Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 1035–1038
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Effects of $LaNiO_3$ buffer layers on preferential orientation growth and properties of $PbTiO_3$ thin films

Xian Yang, Xiaoqing Wu *, Wei Ren, Peng Shi, Xin Yan, Hongsheng Lei, Xi Yao

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

Available online 2 October 2007

Abstract

(1 0 0)- and (1 0 1)-oriented $PbTiO_3$ (PT) thin films on conductive $LaNiO_3$ (LNO)-coated Si(1 1 1) substrates were prepared by a metal-organic decomposition method. It is found that the crystallization states of LNO thin films used as buffer layers have significantly effects on preferential orientation of PT thin films. PT thin films with (1 0 0) orientation could be obtained not only on the crystalline LNO (1 0 0) film, but also on the amorphous LNO thin film. The highly (1 0 0)-oriented PT films show high dielectric constant of 189.4 on LNO (1 0 0) films and 183.1 on amorphous LNO films. The PT capacitors fabricated on the LNO buffer layers display good *P–E* hysteresis loops. The remnant polarization (P_r) and coercive field (E_c) of PT films on amorphous, (1 0 0)- and (1 1 0)-oriented LNO films are 9.35 μC/cm^2 and 162.8 kV/cm, 10.03 μC/cm^2 and 163.3 kV/cm, 11.23 μC/cm^2 and 166.2 kV/cm, respectively.

Keywords: C. Electric properties; MOD process; Oriented growth; $LaNiO_3$ and $PbTiO_3$ films

1. Introduction

Oxide electrodes, prepared by chemical solution deposition for ferroelectric thin films, have been studied by many research groups [1–3]. As a typical member of this family, $LaNiO_3$ (LNO) thin film exhibits good conductivity in room temperature. It has a pseudo-cubic lattice parameter of $a = 3.84$ Å, which is close to the values of ferroelectric films such as $Pb(Zr_xTi_{1-x})O_3$, $Pb_{1-x}La_x(Zr_yTi_{1-y})O_3$ and so on [4,5]. As a buffering layer, oriented LNO thin films can induce oriented growth of ferroelectric thin films [6,7].

In the previous work, LNO thin films with high (1 0 0) and (1 1 0) orientation on Si(1 0 0), Si(1 1 1), SiO_2/Si(1 1 1), Si_3N_4/Si(1 1 1) substrates have been fabricated successfully by different thermal annealing processes [8]. In this paper, preferential orientation $PbTiO_3$ films deposited on amorphous and oriented LNO films have been investigated. Generally, (1 0 0)-oriented or (1 1 0)-oriented LNO films could induce (1 0 0)-oriented or (1 1 0)-oriented PT thin films. At the same time, it was also found that the amorphous LNO layer could induce the oriented growth of PT thin films. The effects of the preferential orientations on dielectric and ferroelectric properties of PT films have been presented and discussed.

2. Experimental procedure

The precursors of LNO and PT thin films were prepared by a modified MOD method. For LNO precursor, lanthanum nitrate [La $(NO_3)_3$ (AR)] and equimolar amount of nickel acetate [$Ni(CH_3COO)_2{\cdot}4H_2O$ (AR)] were used as raw materials and glycol ether [$C_4H_{10}O_2$ (AR)] was used as the solvent. The PT precursor was prepared using lead acetate trihydrate [$Pb(CH_3COO)_2{\cdot}3H_2O$ (AR)] and titanium *n*-butoxide [$C_{16}H_{36}O_4Ti$ (AR)] as raw materials and also glycol ether [$C_4H_{10}O_2$ (AR)] as the solvent. Acetylacetone [$C_5H_8O_2$ (AR)] was added in the PT precursor to make the solution stable. The concentration of the LNO solution and PT precursor solution was 0.3 mol/L and 0.5 mol/L, respectively. A spin-coating technique was used to deposit the LNO and PT thin films. The PT films were spin-coated on the various LNO-coated Si substrates. After each coating, the films were thermally treated at 650 °C for 3 min by RTA process. The PT thin films were obtained by coating five times. Thickness of the PT thin films was about 500 nm.

