaNiO_3$ films with smooth and crack-free surfaces were grown on $SrTiO_3$ (100) and $LaAlO_3$ (100) substrates, while films on MgO (100) and Si (100) substrates showed random orientation. In this study, we conclude that lattice-mismatches between $LaNiO_3$ films and substrates used affect film's properties.

Key words : $LaNiO_3$ thin films, Spin-coating technique. Lattice-mismatches

I. Introduction

In recent years, preparation of the ferroelectric thin film attracts attention for its important application to the integrated circuit memory and the pyroelectric micro sensor. Since the ferroelectric material is crystallographically anisotropy, in order to obtain the film with microscopically uniform properties for the fabrication of high density integrated devices; many efforts were given to the growth of epitaxial or highly-oriented films on lattice-matched substrates.

$LaNiO_3$ (LNO) is a perovskite-related Pauli paramagnetic and metallic oxide down to 0.4 K.[1] The primitive cell of LNO consists of two formula units. First, it has rhombohedral symmetry with lattice parameter of a=0.546 nm and the rhombohedral angle of 60.41°. Second, pseudocubic "a" of this oxide is 0.383 nm and it matches well with "a" of perovskite compounds such as $BaTiO_3$ and Pb $(Zr,Ti)O_3$. Therefore, it is possible to grow epitaxial or highly-oriented LNO films on lattice-matched single crystal substrates such as $LaAlO_3$ (LAO) and $SrTiO_3$ (STO).

At present, most of textured LNO films have been prepared by physical dry process such as pulsed laser deposition (PLD)[2,3] and rf magnetron sputtering.[4-6] A wet chemical solution process provides a simple and versatile alternation for crystalline thin film preparation.[7,8] However, few works have been reported on LNO thin films by chemical solution process.

In this paper, we report on the structural and electrical properties of the LNO film on various substrates and discuss on the basis of lattice-mismatch between the LNO and substrates.

II. Experimental procedure

The LNO film was deposited on various substrates by a spin-coating technique. Starting solution was prepared by mixing commercially available La- and Ni-naphtenates. This solution was diluted with toluene to an appropriate concentration and viscosity for the deposition of smooth film by the spin-coating (concentration: 2.83 mg metal/ml coating solution). The molar ratio of metals in the coating solution was set as La:Ni=1:1. Generally, metal naphtenate solutions are very stable in air, and there is no chemical reaction upon mixing or diluting in contrast to the case of metal-alkoxide solution, which is commonly used in the chemical solution process.

Single-crystals of STO (100), LAO (100) (pseudocubic index, p. i.), MgO (100) and Si (100) were selected as a substrate. Prior to the coating process, substrates were cleaned in neutral solution (Merck), immersed in H_2O_2 solution and rinsed in toluene. Starting solution was spin-coated onto the cleaned substrate at 4000 rpm for 10 sec in air. As-deposited film was dried at 110°C for 30 min and pyrolyzed at 500°C for 10 min in air.

The coating process was repeated five times to prepare the thick layer of LNO. The films studied were typically 0.5 μm thick, confirmed by both weight-gain and observation of the fractured cross-section of films with a scanning electron microscope (SEM). Then, final heat treatment was done in air at 750°C for 30 min, followed by rapid cooling. Crystal structure of the LNO film was determined by the X-ray diffraction (XRD) θ-2θ scan with CuKα radiation. Resistivity was measured by the standard four-point probe method.

III. Results and discussion

Fig. 1 shows XRD θ-2θ scans of the LNO thin film on various substrates annealed at 750°C. Highly $(h00)/(00l)$ oriented LNO thin film was obtained and no evidence of the mis-oriented peak or the metastable pyrochlore

