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Sol–gel derived $LaNiO_3$ thin films on ZrO_2-buffered (1 0 0) Si substrates

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Abstract

Perovskite $LaNiO_3$ (LNO) thin films with a strong (1 0 0)-orientation were fabricated on yttrium-stabilized-zirconia (YSZ)-buffered silicon substrates using a sol–gel method. The YSZ buffer layer showed a stable tetragonal phase, and proved to be effective to suppress inter-diffusion between the Si substrates and the LNO films. Our obtained LNO films on the YSZ buffer layer exhibited a homogenous and smooth surface, with an average grain size below 0.1 μm. The resistivity of the LNO films was in the magnitude order of 10^{-4} Ω cm. The crystallographic orientation and low resistivity make the sol–gel derived LNO films very attractive as the bottom electrode layer for perovskite oxide ceramic thin films.

Keywords: A. Sol–gel processes; C. Electrical conductivity; $LaNiO_3$; Thin film; YSZ

1. Introduction

Ferroelectric thin films have been receiving great attention due to their many applications in various functional devices. Selection of a suitable electrode is critical to integrating quality films into devices. It has been noted that many conductive perovskite oxides, for examples, $YBa_2Cu_3O_{8-\delta}$ (YBCO), $(La_{0.5}Sr_{0.5})CoO_{3-\delta}$ (LSCO) and $SrRuO_3$, have great potentials as the electrode for the improvement of the fatigue and aging of ferroelectric memories [1–3]. The $LaNiO_3$ (LNO), which is a perovskite-type metallic oxide, has also attracted attention as a conducting film [4,5]. LNO has a lattice parameter of 3.84 Å, which matches well with many ferroelectric compositions, such as $PbTiO_3$ (PT) and $Pb(Zr_xTi_{1-x})O_3$ (PZT) perovskite oxides [6,7]. Therefore, LNO film can function not only as a bottom electrode but also as a template to control the structure and orientation of the perovskite oxide films on it.

The orientation in the LNO film can be controlled with single crystal substrates such as $LaAlO_3$ and $SrTiO_3$, or by an oriented buffer layer such as yttrium-stabilized-ZrO_2 (YSZ) and MgO deposited by pulsed laser deposition method (PLD) [8–11]. Yang et al. also reported that the (1 0 0)-oriented LNO films could be grown on amorphous SiO_2/Si and polycrystalline Pt/Ti/SiO_2/Si substrates using a sputtering method [4]. In Miyake et al.'s report, the LNO films prepared on the SiO_2 glass and CeO_2-covered (1 0 0) Si substrates through a sol–gel method also had a strong (1 0 0)-orientation [12].

In this paper, we report the preparation of the (1 0 0)-oriented LNO films on a YSZ-buffered Si substrate. Both the LNO and YSZ films were deposited using a sol–gel method. The YSZ buffer layer was used to suppress interfacial chemical diffusion. Compared with other buffer layer materials, YSZ has superior chemical stability and mechanical property. [13] Epitaxial YSZ films can be grown using pulsed laser frequency (PLF) or metal organic chemical vapor deposition (MOCVD) technique [14,15]. However, few results were reported on the sol–gel derived YSZ film as the buffer layer for oriented LNO. As is well known, sol–gel processing possesses many attractive advantages in thin film preparation, such as low cost, large area uniformity, precise composition control, etc.

2. Experimental procedure

To prepare the YSZ buffer layer, Zr-propoxide was dissolved in acetic acid to obtain a 0.2 M solution. The zirco-

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nia was doped with yttrium oxide by adding 8 mol% yttrium nitrate hexahydrate in order to stabilize its tetragonal phase. The precursor solution was deposited on a (1 0 0) Si substrate by spin-coating, followed by annealing at 650–850 °C for 30 min. The film had a thickness of ~50 nm.

To prepare the LNO film, lanthanum nitrate and nickel acetate were used as the starting chemicals; both were dissolved in acetic acid with a molar ratio of La:Ni = 1:1. The LNO solution of 0.3 M was deposited on the YSZ coated Si substrates by repeating the spin-coating cycles to achieve a thickness of 0.2 μm. The annealing was carried out at 650–800 °C.

