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The electrical properties and phase transformation of PLZST 2/85/13/2 antiferroelectric thin films on different bottom electrode

Xihong Hao, Jiwei Zhai*, Xiujian Chou, Xi Yao

Functional Materials Research Laboratory, Tongji University, Siping Road 1239, Shanghai 200092, China

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Abstract

$Pb_{0.97}La_{0.02}(Zr_{0.85}Sn_{0.13}Ti_{0.02})O_3$ (PLZST 2/85/13/2) antiferroelectric thin films were deposited on Pt(111)/Ti/SiO_2/Si and $LaNiO_3$(LNO)/SiO_2/Si substrates through a modified sol–gel process. The phase structure and microstructure of PLZST 2/85/13/2 antiferroelectric thin films were analysed by x-ray diffraction (XRD), scanning electron microcopy (SEM) and field-emission SEM (FE-SEM). The antiferroelectric nature of the PLZST 2/85/13/2 thin films on two electrodes was demonstrated by the C–V (capacitance–voltage) and P–E (polarization–electric field) measurement. The maximum polarizations for PLZST 2/85/13/2 films on Pt and LNO electrodes were 42 and 18 $\mu C/cm^2$, respectively. The temperature dependence of the dielectric property of the PLZST 2/85/13/2 films was measured under different dc electric fields. Also, the phase transformation of the PLZST 2/85/13/2 films was studied in detail as a function of temperature and dc electric field.

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1. Introduction

In the past decade, (Pb, La)(Zr, Sn, Ti)O_3 (PLZST), and (Pb, Nb)(Zr, Sn, Ti)O_3 (PNZST) thin films with antiferroelectric composition have been studied extensively for their potential use in microactuators and high-energy storage capacitors, because of the small free energy and large electric-field-induced strain between antiferroelectric (AFE) and ferroelectric (FE) phase under a sufficient field. Most of the previous studies on PLZST and PNZST were mainly concentrated on Pt/Ti/SiO_2/Si and $LaNiO_3$ (LNO) buffered Pt/Ti/SiO_2/Si substrates [1–3]. The introduction of a perovskite LNO buffer layer has efficiently improved the electric properties, such as the fatigue property. At the same time, an LNO layer can also lower the crystal temperature because the perovskite LNO with the lattice parameters of 0.384 nm has good structure match with most of perovskite ferroelectric materials [4]. In addition, the resistance of LNO is isotropic and low (~225 μΩ cm at room temperature), which is suitable for use as a bottom electrode directly. In fact, there have been a few papers on ferroelectric thin films, such as PLT [5] and PZT [6], grown on LNO-buffered Si (100) and SiO_2/Si substrates. However, to the best of our knowledge, there have been few reports on antiferroelectric thin films with LNO/SiO_2/Si substrates.

In the present investigation, the effect of LNO and Pt on the bottom electrode on the electric properties and phase transformation of PLZST antiferroelectric thin films was studied. LNO thin films were first fabricated on SiO_2/Si substrates via the metal-organic chemical liquid deposition method (MOCLD). Then, for the first time, a novel and cheap tin source, dibutyloxide of tin [$(H_9C_4)_2SnO$], was selected as a raw material to prepare PLZST 2/85/13/2 antiferroelectric thin films. In contrast to previous extensive reports [7,8], the composition of $Pb_{0.97}La_{0.02}(Zr_{0.85}Sn_{0.13}Ti_{0.02})O_3$ was chosen for study, which was far away from the morphotropic phase boundary (MPB) in the PLZST triaxial phase diagram. The PLZST 2/85/13/2 antiferroelectric thin films were deposited on the Pt(111)/Ti/SiO_2/Si and LNO-buffered SiO_2/Si substrates through the sol–gel process. The dielectric properties and phase

* Corresponding author. Tel.: +86 21 65980544.
E-mail address: apzhai@mail.tongji.edu.cn (J. Zhai).

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transformation of the PLZST 2/85/13/2 thin films with Pt and LNO bottom electrodes were studied in detail as a function of frequency, electric field and temperature.

2. Experimental procedure

The preparation of LNO films took the same procedure as the literature [6], and the starting materials were lanthanum acetate [$La(CH_3COO)_3$] and nickel acetate [$Ni(CH_3COO)_3 \cdot 4H_2O$]. The starting materials were mixed with a mole ratio of La:Ni=1:1 in acetate acid and deionized water (CH_3COOH and H_2O with a volume ratio of 5:1) at 105 °C for 1 h. The concentration of the LNO precursor solution was 0.1 M. The solution was spin-coated on SiO_2/Si substrates at 3000 rpm for 20 s. The thickness of SiO_2 was about 400 nm. 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 650 °C for 1 h to obtain a well-crystallized structure. The thickness of the LNO was about 150 nm.