* Corresponding author. Tel.: +86 29 82668679; fax: +86 29 82668794.
E-mail address: xqwu@mail.xjtu.edu.cn (X. Wu).

0272-8842/$34.00 © 2008 Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2007.09.077

The structures of the LNO and PT thin films were analyzed by a Rigaku D/MAX2400 X-ray diffractometer (XRD) with Cu Kα radiation. The morphologies were observed by a JEOL JSM-6500FE field emission scanning electron microscope (FESEM) and a Digital Instrument atomic force microscope (AFM). The dielectric properties and the ferroelectric *P–E* hysteresis loops of the PT films were measured by an Agilent 4294A precision impedance analyzer and aixACCT TF ANALYZER2000 instrument, respectively.

3. Results and discussion

Fig. 1(a) shows XRD patterns of LNO thin films with (1 0 0) and (1 1 0) orientation as well as amorphous state prepared on Si(1 1 1) substrates by different annealing processes. Thicknesses of all LNO films are about 200 nm. In this paper, we designate the amorphous LNO layer as 'LNO (A)', (1 1 0)- and (1 0 0)-oriented LNO layers as 'LNO(1 1 0)' and 'LNO(1 0 0)', respectively.

Fig. 1(b) shows XRD patterns of PT/LNO (A), PT/LNO (1 0 0) and PT/LNO (1 1 0). The (1 0 0) and (1 1 0)orientation ratios are defined here as $\alpha_{1\,0\,0} = I(1\,0\,0)/[I(1\,0\,0) + I(0\,0\,1)]$ and $\alpha_{1\,0\,1} = I(1\,0\,1)/[I(1\,1\,0) + I(1\,0\,1)]$, respectively. It can be seen that both (1 0 0) orientation and amorphous LNO films can induce high (1 0 0)-oriented growth of the PT films. PT(1 0 0)/LNO(A) films exhibit higher (1 0 0) orientation than that of PT(1 0 0)/LNO(1 0 0). While LNO(1 1 0) films induce (1 0 1)-oriented growth of the PT films. The value of $\alpha_{1\,0\,0}$ is 0.70 and 0.78 for PT(1 0 0)/LNO(A), PT(1 0 0)/LNO(1 0 0), respectively. The $\alpha_{1\,0\,1}$ is around 0.69 for the PT(1 0 1)/LNO(1 1 0) films. For PT(1 0 0)/LNO(1 0 0) and PT(1 0 1)/LNO(1 1 0) thin films, it is easy to understand that (1 0 0)- and (1 1 0)-oriented LNO films lead to the oriented PT thin films with corresponding orientation due to the lattice matching. However, it is slightly difficult to explain the (1 0 0)-oriented PT thin films induced by the amorphous LNO films. Further study to understand the crystallization mechanism is under way.

