

Improved dielectric properties of (110)-preferred (Pb, La) (Zr, Sn, Ti)O₃ antiferroelectric thin films on metalorganic decomposition-derived LaNiO₃ buffer layer

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ABSTRACT

In the present investigation, LaNiO₃ (LNO) perovskite thin films were firstly deposited on Pt(111)/Ti/SiO₂/Si substrates through the metalorganic decomposition technique, then (Pb_{0.97}La_{0.02})(Zr_{0.87}Sn_{0.10}Ti_{0.03})O₃ (PLZST 2/87/10/3) antiferroelectric thin films were subsequently grown on Pt(111)/Ti/SiO₂/Si and LNO-buffered Pt(111)/Ti/SiO₂/Si substrates via the sol–gel method, respectively. The effect of LNO buffer layer on the microstructure and electrical properties of PLZST 2/87/10/3 antiferroelectric thin films were studied in detail. XRD patterns and SEM pictures indicated that PLZST 2/87/10/3 antiferroelectric thin films grown on LNO buffer layer displayed a (110)-preferred orientation and had a uniform surface structure. The results of dielectric measurements illustrated that PLZST 2/87/10/3 antiferroelectric thin films on LNO-buffered Pt(111)/Ti/SiO₂/Si substrates had improved dielectric properties.

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1. Introduction

In the last two decades, doped lead zirconate titanate stannate antiferroelectric (AFE) materials have received increasing attention due to their larger electric-induced strain and unique double hysteresis loops, which have the potential usage in microelectric system, especially for higher energy storage applications and high-strain transducers/actuators [1,2]. Generally, most studies on the lead-contained AFE thin films were usually fabricated on Pt/Ti/SiO₂/Si substrates directly. However, ferroelectric (FE) or AFE thin films grown on Pt electrode directly often displayed unsatisfactory performance against fatigue after long polarization switching cycles, which limited their usage in practical application [3]. Besides, the formation of hillocks from Pt electrode often made the capacitors short electrically. It was found that the conductive perovskite oxide layer, such as SrRuO₃, (La, Sr)CoO₃, (La, Sr)MnO₃ and LaNiO₃ (LNO) were the excellent alternatives for solving above problems [4]. Among these oxides, LaNiO₃ is the most promising electrode material for the following reasons [5]. LNO with a lattice parameter of 0.38 nm has the similar structure as most of the perovskite FE and AFE materials, so LNO can function as a template for the growth of subsequent deposited layers at lower temperature. At the same time, LNO with very

simple chemical composition can be easily prepared on different substrates at moderate temperature.

Recently, the studies on deposition (100)-preferred FE thin films on silicon substrates with LNO electrode from the chemical liquid decomposition process were carried out [3,6]. The results indicated that FE films on LNO/Si substrates always suffered the larger dielectric loss at higher frequency compared with films on Pt/Ti/SiO₂/Si substrates. This problem was induced by the larger resistance of LNO in contrast to that of Pt electrode [7]. To overcome this shortcoming, Zhai et al. [8,9] had grown Pb(Nb,Zr,Sn,Ti)O₃ (PNZST) and (Pb,La)(Zr,Sn,Ti)O₃ (PLZST) [10] AFE thin films with (100)-preferred orientation on LNO-buffered Pt/Ti/SiO₂/Si substrates. It was demonstrated that AFE thin films with this kind of heterostructure displayed an improved dielectric behaviors, such as larger dielectric constant, enhanced polarization, smaller dielectric loss and declined leakage current. However, in their studies LNO layers were obtained from the magnetron sputtering technique, which involved a very expensive apparatus. In fact, the chemical liquid technique possesses many attractive advantages for thin films preparation, such as low cost, larger area uniformity and simple coating course [11].

