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Preparation and evaluation of $LaNiO_3$ thin film electrode with chemical solution deposition

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Abstract

$LaNiO_3$ (LNO) thin films were prepared onto Si substrate by chemical solution deposition. The orientation of the LNO films was controlled by changing concentration of precursor solution. The resistivity of the resultant LNO films was $1.82 - 2.57\times10^{-3}\Omega$cm. The obtained 0.3 M-LNO film was flat surface, highly (100) orientation, and had a low resistivity of $1.85\times10^{-3}\Omega$cm. $PbZr_{0.53}Ti_{0.47}O_3$ was fabricated onto the resultant 0.3 M-LNO electrode, and the sample showed a good ferroelectric property.

Keywords: Chemical solution deposition; Electrical conductivity; $LaNiO_3$; Perovskite

1. Introduction

Perovskite lead zirconate titanate (PZT) thin film has been studied for ferroelectric memories because of its low operating voltage and high switching speed.[1–3] Platinum metal film is usually used as an electrode for PZT ferroelectric thin film. However, when Pt is used as an electrode, it is hard to apply because of its fatigue property.[4] $LaNiO_3$ (LNO) has a pseudo cubic perovskite structure, the lattice constant is 3.84Å and it is close to the PZT structure and lattice constant (4.04Å). Furthermore, LNO has a good metallic property.[5–8] Therefore, LNO film is one of candidate of an electrode for ferroelectric PZT film.

In this study, we try to fabricate an LNO film with chemical solution deposition, and to control an orientation of the resultant LNO film. PZT films were also deposited onto the obtained a-axis oriented LNO film, and a ferroelectric property was measured.

2. Experimental procedure

Lanthanum nitrate $[La(NO_3)_3{\cdot}6H_2O]$ and Nickel acetate $[Ni(CH_3COO)_2{\cdot}4H_2O]$ were used as the starting materials. These were dehydrated $[La(NO_3)_3{\cdot}6H_2O]$ at 100 °C for 12h and $[Ni(CH_3COO)_2{\cdot}4H_2O]$ at 200 °C for 3 h, respectively. These were dissolved and refluxed in 2-methoxy ethanol and 2-amino ethanol (mixing ratio of 9/1), and the precursor LNO sol was obtained. Three kinds concentration (0.1, 0.3 and 0.5 M) of the precursor solutions were prepared.

The precursor film was deposited on a silicon wafer by spin coated at 3000 rpm and 30 s. The precursor film was pre-annealed at 350 °C to remove organic components, and annealed at 700 °C by rapid thermal annealing (RTA), the rising temperature speed was 200 °C/min. These processes were repeated until the resultant LNO films were about 300 nm in thickness. The thickness of one time coating using 0.1, 0.3 and 0.5 M precursor solution were 22, 41, and 72 nm, respectively.

The crystallographic structure of the obtained films was characterized by XRD using RIGAKU RINT2000. The thickness and surface morphology of the film were confirmed by scanning electron microscopy with Jeol JSM-5600. The resistivity of the LNO films was measured by a standard four-point probe method.

A PZT film was deposited onto the obtained LNO film by previous reported method,[1,9] and the composition was $PbZr_{0.53}Ti_{0.47}O_3$ (morphotropic phase boundary composition; MPB). The structure of the PZT film

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was characterized by XRD, and a ferroelectric property of one was measured using Radiant Technology RT6000.

3. Results and discussion

Fig. 1 shows the XRD patterns for the obtained LNO thin films with 3 kind concentrations of precursor solutions. The resultant LNO film using 0.1 M precursor solution exhibited (110) preferred orientation. The resultant LNO films using 0.3 and 0.5 M precursor solution showed (100) preferred orientation. In particular, the 0.3 M-LNO film was strongly oriented to the (100), and the other peaks of LNO were not observed. The LNO film using 0.5 M precursor solution was also strongly oriented to the (100). However, the other peaks of the 0.5 M-LNO film were observed. The film thickness of one layer coating was thick, and nucleation was occurred at the various sites in the precursor film.

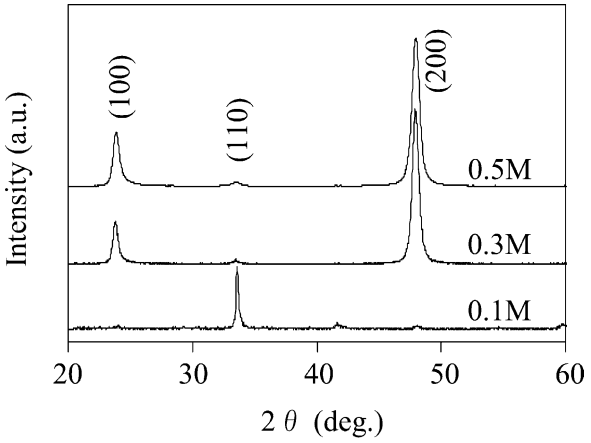

Fig. 1. XRD patterns for the $LaNiO_3$ films derived from different concentration of precursor solutions.