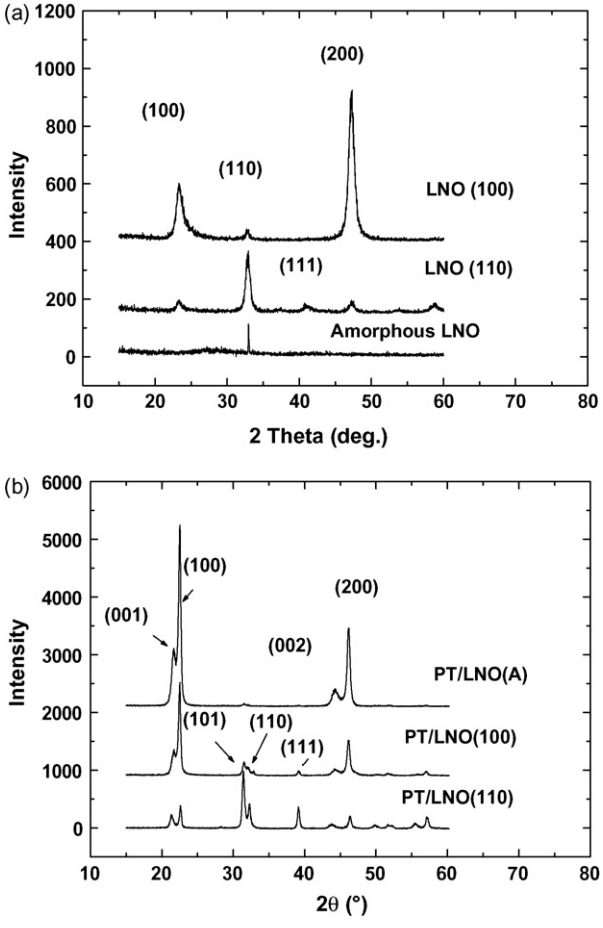

Fig. 1. XRD patterns of various LNO (a) and PT films on various LNO (b).

The FESEM photos of PT(1 0 0)/LNO(A), PT(1 0 0)/LNO(1 0 0) and PT(1 0 1)/LNO(1 1 0) are shown in Fig. 2. All the films display crack-free surfaces. The PT(1 0 0)/LNO(1 0 0) shows a compact surface and small grain size. While the surfaces of PT(1 0 1)/LNO(1 1 0) and PT(1 0 0)/LNO(A) films are looser and have larger grains. The AFM analysis results suggest that the root-mean-surface (RMS) roughness of the PT(1 0 0)/LNO(1 0 0), PT(1 0 1)/LNO(1 1 0) and PT(1 0 0)/LNO(A) films are 3.648, 3.985 and 5.729 nm, respectively. The surfaces of LNO buffer layers with different orientation and crystallization states have significant effect on the morphologies of the PT thin films, as reported by our previously work [8]. The cross-section images of the PT thin films in Fig. 2 exhibit the sharp boundaries between PT films and LNO films for the PT(1 0 0)/LNO(1 0 0) and PT(1 0 1)/LNO(1 1 0). While such a boundary of PT(1 0 0)/LNO(A) is not distinct. There is the possible interface diffusion between PT film and LNO film.

Fig. 3 shows the frequency dependence of dielectric constant and dielectric loss of the PT thin films with a configuration of Au/PT/LNO/Si. The orientation and electrical properties of PT/LNO films are listed in Table 1. It can be seen that PT(1 0 0)/LNO(A) and PT(1 0 0)/LNO(1 0 0) have similar dielectric constants and losses. The dielectric constant at 1 kHz is about 190, which is much larger than that of the PT films with a random orientation. It is attributed to the highly (1 0 0) orientation of the PT films. Meanwhile, the PT(1 0 1)/LNO(1 1 0) shows moderate value (1 1 0) due to its (1 0 1) preferential orientation. The dielectric losses of PT(1 0 0)/LNO(A), PT(1 0 0)/LNO(1 0 0) and PT(1 0 1)/LNO(1 1 0) are slightly larger than that of the PT films deposited on Pt electrode (∼0.02) [9]. Otherwise, from 100 kHz to 1 MHz, the dielectric constant curve has a drastic drop while loss tangent curve rises strongly. It is caused by the measurement equipment used (Agilent 4294A).

Fig. 4 gives the *P–E* hysteresis loops of the oriented PT films. The values of remnant polarization (P_r) and coercive field (E_c) of PT(1 0 0)/LNO(1 0 0), PT(1 0 0)/LNO(A) and PT(1 0 1)/LNO(1 1 0) are very close, as seen in Table 1. It can be also seen from Fig. 4, the breakdown field (E_b) of PT(1 0 0)/LNO(A) is smaller than those of the PT(1 0 0)/