To the best of our knowledge, in the former studies AFE films deposited on the LNO buffer layer often displayed (100)-preferred orientation. However, the antipolar direction for lead-based AFE materials is along the pseudocubic <110> [9]. Hence, AFE thin films with (110)-preferred orientation should have more excellent properties. In the present investigation, (110)-oriented LNO

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thin films, as a template, were firstly grown on Pt(111)/Ti/SiO₂/Si substrates by the metalorganic decomposition (MOD) process, and then PLZST 2/87/10/3 AFE thin films were deposited on LNO/Pt/Ti/SiO₂/Si and Pt/Ti/SiO₂/Si substrates through the sol-gel technique, respectively. Contrary to previous extensive reports, the composition of (Pb_{0.97}La_{0.02})(Zr_{0.87}Sn_{0.10}Ti_{0.03})O₃ was chosen to study, which was located in the AFE orthorhombic region far away from the morphotropic phase boundary in the PLZST triaxial phase diagram. This kind of AFE materials exhibit a “squared” polarization–electric field (*P*–*E*) loop, which have a larger energy storage density and are more suitable for the application in high-energy storage capacitors. The effect of LNO buffer layer on the structure and electrical properties of PLZST 2/87/10/3 films were investigated in detail.

2. Experimental procedure

The preparation of LNO films was from the MOD procedure similar to Ref. [12], and the starting materials were lanthanum acetate [La(CH₃COO)₃] and nickel acetate [Ni(CH₃COO)₃ · 4H₂O]. The starting materials with a mole ratio of La:Ni=1:1 were mixed in acetate acid and deion water (CH₃COOH and H₂O with a volume ratio of 5:1) at 105 °C for 1 h. The concentration of the final LNO precursor solution was 0.1 M. The solution was spin coated on Pt/Ti/SiO₂/Si substrates at 3000 rpm for 20 s. Then the wet films were heat treated at 450 °C for 20 min. This procedure was repeated 15 times. Finally, the LNO films were annealed at 700 °C for 1 h to obtain a well-crystallized structure. The final thickness of the LNO was about 150 nm.

(Pb_{0.97}La_{0.02})(Zr_{0.87}Sn_{0.10}Ti_{0.03})O₃ (PLZST 2/87/10/3) AFE thin films were prepared by the sol-gel method from raw materials lead acetate trihydrate [Pb(CH₃COO)₂ · 3H₂O], lanthanum acetate [La(CH₃COO)₃], zirconium propoxide [Zr(OC₃H₇)₄], titanium isopropoxide [Ti[OCH(CH₃)₂]₄] and tin acetate [Sn(CH₃COO)₄]. Acetate was selected as a solvent. At first, lead acetate trihydrate, tin acetate, lanthanum acetate hydrate and acetic acid were mixed in a ratio according to the predetermined number. In order to compensate the lead loss during annealing and to prevent the formation of a pyrochlore phase, 10% excess lead were added. The mixed solution was distilled at 110 °C for 1 h to remove water. When the mixed solution was cooled to room temperature, zirconium propoxide and titanium isopropoxide were added in turn and mixed for 30 min. During the mixing process distilled water was added in the proportion of 20 ml of distilled water to 1 ml of lead to stabilize the solution. Finally, the solution was adjusted to 0.3 M using acetic acid and small amount of 2-methoxyethanol. The addition of 2-methoxyethanol lowered the surface tension of the solution and could improve the wettability of the solution. Then PLZST 2/87/10/3 films were grown on LNO-buffered Pt(111)/Ti/SiO₂/Si and Pt(111)/Ti/SiO₂/Si substrates also by the spin-coating method. Each PLZST 2/87/10/3 layer was spin coated at 3000 rpm for 20 s and pyrolyzed at 450 °C for 10 min. The spin coating and heat treatment were repeated several times to obtain the desired thickness. A capping layer consisting of 0.4 M PbO precursor solution, which was prepared from lead acetate trihydrate, was added before the films went through a final anneal at 700 °C for 30 min to form the perovskite phase. This capping layer served the purpose of preventing excessive lead loss and ensuring the formation of a pure perovskite phase of PLZST 2/87/10/3. More detailed fabricated process can be found in Ref. [8,11]. The final thickness of the PLZST 2/87/10/3 thin films was about 580 nm. Gold pads of 0.5 mm in diameter were coated on the film surface as top electrodes by dc sputtering for the measurements of electrical properties.