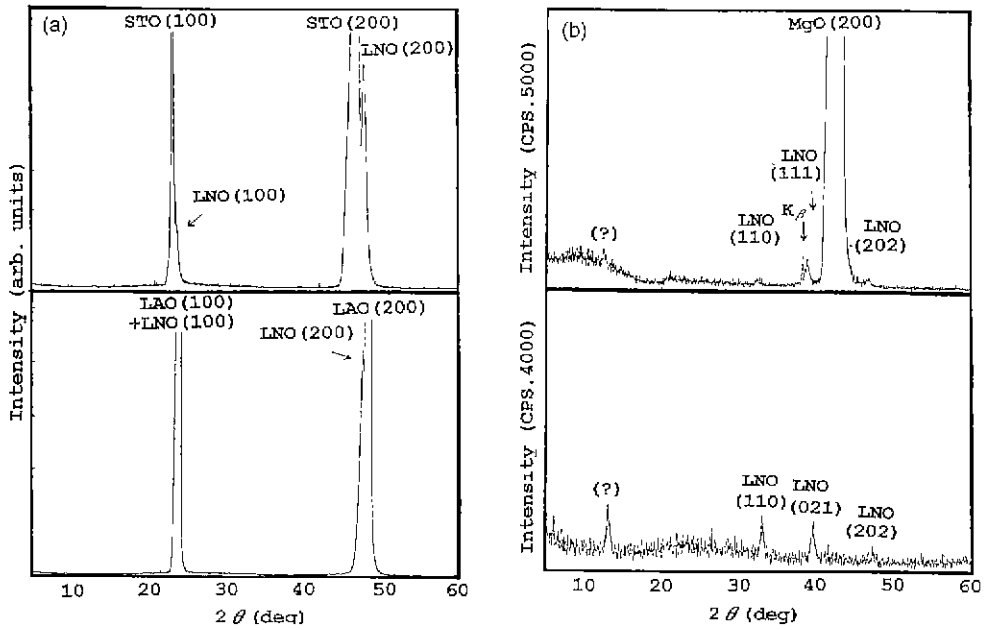

Fig. 1. XRD θ-2θ scans of LNO Films on STO and LAO (a) and MgO and Si (b) Annealed at 750°C.