X-ray diffraction analysis (Bruker GADDS, D8-ADVANCED) was carried out to determine the structure of the films annealed at different temperatures. The morphology of the LNO films was examined using Field Emission Scanning Electron Microscopy (JSM-6700F). Secondary Ion Mass Spectrometry (ION-ToF GmbH, ToF-SIMS-IV) was used to investigate the inter-diffusion. The resistivity of the LNO electrode was measured with a 4-point probe system (MCP-T360).

3. Results and discussion

3.1. YSZ buffer layer

A stable single phase is desired in the ZrO_2 films as the buffer layer. Fig. 1 shows the XRD patterns of the undoped ZrO_2 and YSZ films annealed at different temperatures. As shown in Fig. 1A, both tetragonal and monoclinic phases exist in the undoped ZrO_2 through various annealing temperatures from 650 to 850 °C. In contrast, the YSZ film exhibits a single tetragonal phase through all the examined temperatures range, as shown in Fig. 1B.

SIMS analysis confirmed that the YSZ layer suppressed diffusion of LNO, especially lanthanum, towards the Si substrate. Figs. 2 and 3 show SIMS depth profiles of LNO films grown on Si and YSZ-buffered Si substrates, respectively.

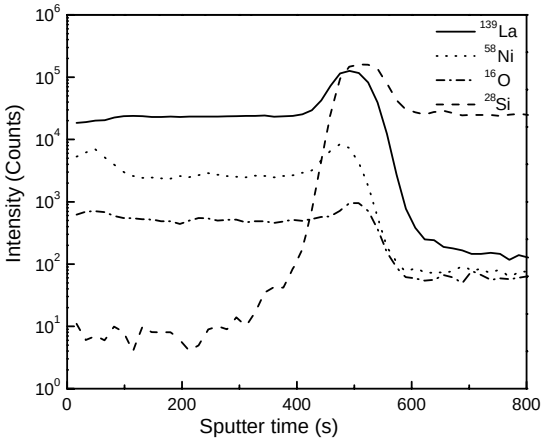


Fig. 2. Composition depth profiles of the LNO film deposited on a Si substrate, obtained by secondary ion mass spectrometry, 700 °C for 1 h.

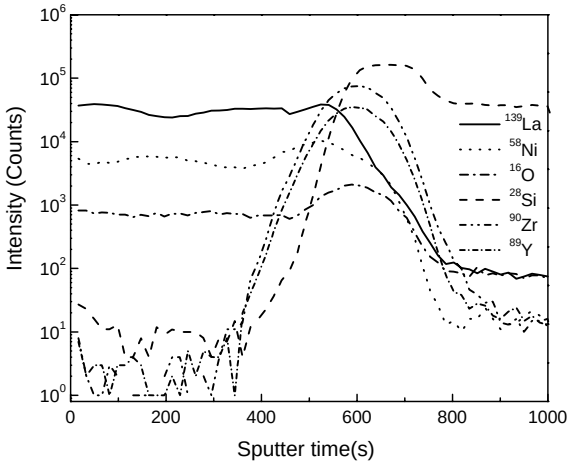


Fig. 3. Composition depth profiles of the LNO film deposited on a YSZ/Si substrate, obtained by secondary ion mass spectrometry, 700 °C for 1 h.

As revealed in Fig. 2, for the LNO grown directly on the Si substrate, both the La and Ni concentrations at the LNO–Si interface are relatively high, indicating a strong interaction between the LNO and Si. It is also apparent that La diffuses into the Si substrate. In contrast, for the LNO grown

