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Characteristics of oriented $LaNiO_3$ thin films fabricated by the sol–gel method

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Abstract

We fabricated $LaNiO_3$ (LNO) thin films on SiO_2 glass, (100) $SrTiO_3$ (STO), (100) Si and CeO_2-covered (100) Si substrates by the sol–gel method. The deposited films were heat-treated at 700°C with various conditions, duration and atmosphere. Preferentially (100)-oriented, polycrystalline LNO films were obtained on STO and Si. It was also found that orientated films could be formed even on SiO_2 glass and CeO_2-covered (100) Si substrates by altering the heating process. We investigated a relationship between the resistance and the crystallite size of the LNO films. The sheet resistance of LNO decreased with increasing crystallite size of LNO. The resistivity and sheet resistance of LNO/STO at 300 K were 340 μΩ·cm and 33.8 Ω/□, respectively, and those values of LNO/CeO_2/Si at 300 K were 460 μΩ·cm and 28.8 Ω/□.

Keywords: CeO_2; Electrical conductivity; Films; Perovskites; Sol–gel processes

1. Introduction

Perovskite ferroelectric thin films have been attracting much attention for applications to a ferroelectric random access memory (FeRAM). Although a metal film like Pt or Ir is often used as an electrode, it has weak adhesion to a Si wafer and tends to cause ferroelectric fatigue due to oxygen deficiency.[1] Oxides, especially perovskite-type oxides, with metallic conductivity have been studied as an alternative electrode. $LaNiO_3$ (LNO) has the pseudo-cubic perovskite structure ($a = 3.84$ Å), low resistivity (225 μΩ·cm) and good metallic conductivity.[2,3] (100)-oriented LNO films can be utilized to control orientation of the perovskite-type ferroelectric thin film deposited successively. Therefore, highly (100)-oriented LNO is a promising candidate for the electrode as well as the substrate for the ferroelectric thin films.[4–10] In this work we investigated first the effects of sol–gel processing parameters on the orientation and the electrical properties of LNO thin films. Then $LaNiO_3/CeO_2/Si$ structure was prepared as an MIS (Metal-Insulator-Semiconductor) structure.

2. Experimental procedure

$La(NO_3)_3 \cdot 6H_2O$ (0.002 mol) was dissolved in 2-methoxyethanol (9 ml) and monoethanolamine (MEA) (1 ml), and then $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.002 mol) was added to the solution. The resultant solution was deposited on SiO_2 glass, (100) $SrTiO_3$ (STO), (100) Si and CeO_2-coated (100) Si substrates by the spin-coating technique at 2700 rpm for 30 s. After deposition, the deposited substrates were heated at 700°C for 1–20 min in air. Two kinds of heating processes were adopted. In one process, the deposited substrate was put on a plate at room temperature and then heated so that the films could be heated uniformly in the furnace (process 1). In the other process, the deposited substrate was put on a pre-heated plate at 700°C so that the film should be heated first from the bottom of the substrate (process 2). After repeating the deposition 5 times, the sample was finally annealed at 700°C in a flowing oxygen atmosphere. To form the CeO_2 insulator layer, $Ce(NO_3)_3 \cdot 6H_2O$ (0.0015 mol) was dissolved in acetylacetone (10 ml). The solution was refluxed at 100°C for 1 h in the presence of zeolite to remove H_2O. CeO_2 thin films were deposited on (100) Si by the spin-coating technique. The deposited substrate was heated at various temperatures between 400 and 700°C for 1 min by rapid heating in

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air, this procedure was repeated 5 times, and finally the sample was annealed for 1 h at the same temperature in air. The phases were identified by an X-ray diffraction (XRD) θ-2θ scan using CuK_α radiation. The crystallite size of LNO was calculated by Scherrer formula from XRD profiles of the films. Surface and thickness of the films were observed by field emission scanning electron microscopy (FESEM). The resistivity of the sheet was measured by the four-points method where the sheet resistance (ρ_s) is defined by volume resistivity ρ and thickness of the sample t as $\rho_s = \rho/t$ and unit is expressed by Ω/□. The electrical resistivity (ρ) of LNO was measured by the four probe method.