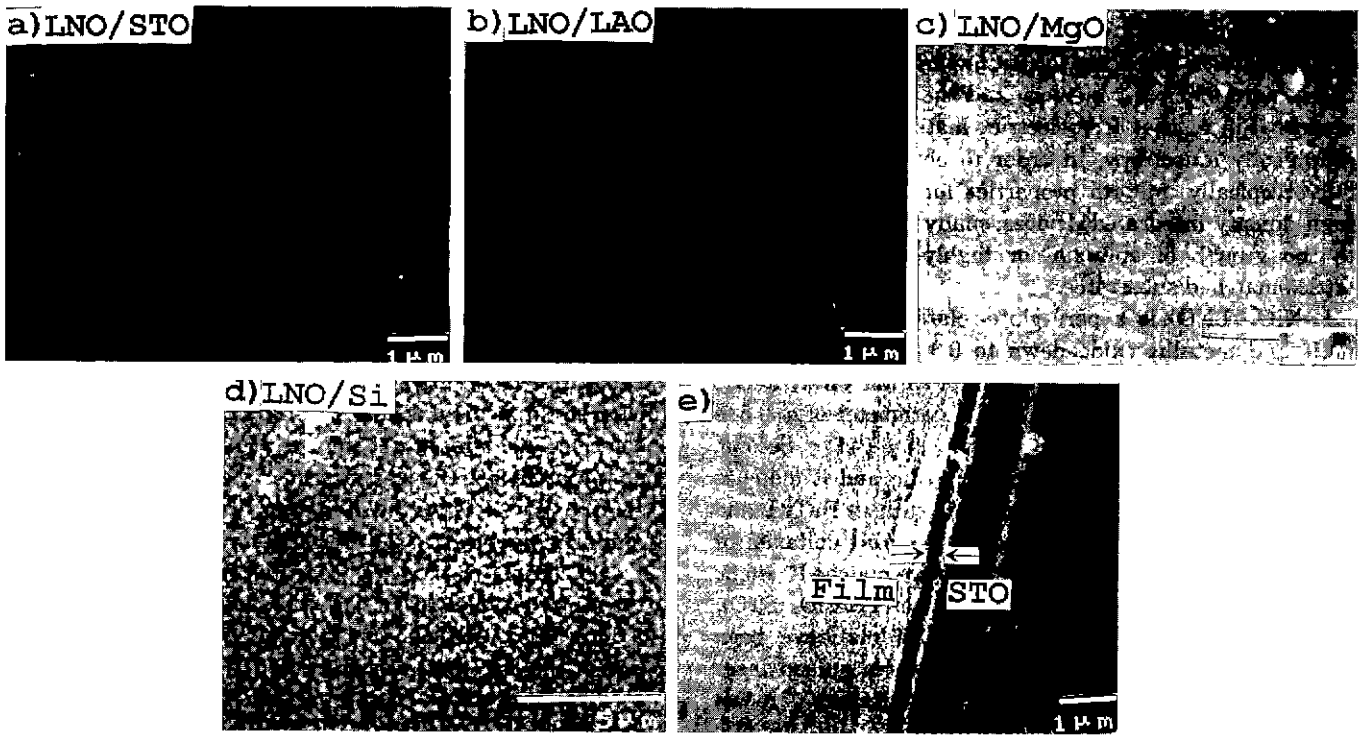

Fig. 2. SEM Photographs of Free Surfaces of LNO Films Annealed at 750°C on Various Substrates.

phase was observed for the films on STO and LAO substrates. On the other hand, the films on MgO (100) and Si (100) substrates showed mis-oriented peaks such as (110), (202) and (111). Moreover, an unknown peak was observed in the film on MgO and Si substrates. We will fully discuss this difference crystallinity of the film in later chapter.

SEM photographs of the free surface and the fractured cross-section for the LNO films on various substrates are shown in Fig. 2. Confirmed by XRD θ-2θ scanning, the films with high orientation on STO and LAO substrates had smooth and crack-free surface, and its fractured cross-section was dense and uniform, as shown in Fig. 2 (a), (b) and (e). However, the films on MgO and Si substrates were the randomly-oriented structures and showed numerous grain bounderies.

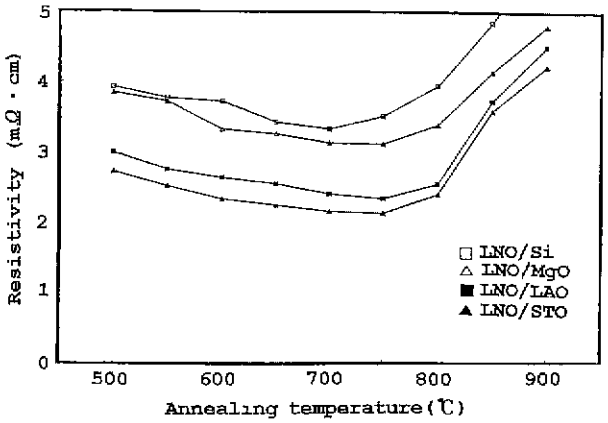

Fig. 3. Plot of the Resistivity of LNO Films on Various Substrates According to the Annealing Temperature.

Resistance measurement depending upon a temperature was carried out using a closed refrigeration system. Fig. 3 shows a plot of resistivity as a function of annealing temperature for the LNO film deposited on STO (100), LAO (100), MgO (100) and Si (100) substrates in air. Measurements of resistivity for films versus temperature were carried out using four-point probe method. A minimum resistivity is achieved for the film on STO annealed at 750°C. The LNO film with random orientation on MgO (100) and Si (100) substrates exhibited higher resistivity than that of the highly-oriented one.

High resistivity of the randomly-oriented films may be due to the effect of grain boundary as shown in microscophical results (Fig. 2). Moreover, in all the films, resistivity increased abruptly up to the annealing temperature of 800°C. We assume that the increase of resistivity at high temperature, i. e., 800°C, might be due to the decomposition of nickel compound.[9]

Fig. 4 shows a plot of resistivity versus temperature for a 0.5 μm-thick LNO films on STO, LAO, MgO and Si substrates annealed at 750°C. The temperature dependence (dρ/dT) shows good metallic behavior which is important for electrode application. The ρ_{300K}/ρ_{100K} of LNO/STO and