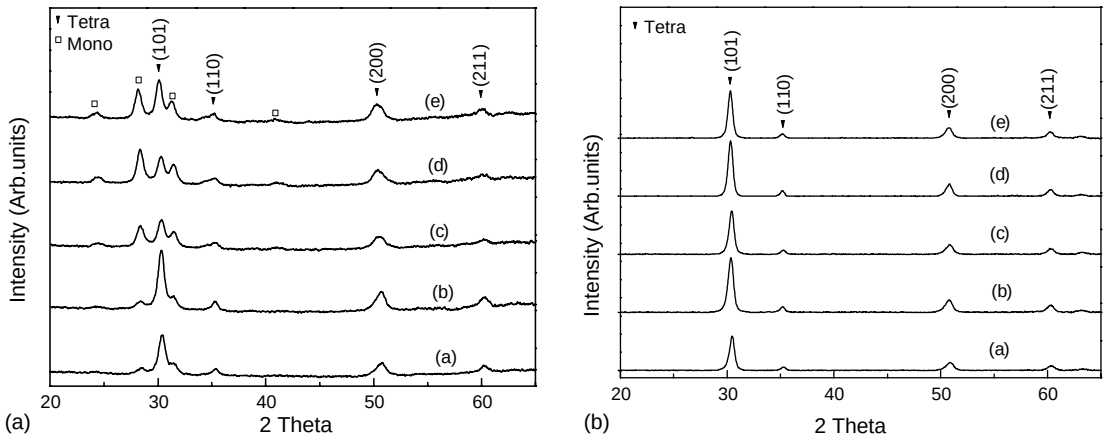


Fig. 1. XRD patterns of the ZrO_2 (A) and YSZ (B) layers annealed at (a) 650 °C, (b) 700 °C, (c) 750 °C, (d) 800 °C, and (e) 850 °C for 30 min.

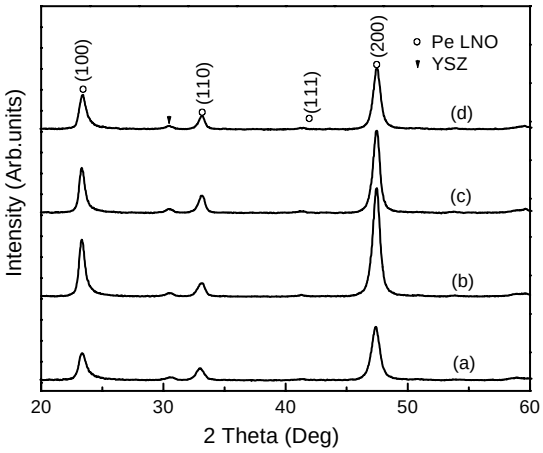


Fig. 4. XRD patterns of the LNO films annealed at different temperatures: (a) 650 °C, (b) 700 °C, (c) 750 °C, and (d) 800 °C for 1 h.

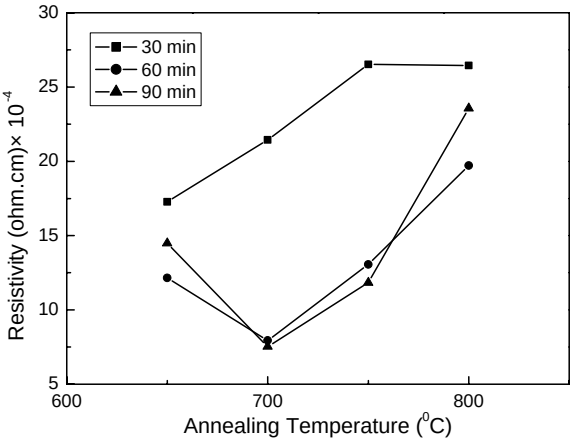


Fig. 6. Resistivity of the LNO films grown on a YSZ/Si substrate, annealed at different temperatures for different time.

on the YSZ-coated Si substrate, the concentration of La and Ni at the LNO–YSZ/Si interface is substantially reduced, and the diffusion of La into Si is suppressed, as shown in Fig. 3.