The (100) oriented LNO film was observed on the some previous reports,[6,8,10] and it assumes that the (100) plane is the preferred orientation plane of an LNO film. When 0.1 M-LNO solution was used to fabricate the film, the film thickness of one layer coating was thin, and a large stress was applied to the film. Therefore, it considered that the orientation direction was changed to the (110) direction.

Fig. 2 shows the surface morphology of the resultant LNO films. The 0.1 M-LNO film surface looks rough. The film thickness of one layer coating was thin, and a lot of times coating needed to become 300 nm thickness. A lot of thermal stress was applied to the film from the substrate. Therefore, it assumed that the surface of the 0.1 M-LNO film was roughed.

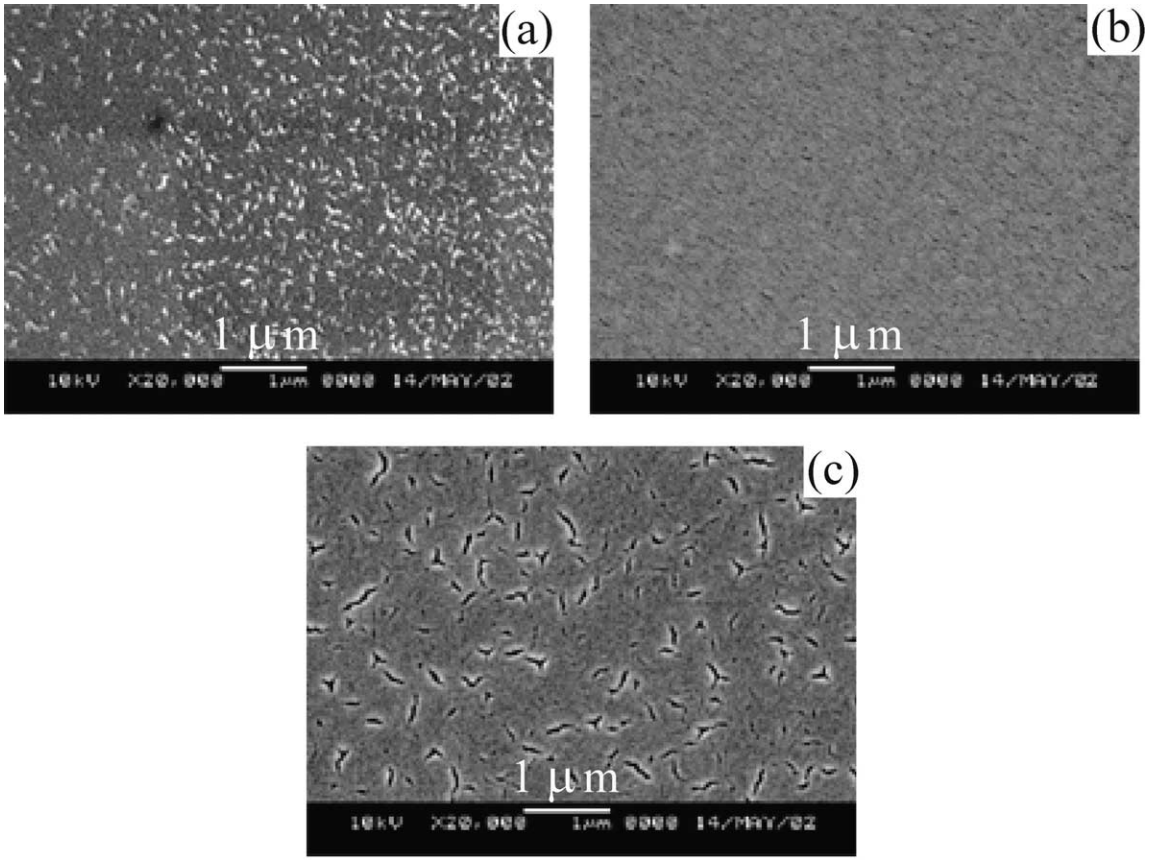

Fig. 2. Surface morphology of the $LaNiO_3$ films derived from (a) 0.1 M, (b) 0.3 M and (c) 0.5 M concentration of precursor solutions.