The X-ray diffraction (XRD) patterns of LNO and PLZST 2/87/10/3 films on the different bottom electrodes were obtained using a Bruker D8 advance diffractometer. The microstructure of the PLZST 2/87/10/3 films was examined through scanning electron microscopy (SEM). The field-induced hysteresis loops of the PLZST 2/87/10/3 thin films were measured by a Sawyer–Tower circuit. The temperature, frequency and dc electric field-dependent dielectric properties of the AFE films were investigated using an Agilent 4284A LCR meter. The current-field (*J*–*E*) characters of the films were tested by a Keithley 6517A electrometer at room temperature.

3. Results and discussion

Fig. 1 presents the XRD patterns of LNO layers and PLZST 2/87/10/3 AFE thin films on Pt(111)/Ti/SiO₂/Si and LNO-buffered Pt(111)/Ti/SiO₂/Si substrates, respectively. The LNO films deposited on Pt(111)/Ti/SiO₂/Si substrates show a (110)-preferred orientation with a very weak crystallization intensity. From the XRD results, it can be considered that PLZST 2/87/10/3 films on Pt(111)/Ti/SiO₂/Si substrates have a (111)-preferred orientation, since (111) peak is the strongest one. However, films on LNO-buffered substrates display a (110)-preferred orientation and (111) peak is undetected. In order to estimate the orientation degree of the PLZST films on the two kinds of substrates, orientation factor, $\alpha_{(100)}$ and $\alpha_{(110)}$, are given according to the following well-known formulas:

$$\alpha_{(100)} = \frac{I_{(100)}}{I_{(100)} + I_{(110)} + I_{(111)}}$$

$$\alpha_{(110)} = \frac{I_{(110)}}{I_{(100)} + I_{(110)} + I_{(111)}}$$

The calculated values of $\alpha_{(100)}$ and $\alpha_{(110)}$ are 0.85 and 0.73 for PLZST films on Pt(111)/Ti/SiO₂/Si and LNO/Pt(111)/Ti/SiO₂/Si substrates, respectively. The (111)-preferred orientation of PLZST 2/87/10/3 films can be explained by the formation of a transient intermetallic phase Pt₃Pb at the interface between PLZST 2/87/10/3 films and Pt(111)/Ti/SiO₂/Si substrates during heat treatment [13]. Pt₃Pb with preferred-(111) orientation function as a

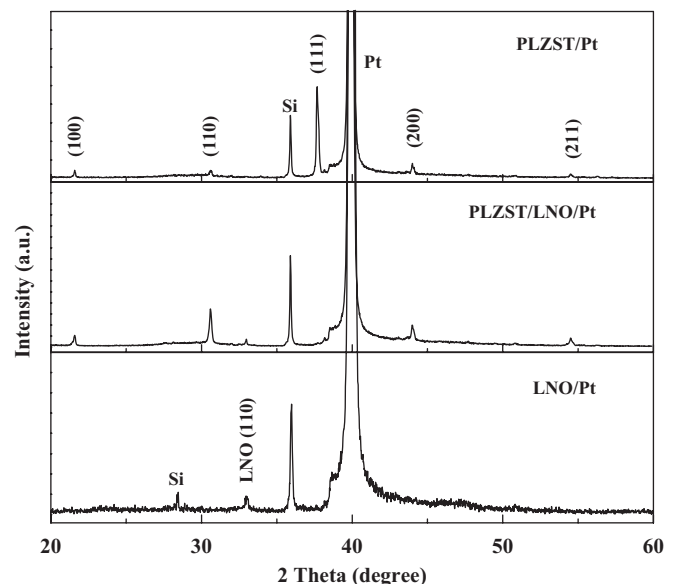


Fig. 1. XRD patterns of the LNO buffer layer and PLZST 2/87/10/3 thin films grown on Pt(111)/Ti/SiO₂/Si(100) and LNO/Pt(111)/Ti/SiO₂/Si substrates.

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