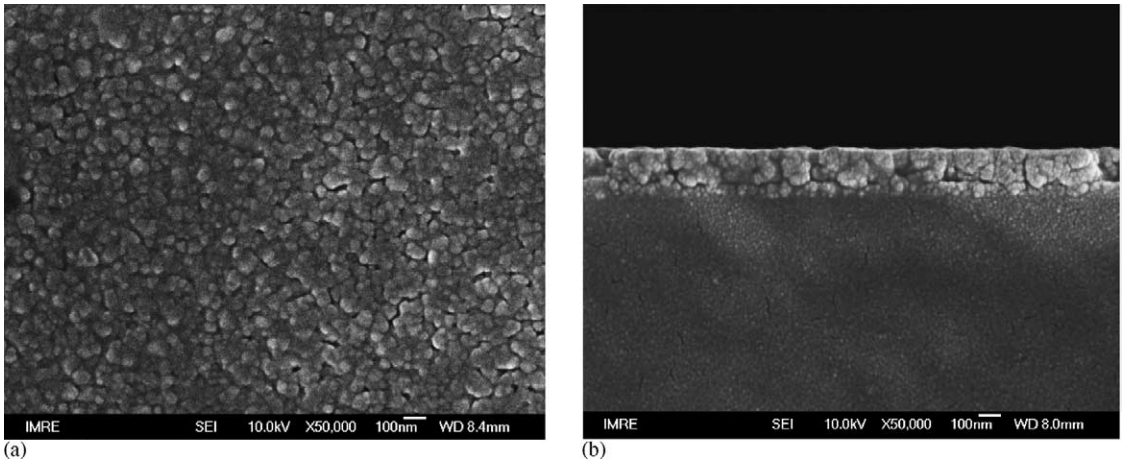
3.2. Structure and morphology of LNO on YSZ

Although the tetragonal phase of the YSZ layer exhibits random orientation, the LNO films grown on the YSZ layer have the perovskite structure with a strong (1 0 0)-orientation, as shown in Fig. 4. It has been reported that the (1 0 0)-plane of LNO, which has the smallest surface energy, can develop parallel to the substrate surface when adhesive bonding between the film and substrate is strong [12,16]. Therefore, the (1 0 0)-oriented nuclei might tend to grow more rapidly than the others.

SEM picture reveals that the morphology of the LNO film is homogeneous with an average grain size below 0.1 μm. The thickness of the film is around 0.2 μm (Fig. 5).

3.3. Resistivity of LNO on YSZ

In order to achieve good conductivity, the LNO films deposited on the YSZ/Si substrates were annealed at different conditions. The resistivity of the LNO films, dependent on the annealing temperature and time, is presented in Fig. 6. In general, lower resistivity can be obtained in the films annealed for a longer time than 30 min. However, a high temperature above 700 °C is not favorable for obtaining a good conductivity. As shown in Fig. 6, when the LNO film is annealed above 700 °C, resistivity increases with the annealing temperature. The resistivity at room temperature for the LNO film annealed at 700 °C for 1 h shows the lowest resistivity of $7.6 \times 10^{-4}\,\Omega\,\text{cm}$, which is consistent with the good crystallization as shown in Fig. 4. The resistivity value is comparable to those of LNO films obtained by physical techniques, such as radio frequency magnetron sputtering and pulsed laser ablation [4,17].



(a) (b)

Fig. 5. SEM images of the LNO film grown on a YSZ/Si substrate: surface (A) and cross-section (B), annealed at 700 °C for 1 h.

4. Conclusions

Highly (1 0 0)-oriented $LaNiO_3$ thin films were fabricated on YSZ-buffered Si substrates through a sol–gel method. The YSZ buffer layer exhibits a stable single tetragonal phase through the annealing temperature from 650 to 850 °C, and it has proved to be effective in suppressing the interfacial diffusion between the LNO film and the Si substrate. The LNO film annealed at 700 °C for 1 h shows a low resistivity of $7.6 \times 10^{-4}\ \Omega$ cm. The low resistivity and the strong (1 0 0)-orientation make the sol–gel derived LNO film an attractive candidate for the bottom electrode and the seeding layer as well in the fabrication of the perovskite-type ferroelectric thin films.

