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Growth of highly c-axis-oriented $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin films on $LaNiO_3$ electrodes by pulsed laser ablation

Tao Yu *, Yan-Feng Chen, Zhi-Guo Liu, Si-Bei Xiong, Li Sun, Xiao-Yuan Chen, Nai-Ben Ming

National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093 and Center for Advanced Studies in Science and Technology of Microstructures, Nanjing 210093, China

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Abstract

Highly *c*-axis-oriented ferroelectric $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) thin films have been fabricated on epitaxial metallic $LaNiO_3$ (LNO) electrodes deposited on (001)$SrTiO_3$ (STO) and (001)$LaAlO_3$ (LAO) single crystal substrates by pulsed laser ablation (PLA). The LNO thin film surfaces, which would influence the growth and ferroelectric properties of PZT thin films, were analyzed by X-ray photoelectron spectroscopy (XPS). *P–E* hysteresis loop of PZT in the trilayer Ag/PZT/LNO/STO were measured using the Sawyer–Tower circuit. The remnant polarization P_r and coercive field E_c at room temperature were 25.2×10^{-6} C/cm^2 and 24.6 kV/cm (at 7.5 V, 50 Hz) respectively.

Keywords: Ferroelectric thin film; $LaNiO_3$; Pulsed laser ablation

Ferroelectric thin films have recently attracted much attention, primarily because of their potential use as high speed nonvolatile ferroelectric random access memories (NVFRAM) [1]. Among various ferroelectric materials, the $PbZr_xTi_{1-x}O_3$ (PZT) class of perovskites and its derivatives are being intensively examined as memory materials [2]. The thin films of these materials have been prepared by different techniques such as sol–gel processing, rf sputtering, metal-organic chemical vapor deposition (MOCVD) and pulsed laser ablation (PLA) in the last few years [2–5]. Among these techniques, PLA shows some advantages such as lower deposition temperature, lower thermal budget, excellent stoichiometry transfer from target to substrate and the possibility of preparing epitaxial films.

It is important to fabricate high quality ferroelectric thin films on proper electrode materials in the NVFRAM application. Recent studies revealed that the metallic oxides, such as $YBa_2Cu_3O_{7-x}$ (YBCO), $La_{0.5}Sr_{0.5}CoO_3$ (LSCO), RuO_2 and IrO_2, could be used as electrode materials [6–9]. Furthermore, these metallic oxide electrodes yield ferroelectric memories with better fatigue properties compared to conventionally used platinum electrodes [6,7].

$LaNiO_3$ (LNO) without any doping is a Pauli paramagnetic material and a n-type metallic oxide (the resistivity at 300 K is near 10^{-5} Ω.m). It has a perovskite structure with the pseudocubic lattice parameter $a = 3.84$ Å, which is close to the "*a*"-

* Corresponding author.

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parameter of PZT. So it is a favorable candidate as a conductive bottom electrode for epitaxial growth of ferroelectric thin films. Epitaxial LNO films have been fabricated and textured $Bi_2VO_{5.5}$ thin films have recently been grown on LNO electrodes by PLA [10,11]. In this paper we report on the growth and ferroelectric properties of highly *c*-axis-oriented PZT thin films on LNO/(001)$SrTiO_3$ and LNO/(001)$LaAlO_3$ substrates by the PLA method. In addition, the LNO thin film surface which would influence the growth and ferroelectric properties of PZT thin films has been analyzed by X-ray photoelectron spectroscopy (XPS).

The PLA processes were performed using a Lambda Physik LPX205i KrF excimer laser system with 248 nm radiation, 30 ns pulse width and 5 Hz pulse frequency. In our experiment, the average laser pulse energy density was 200 mJ/mm^2. The PZT and LNO targets used in this work were prepared by the standard sintering method. The nominal composition of PZT was $Pb(Zr_{0.53}Ti_{0.47})O_3$. The substrates were (001)$SrTiO_3$ (STO) and (001)$LaAlO_3$ (LAO) single crystals. During laser ablation, the substrates were mounted on a resistively heated stage whose temperature could be varied from 25 to 800°C. LNO films were fabricated at 700°C in 30 Pa oxygen partial pressure for 30 min. After deposition, the films were kept in 0.2 atm oxygen pressure for 30 min and then cooled to room temperature at a rate of about 10°C/min. A portion of the film was masked by Al foil. Subsequently, the deposition of PZT was carried out under the same conditions as that of LNO. The thickness of the film was typically about 300 nm.