The 0.3 M-LNO film showed a flat surface. On the 0.5 M-LNO film surface was observed some cracks. The film thickness of one layer coating was thick in the precursor film using 0.5 M-LNO solution, and strain was generated while to removing organic components or annealing. Therefore, it was considered that some cracks were yielded in the resultant 0.5 M-LNO film.

The electrical resistivity of the obtained 0.1, 0.3 and 0.5 M-LNO films were 2.57×10^{-3}, 1.85×10^{-3} and $1.82\times10^{-3}\Omega$cm, respectively. These were close to the reported value,[5-8,10] and the obtained LNO films were able to apply for the electrode.

LNO films were successfully deposited by the CSD method. In particular, the 0.3 M-LNO film showed a low resistivity, flat surface, and highly (100) preferred orientation. Therefore, to fabricate an LNO film, it was considered that the 0.3 M concentration of precursor solution was the optimal deposition condition as an electrode for a ferroelectric material. We fabricated a PZT film onto the 0.3 M-LNO electrode and tried to evaluate the ferroelectric and electrode property.

Fig. 3 shows the obtained crystalline PZT film onto the LNO film. The PZT film showed (100)/(001) preferred orientation. PZT lattice parameter is close to LNO lattice parameter. The prepared LNO film electrode was (100) orientation, and it considered that the PZT film was grown epitaxally onto the LNO electrode. This result suggested that a PZT film orientation could be controlled on an LNO electrode.

A ferroelectric property for the obtained PZT film onto the LNO electrode was measured (Fig. 4). The PZT/LNO film showed a hysteresis loop, and the film exhibited the remanent polarization of 10 $\mu C/cm^2$, the coercive field of 50 kV/cm. This result showed the obtained film exhibited a ferroelectric property, and the 0.3 M-LNO film worked as an electrode for a ferroelectric film.

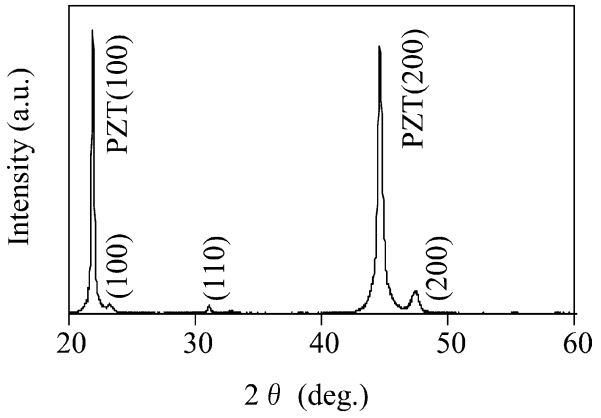

Fig. 3. XRD patterns for the PZT film onto the resultant $LaNiO_3$ film.

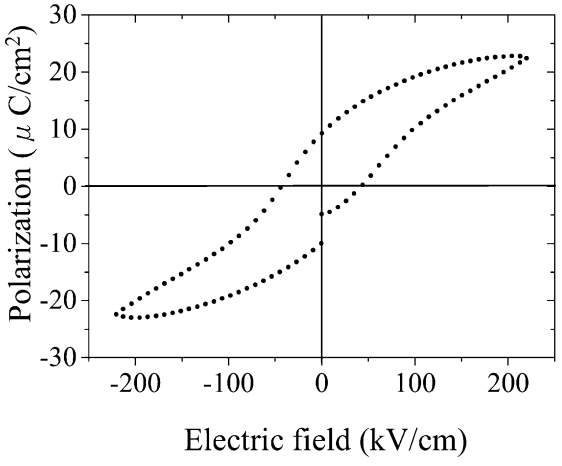

Fig. 4. P–E Hysteresis loop of the PZT film onto the resultant $LaNiO_3$ film.

4. Conclusion

Orientation of the LNO film was controlled by changing concentration of the precursor solution. The resistivity of the resultant LNO films was 1.82–$2.57\times10^{-3}\Omega$cm. In particular, the 0.3 M-LNO film was flat surface, (100) preferred orientation, and low resistivity. That is, 0.3 M-LNO film was much more suitable for an electrode for ferroelectric films. PZT films were deposited by CSD onto the 0.3 M-LNO film. The PZT/LNO film was oriented to (100)/(001), and the resultant PZT film showed a ferroelectric property.

In this study, we showed that both an electrode film and a ferroelectric film could be fabricated by only chemical solution deposition.

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