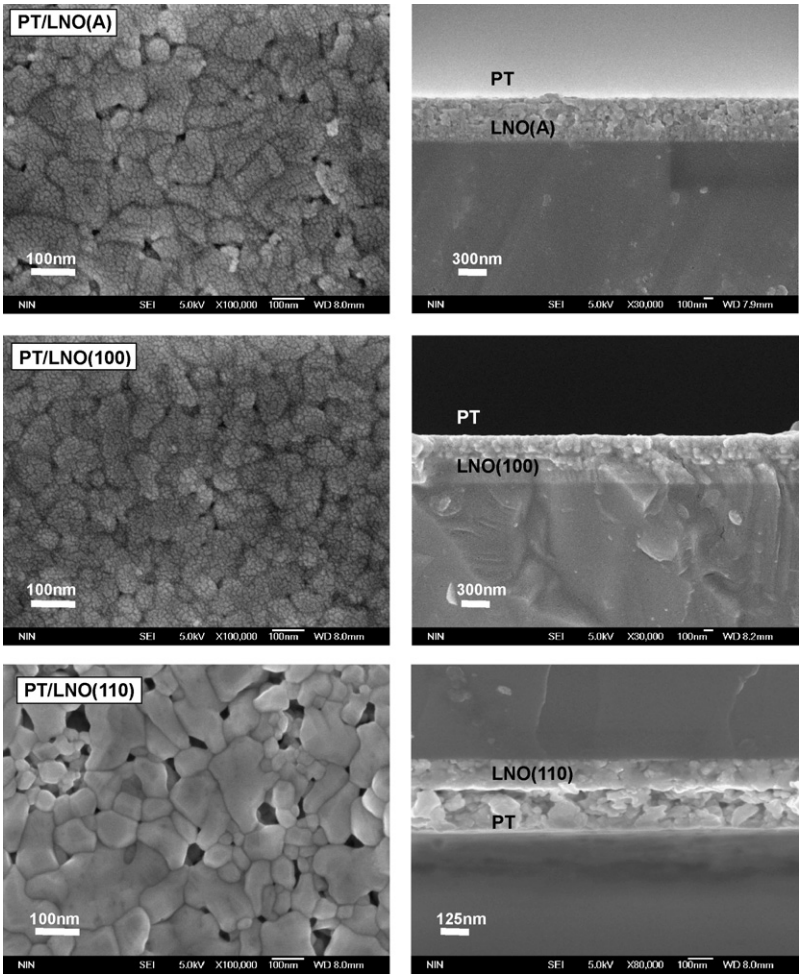

Fig. 2. FESEM images of PT/LNO films.

LNO(1 0 0) and PT(1 0 1)/LNO(1 1 0), which may be due to thinner PT films caused by the diffusion between LNO and PT. Meanwhile, at lower applied fields, the values of E_c and P_r of PT(1 0 0)/LNO(A) samples are close with those of the PT(1 0 0)/LNO(1 0 0) and PT(1 0 1)/LNO (1 1 0) samples because the larger dielectric loss makes the curves 'fat'.

From the above discussion, we can suggest that the orientation of PT thin films have a significant effect on the dielectric constants.

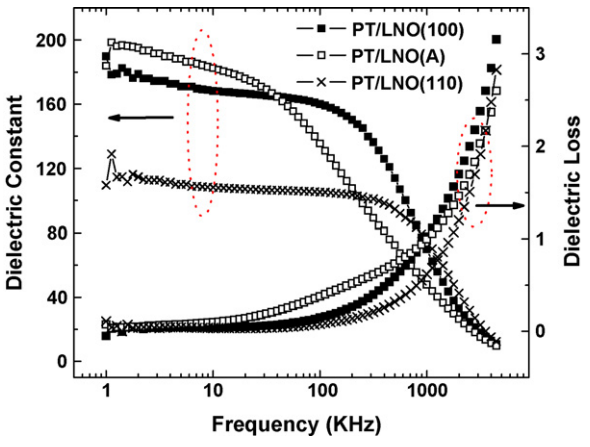

Fig. 3. Frequency dependence of dielectric constant and loss tangent of PT/LNO films.

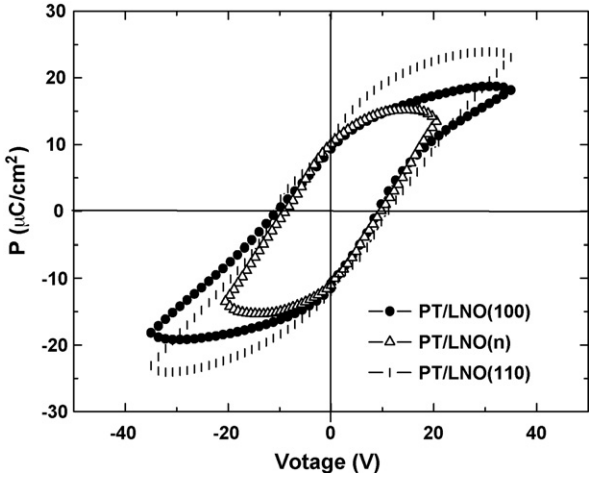

Fig. 4. The polarization–voltage hysteresis loops of PT/LNO films.