3. Results

Fig. 1 shows the XRD θ–2θ scan profiles of LNO deposited on (a) SiO_2 glass, (b) STO and (c) Si substrates with heating at 700°C for 10 min through process 1 and annealing at 700°C in a flowing oxygen for 1 h. The strong (100) and (200) peaks of LNO (pseudo-cubic) are observed in LNO/STO and LNO/Si. We calculated orientation factor F as defined by Lotgering.[11] The F values were (a) $F=0.07$, (b) $F=0.97$ and (c) $F=0.99$ for LNO/SiO_2 glass, LNO/STO and LNO/Si, respectively. This result indicates that the growth of LNO is affected by the substrate structure; STO ($a=3.95$ Å) and Si ($a=5.43$ Å) have an excellent lattice match with LNO ($a=3.84$ and $\sqrt{2}a=5.43$ Å). The resistivity and sheet resistance of LNO/STO at 300 K were 340 μΩ·cm and 33.8 Ω/□, respectively, and those of LNO/Si were 630 μΩ·cm and 43.5 Ω/□, respectively. These values were lower than those of LNO/SiO_2, 1528 μΩ·cm and 90.3 Ω□, with relatively small F.

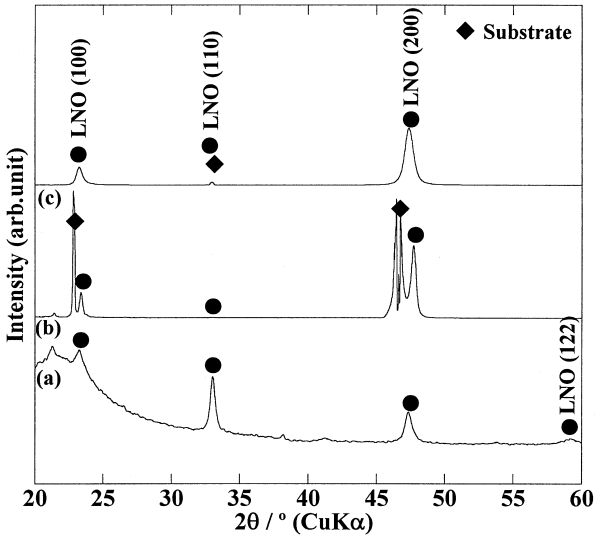

Fig. 1. θ–2θ XRD profiles of $LaNiO_3$ thin films on (a) SiO_2 glass, (b) (100) $SrTiO_3$ and (c) (100) Si substrates heated at 700°C and annealed at 700°C for 1 h in a flowing oxygen by process 1.

We fabricated LNO thin films on SiO_2 glass substrates by process 2. Fig. 2 shows the XRD θ–2θ scan profiles of LNO films heated at 700°C for (a) 1 min, (b) 5 min, (c) 10 min and (d) 20 min and annealed in a flowing oxygen for 5 h. The LNO films made by process 2 have the higher degree of (100)-orientation than those made by process 1. The orientation factor of films was between $F=0.91$ and 0.95. In spite of almost the same in the F values, the sheet resistance of the films was different; 53.5, 114, 88.6 and 128 Ω/□ for the samples in Fig. 2(a), (b), (c) and (d), respectively. The F values, the crystallite size and the sheet resistance of LNO/SiO_2 films were exhibited in Table 1. This difference is originated from crystallite size of LNO. The relationship between crystallite size and sheet resistance will be discussed later in detail.