As-deposited LNO films on STO and LAO exhibited a dense, shiny and dark appearance. The PZT films deposited on LNO/STO and LNO/LAO were transparent and blue in color. Fig. 1 is a scanning electron micrograph (SEM) of the surface of the PZT film on LNO/STO. Fig. 1 shows that the surface of PZT film is smooth over large area and there are a few droplets with the size of 0.2 μm. The X-ray energy dispersion analysis (EDAX) study was carried out on a PZT film. The Pb:Zr:Ti ratio was 1.00:0.72:0.39 with an experimental error of 3%, indicated that the PZT film was close to the desired stoichiometry.

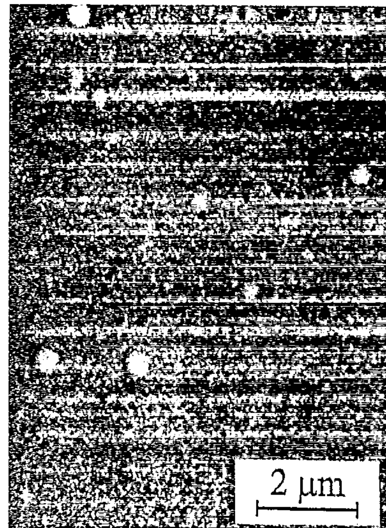
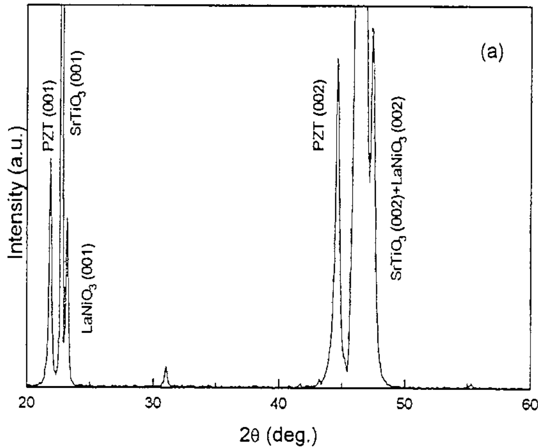


Fig. 1. Scanning elecron micrograph (SEM) of the surface of PZT film on LNO/STO.

The structures of PZT/LNO/STO and PZT/LNO/LAO were then characterized by X-ray diffraction (XRD) using Cu K_α radiation on a Rigaku diffractometer. Fig. 2 is the XRD pattern of a PZT thin film deposited on LNO/STO (Fig. 2a) and on LNO/LAO (Fig. 2b). In Fig. 2a and 2b, only the (001) and (002) peaks of PZT and LNO can be recognized. The XRD Φ scans have also been carried out on LNO/STO and LNO/LAO; the results indicated that the LNO films were epitaxially grown on STO and LAO substrates. So Fig. 2 reveals that the PZT films were highly *c*-axis-oriented or epitaxially grown on the epitaxial LNO electrodes. In addition, diffraction peaks from oxygen or lead deficient pyrochlore phases are not observed, indicating good phase purity of PZT. Similarly, diffraction peaks from other phases are not observed, suggesting the absence of any significant chemical reaction at the interface.

X-ray photoelectron spectroscopy (XPS) analysis was performed to characterize the surface of epitaxial LNO electrode. Fig. 3 is the O1s region of the XPS of LNO thin film. In Fig. 3, two peaks can be found. One peak of lower binding energy corresponds to the lattice oxygen in LNO. Another peak of higher binding energy arises from surface disorder or O^- ions on the surface of the LNO thin film [12]. Because the depth of XPS analysis is limited (< 2 nm), Fig. 3 indicates that there were oxygen vacan-