Table 1
The properties of oriented PT films

Samples	Orientation ratio	ε_r	tan δ	P_r ($\mu C/cm^2$)	E_c (kV/cm)	E_b (kV/cm)
PT(1 0 0)/LNO(A)	$\alpha_{1\,0\,0} = 0.70$	183.1	0.056	9.35	162.8	409.8
PT(1 0 0)/LNO(1 0 0)	$\alpha_{1\,0\,0} = 0.78$	189.4	0.043	10.03	163.3	688.3
PT(1 0 1)/LNO(1 1 0)	$\alpha_{1\,0\,1} = 0.69$	114.3	0.041	11.23	166.2	699.6

4. Conclusions

Highly (1 0 0)-oriented PT films were successfully prepared using the LNO films with different orientation and crystallization as buffer layers and electrodes. The PT thin films prepared on the amorphous LNO films exhibit (1 0 0) highly preferential orientation. The PT thin films possess good dielectric and ferroelectric properties. The results suggest that LNO is a promising electrode material and also a good buffer layer or seed layer for highly oriented growth of ferroelectric thin films.

Acknowledgements

This work was supported by the Natural Science Foundation of China (No. 60377035) and the Key Science and Technology Research Project from the Ministry of Education of China (Grant No. 03155).

References

[1] Y. Ling, W. Ren, X.Q. Wu, L.Y. Zhang, X. Yao, Preparation and properties of conductive $LaNiO_3$ thin films by a thermal decomposition of water-based solutions, Thin Solid Films 311 (1997) 128–132.

[2] J.K. Li, X. Yao, L.Y. Zhang, The preparation of the single-phase perovskite conductive $LaNiO_3$ films on different substrates, Proc. SPIE 5774 (2004) 184–187.

[3] J. Yu, J.L. Sun, X.J. Meng, Z.M. Huang, J.H. Chu, D.Y. Tang, Ultraviolet–infrared optical properties of highly (1 0 0)-oriented $LaNiO_3$ thin films on Pt–Ti–SiO_2–Si wafer, J. Appl. Phys. 90 (6) (2001) 4439–4448.

[4] Q. Zou, H.E. Ruda, B.G. Yacobi, Improved dielectric properties of lead zirconate titanate thin films deposited on metal foils with $LaNiO_3$ buffer layers, Appl. Phys. Lett. 78 (9) (2001) 1282.

[5] A. Lin, X. Hong, V. Wood, A.A. Verevkin, R.A. McKee, F.J. Walker, E.D. Specht, Epitaxial growth of $Pb(Zr_{0.2}Ti_{0.8})O_3$ on Si and its nanoscale piezoelectric properties, Appl. Phys. Lett. 2034 (2001) 78–81.

[6] R. Ramesh, D.G. Schlom, Orienting Ferroelectric films, Science. 296 (2002) 1975–1976.

[7] C.R. Cho, D.A. Payne, S.L. Cho, Solution deposition and heteroepitaxial crystallization of $LaNiO_3$ electrodes for integrated ferroelectric devices, Appl. Phys. Lett. 71 (1997) 3013.

[8] X. Yang, X.Q. Wu, W. Ren, X. Yao, Preparation and properties of highly oriented $LaNiO_3$ thin films on different substrates, Ferroelectrics 357 (2007) 617–621.

[9] A.D. Li, D. Wu, C.Z. Ge, H. Wang, M. Wang, M. Wang, Z.G. Liu, N.B. Ming, Structural and electrical properties of $PbTiO_3$ thin films on conductive oxide $LaNiO_3$-coated Si substrates prepared by sol–gel method, Thin Solid Film 375 (2000) 220–223.