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References

[1] J.F.M. Cillessen, R.B. Wolf, A.E.M. De Veirman, Hetero-epitaxial oxidic conductor $La_{1-x}Sr_xCoO_3$ prepared by pulsed laser deposition, Appl. Surf. Sci. 69 (1993) 212–215.
[2] J.T. Cheung, P.E.D. Morgan, D.H. Lowndes, S.Y. Zheng, J. Breen, Structural and electrical properties of $La_{0.5}Sr_{0.5}CoO_3$ epitaxial films, Appl. Phys. Lett. 62 (1993) 2045–2048.
[3] C.B. Eom, R.B. Van Dover, J.M. Philips, K.J. Werder, J.H. Marshall, C.H. Chen, R.J. Cara, R.M. Fleming, P.K. Fork, Fabrication and properties of epitaxial ferroelectric heterostructures with ($SrRuO_3$) isotropic metallic oxide electrodes, Appl. Phys. Lett. 63 (1993) 2570–2572.
[4] C.-C. Yang, M.-S. Chen, T.-J. Hong, C.-M. Wu, J.-M. Wu, Preparation of (1 0 0)-oriented metallic $LaNiO_3$ thin films on Si substrates by radio frequency magnetron sputtering for the growth of textured $Pb(Zr_{0.53}Ti_{0.47})O_3$, Appl. Phys. Lett. 66 (20) (1995) 2643–2645.
[5] S.S. Kim, T.S. Kang, J.H. Je, Microstructures of $LaNiO_3$ films grown on Si(0 0 1) by pulsed laser deposition, Thin Solid Films 405 (2002) 117–121.
[6] S.-Y. Chen, I.-W. Chen, Texture development, microstructure evolution, and crystallization of chemically derived PZT thin films, J. Am. Ceram. Soc. 81 (1998) 97–105.
[7] V.R. Palker, S.C. Purandare, R. Pinto, Ferroelectric thin films of $PbTiO_3$ on silicon, J. Phys. D: Appl. Phys. 32 (1999) R1.
[8] K.M. Satyalakshmi, R.M. Mallya, K. Ramanathan, X.D. Wu, B. Brainard, D.C. Gautier, N.Y. Yasanthacharya, M.S. Hegde, Epitaxial metallic $LaNiO_3$ thin films grown by pulsed laser deposition, Appl. Phys. Lett. 62 (1993) 1233–1235.
[9] F. Sanchez, C. Ferrater, X. Alcobe, J. Bassas, M.V. Garcia-Cuenca, M. Varela, Pulsed laser deposition of epitaxial $LaNiO_3$ thin films on buffered Si (1 0 0), Thin Solid Films 384 (2001) 200–205.
[10] X.Y. Chen, K.H. Wong, C.L. Mak, J.M. Liu, X.B. Yin, M. Wang, Z.G. Liu, The orientation-selective growth of $LaNiO_3$ on Si(1 0 0) by pulsed laser deposition using a MgO buffer, Appl. Phys. A 75 (2002) 545–549.
[11] F. Sanchez, M.V. Garcia-Cuenca, C. Ferrater, M. Varela, Epitaxial growth of yttria-stabilized zirconia buffer layers on X-cut $LiNbO_3$ for superconducting electrodes, Appl. Phys. A 75 (2002) 381–385.
[12] S. Miyake, S. Fujihara, T. Kimura, Characterization of oriented $LaNiO_3$ thin films fabricated by the sol–gel method, J. Eur. Ceram. Soc. 21 (2001) 1525–1528.
[13] J. Moon, H. Choi, H. Kim, C. Lee, The effects of heat treatment on the phase transformation behavior of plasma-sprayed stabilized ZrO_2 coating, Surf. Coat. Technol. 155 (2002) 1–10.
[14] C.-H. Chen, N. Wakiya, K. Shinozake, N. Mizutani, Effects of thermal coefficient and lattice constant mismatches on mosaic dispersion of heteroepitaxial YSZ/Si(0 0 1) thin films, J. Phys. D: Appl. Phys. 35 (2002) 151–156.
[15] B.-H. Ju, J.-W. Sn, H.-J. Kim, D.-W. Lee, C.-H. Jung, S.-D. Par, C.-J. Kim, Fabrication of YSZ buffer layer by single source MOCVD technique for YBCO coated conductor, Physica C 392–396 (2003) 867–872.
[16] M. Mashita, M. Yoshida, Handbook of Thin Film Engineering, Kdansha, 1998, p. 188.
[17] T. Yu, Y.F. Chen, Z.G. Liu, X.Y. Chen, L. Sun, N.B. Ming, L.J. Shi, Epitaxial growth of conductive $LaNiO_3$ thin films by pulsed laser ablation, Mater. Lett. 26 (1996) 73–76.