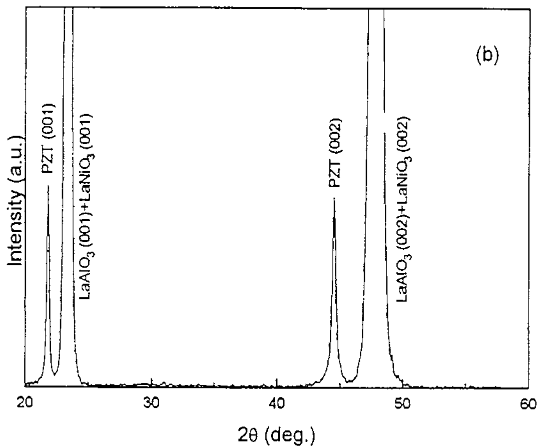


Fig. 2. XRD pattern of PZT thin film deposited (a) on LNO/STO and (b) on LNO/LAO substrates.

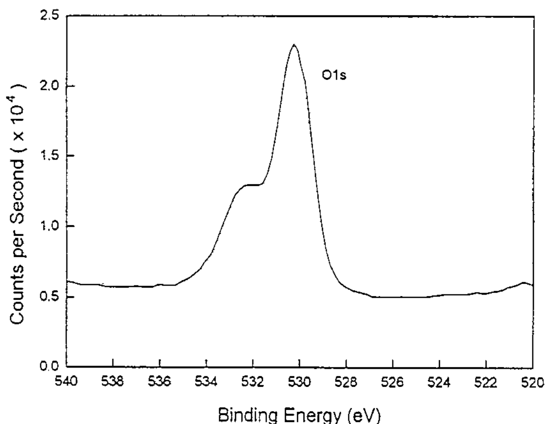


Fig. 3. The O1s region of XPS of epitaxial LNO thin film.

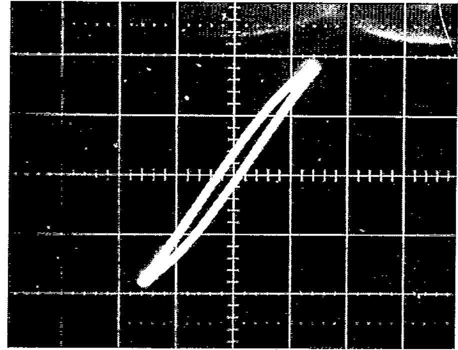


Fig. 4. The $P-E$ hysteresis loop of PZT in the Ag/PZT/LNO/STO heterostructure.

cies or adsorbed oxygen on the surface layer of the epitaxial LNO thin film. In NVFRAM applications, the exact reasons for the superior fatigue characteristics of capacitors with metallic oxide top and bottom electrodes, as compared to Pt electrodes, are not clear. Ramesh et al. attributed the better performance to the nature of the electrode–ferroelectric interface and not to phenomena occurring in the bulk [7]. So the oxygen vacancy or chemically adsorbed oxygen on the LNO surface may influence the ferroelectric properties of ferroelectric thin films deposited on the LNO electrode.

The ferroelectric behavior of PZT thin films in the PZT/LNO/STO and PZT/LNO/LAO heterostructures was demonstrated via $P–E$ hysteresis loop measurements by using a Sawyer–Tower circuit. In this experiment, a thin layer of Ag with an area of 1 mm^2 deposited by vacuum evaporation was used as the top electrode. Fig. 4 is the $P–E$ hysteresis loop of PZT in the Ag/PZT/LNO/STO heterostructure. The remnant polarization (P_r) as well as the coercive field (E_c) were found to increase with the increase in the switching voltage. The remnant polarization P_r and coercive field E_c measured in our specimen at room temperature were 25.2×10^{-6} C/cm^2 and 24.6 kV/cm (at 7.4 V, 50 Hz) respectively. The smaller P_r and E_c indicated that the PZT thin film was highly c-axis-oriented but not completely epitaxial on the LNO electrode. We also attribute the smaller P_r and E_c to the diffusion of Ag (top electrode) into the PZT thin film.

In summary, highly c-axis-oriented ferroelectric PZT thin films have been successfully fabricated on a metallic LNO electrode epitaxially grown on

$SrTiO_3$ and $LaAlO_3$. XPS analysis demonstrated that there were oxygen vacancies or chemically adsorbed oxygen on the surface of the epitaxial LNO electrode. The ferroelectric properties of PZT in the trilayer Ag/PZT/LNO/STO were determined by $P-E$ hysteresis measurements.

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