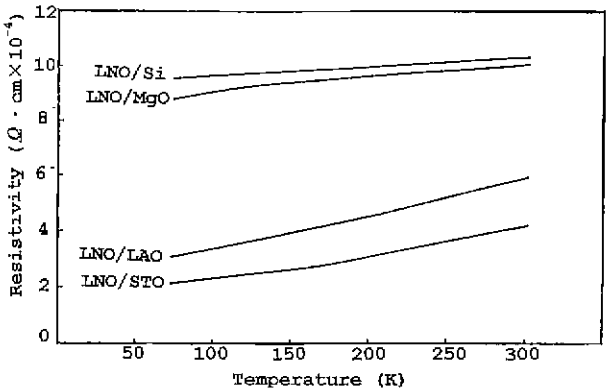

Fig. 4. Temperature Dependence of Resistivity for LNO Films on Various Substrates.

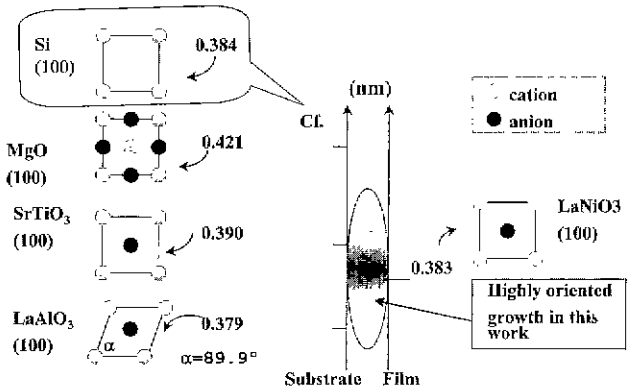

Fig. 5. Schematic Drawing of Arrangement of Ions for $LaNiO_3$ and Substrates Used.

LNO/LAO was about 1.83 and 1.73, respectively, which were comparable to the LNO film by physical method (1.7 for the LNO/STO).[3] The resistivities at room temperature for LNO/STO and LNO/LAO were 4.2×10^{-4} Ω cm and 6.04×10^{-4} Ω·cm, respectively, which are larger than 3.7×10^{-4} Ω·cm of the LNO/Si by physical method.[3] Generally, a non-stoichiometry of LNO, i. e., oxygen deficiency, comprises the increase of resistivity. Thus, in this study, reduction atmosphere owing to the pyrolysis of organic component during annealing caused oxygen deficiency, then, decreased the resistivity of the LNO.

Fig. 5 shows the schematic drawing for ionic arrangements of LNO and substrates. STO has a cubic structure with the lattice parameter of 0.390 nm. LAO has a rombohedral structure with very small distortion (α= 89.9°). STO (100) and LAO (100) substrates gave the highly-orientated LNO films, while the films prepared on MgO (100) and Si (100) substrates exhibited random orientation.

We assume that the difference of lattice-mismatchs between the film and substrate provoked orientational difference of the film. Preferential growth behavior of the LNO/STO and LNO/LAO can be easily understood by the small lattice-mismatch between the pseudocubic LNO film and substrate. On the contrary, MgO (100) has a cubic structure with lattice parameter of a=0.421 nm, thus, too large lattice-mismatch between the LNO and MgO in the case of LNO/MgO (100) causes the oriented growth of LNO to be difficult. Furthermore, the nearest atom of Si (100), i. e., $a/\sqrt{2}$=0.384 nm, is very close to the lattice parameter of LNO. However, in this study, interaction between LNO and Si reacted the oxygen diffusion, thus it is difficult to obtain the highly-oriented LNO film.

Conclusively, a highly-oriented LNO can obtain in the case of small lattice-mismatch and non-interaction between the LNO and substrate.

IV. Summary

LNO films were deposited by spin-coating technique

on various substrates using the metal naphthenates as starting materials. By θ-2θ scan, the highly-oriented LNO film with smooth and crack-free surface prepared on STO and LAO substrates, while the film on MgO and Si exhibited random orientation. The highly-oriented LNO films on STO and LAO showed a good metallic character and small lattice-mismatch between the LNO and STO and LAO substrates gave a highly-oriented LNO.

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