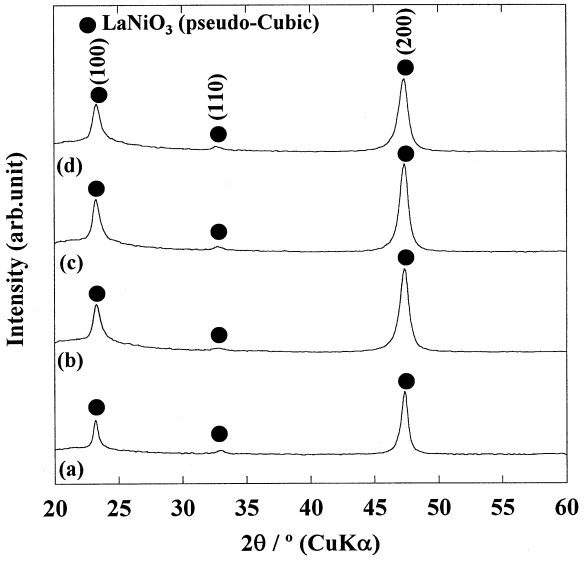

Fig. 2. θ–2θ XRD profiles of $LaNiO_3$ thin films on SiO_2 glass substrates heated at 700°C for (a) 1 min, (b) 5 min, (c) 10 min and (d) 20 min and annealed at 700°C for 5 h in a flowing oxygen by process 2.

Table 1
The orientation factor, the crystallite size and the sheet resistance of the LNO films on SiO_2 glass substrate made by process 2

Heating time (min)	Annealing time (h)	Orientation factor F	Crystallite size (nm)	Sheet resistance ρ_s (Ω/□)
1	–	0.65	6.9	1680
1	5	0.91	17.5	53.5
1	10	0.95	19.5	55.6
5	–	0.86	9.2	256.6
5	5	0.92	13.4	114
5	10	0.94	14.1	101
10	–	0.90	12.1	136.4
10	5	0.92	13.0	88.6
10	10	0.95	13.0	80.1
20	–	0.90	10.9	126.6
20	5	0.90	13.4	128.0
20	10	0.95	13.6	106.1

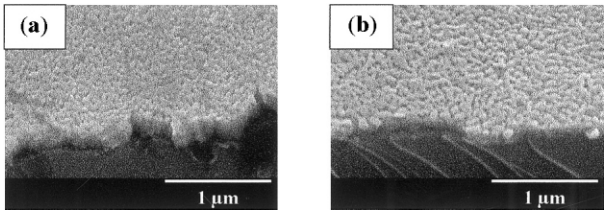

Fig. 3. FESEM photographs of $LaNiO_3$ thin films on SiO_2 made by (a) process 1 and (b) process 2 with heating for 10 min and annealing 1 h in a flowing oxygen.

Fig. 3 shows FESEM photographs of the LNO/SiO_2 made by process (a) 1 and (b) process 2 with heating for 10 min and annealing for 1 h at 700°C in a flowing oxygen. The surface of the film made by process 2 is more porous than that made by process 1. However, the sheet resistance of the LNO film made by process 2 was lower than that by process 1. Thicknesses of the films made by processes 1 and 2 were 200 and 160 nm, respectively. The thickness of the other films made by each process was almost the same, regardless of the heating and annealing conditions.

The CeO_2 thin films fabricated at various temperatures exhibited a high degree of orientation to the <100> direction (Table 2). LNO thin films were fabricated on the CeO_2 films by heating at 700°C for 1 min by process 2 and annealing at 700°C for 5 h in a flowing oxygen. The F values of CeO_2 films, the crystallite size and the sheet resistance of LNO/CeO_2 films are shown in Table 2. Fig. 4 shows the θ–2θ scan profiles of the LNO/CeO_2/Si structures. Strong (100) and (200) peaks of LNO are observed despite the different F values of CeO_2 films. The sheet resistance of LNO were (a) 28.8, (b) 28.8, (c) 34.3 and (d) 37.0 Ω/□ for the sample shown in Fig. 4 (a), (b), (c) and (d), respectively. These values were as low as that of LNO/STO made by process 1. However, the resistivity was 460 μΩ·cm and thickness was about 180 nm for the sample (a).

4. Discussion

First, we discuss the difference in the degree of orientation of LNO/SiO_2 films made by processes 1 and 2. In

Table 2
The crystallite size and the sheet resistance of the LNO films on CeO_2/Si substrates

Fabrication temperature of CeO_2 on (100) Si substrate	Orientation factor of the CeO_2 films	Crystallite size of the LNO film (nm)	Sheet resistance ρ_s of the LNO film (Ω/□)
400°C	0.62	23.8	28.8
500°C	0.58	22.6	28.8
600°C	0.87	22.2	34.3
700°C	0.82	24.7	37.0

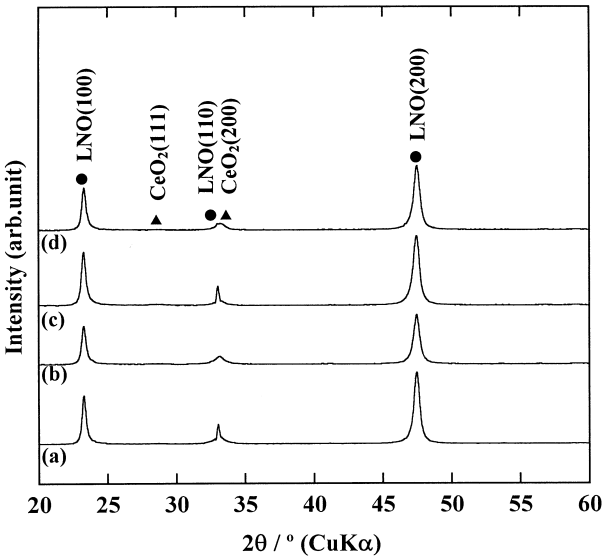

Fig. 4. θ–2θ XRD profiles of $LaNiO_3$ thin films heated at 700°C and annealed at 700°C for 5 h in a flowing oxygen by process 2 on CeO_2-covered Si substrates fabricated at (a) 400°C, (b) 500°C, (c) 600°C and (d) 700°C.

the case of process 2, most of LNO would nucleate heterogeneously from the substrate side. The (100)-plane of LNO which has the smallest surface energy could develop parallel to the substrate surface because grains in the film grow flat and outer surface is composed of the plane with the smallest surface energy, when adhesive bonding between the film and substrate is strong.[12,13] Therefore, the (100)-oriented LNO films could be fabricated even on the amorphous substrate. Grains in the film made by process 1 would nucleate homogeneously, resulting in the small degree of (100)-orientation.

Secondly, we discuss the effect of heating time during the deposition procedure on the sheet resistance. Fig. 5

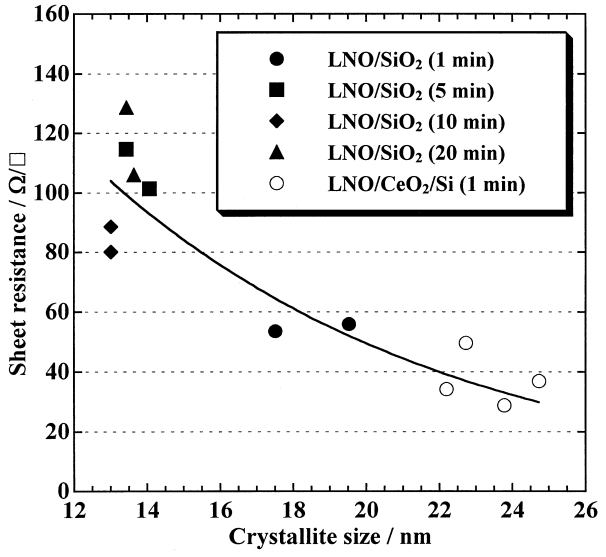

Fig. 5. Effect of crystallite size of $LaNiO_3$ thin films on sheet resistance.

shows the relationship between the sheet resistance and the crystallite size of the LNO films. It is clearly shown that the sheet resistance decreases with increasing crystallite size of LNO. For the LNO/SiO_2 film, the crystallite size of LNO after annealing tends to increase with decreasing heating time during the deposition procedure. Before annealing the crystallite size of LNO/SiO_2 with short heating time (1 min) was smaller than that with longer heating time (5, 10 and 20 min), but that with short heating time was bigger than that with long heating time after annealing (Table 1). This is because small grains have large surface energy which acts as a driving force for grain growth of the LNO during annealing.

5. Conclusions

Highly (100)-oriented $LaNiO_3$ thin films were fabricated on (100)$SrTiO_3$, (100)Si and SiO_2 glass substrates by the sol–gel method. Among them, the LNO/STO showed the lowest resistivity of 340 μΩ·cm. (100)-Oriented LNO/CeO_2/Si MIS structure with the sheet resistance of 28.8 Ω/□ could also be obtained. It was revealed that the electrical property of the films mainly depended on the crystallite size of LNO.

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