$Pb_{0.97}La_{0.02}(Zr_{0.85}Sn_{0.13}Ti_{0.02})O_3$ (PLZST 2/85/13/2) anti ferroelectric thin films were prepared from raw materials lead acetate trihydrate [$Pb(CH_3COO)_2 \cdot 3H_2O$], lanthanum acetate [$La(CH_3COO)_3$], zirconium propoxide [$Zr(OC_3H_7)_4$], titanium isopropoxide [$Ti[OCH(CH_3)_2]_4$ and dibutyloxide of tin [$(H_9C_4)_2SnO$]. Acetate was selected as a solvent. At first, lead acetate trihydrate (with 10% excess in order to compensate Pb loss during annealing and prevent the formation of the pyrochloren phase), dibutyloxide of tin, lanthanum acetate hydrate, and acetic acid were mixed in a ratio according to a predetermined number. 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 and mixed for 30 min. During the mixing process, distilled water was added in the proportion of 20 M of distilled water to 1 M of lead to stabilize the solution. Finally, the solution was adjusted to 0.2 M using the propanol. The addition of propanol lowered the surface tension of the solution and could improve the wettability of the solution. Then PLZST 2/85/13/2 films were grown on LNO-buffered SiO_2/Si and Pt/Ti/SiO_2/Si substrates also using the spin-coating method. The thicknesses of Pt, Ti and SiO_2 were 260, 30 and 540 nm, respectively. Each PLZST 2/85/13/2 layer for both substrates 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. At last, the films went through a final anneal at 650 °C and 700 °C for 30 min for the LNO and Pt bottom electrodes, respectively, to form the perovskite phase. The final thickness of the PLZST 2/85/13/2 thin films was about 350 nm. Gold pads of 0.50 mm in diameter were coated on the film surface by dc sputtering as top electrodes.

The x-ray diffraction (XRD) patterns of the PLZST 2/85/13/2 films on the different bottom electrodes were obtained using a Bruker D8 advance diffractometer. The microstructure and the surface component of the PLZST 2/85/13/2 films were examined through scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The grain size of the PLZST 2/85/13/2 films was observed through field-emission scanning electron microscopy (FE-SEM). The field-induced hysteresis loops of the PLZST 2/85/13/2 thin films were measured by a modified Sawyer–Tower circuit. The temperature, frequency and dc electric field dependent of the dielectric properties of the antiferroelectirc films were measured using an Agilent 4284A *LCR* meter.

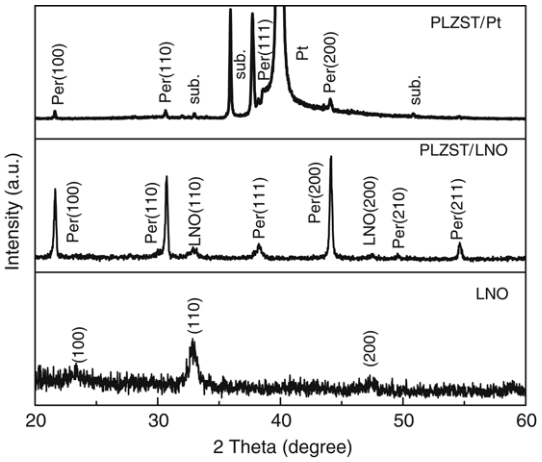

Fig. 1. XRD patterns of PLZST 2/85/13/2 thin films grown on LNO/SiO_2/Si and Pt(111)/Ti/SiO_2/Si substrates, annealed at 650 °C and 700 °C for 30 min, respectively.

3. Results and discussion

XRD patterns taken at room temperature from PLZST 2/85/13/2 thin films on Pt and LNO bottom electrodes and from LNO on SiO_2/Si substrate are shown in Fig. 1. The results show that PLZST 2/85/13/2 films on Pt and LNO bottom electrodes after being annealed at 700 °C and 650 °C for 30 min, respectively, had crystallized well and displayed a better perovskite structure. It was clearly seen that PLZST 2/85/13/2 films on Pt (111)/Ti/SiO_2/Si substrates had a preferred (111) orientation, but films on LNO/SiO_2/Si substrates showed a polycrystalline structure without any obvious preferred orientation. The (111)-preferred orientation of PLZST 2/85/13/2 films can be explained by the formation of Pt_3Pb at the interface of PLZST 2/85/13/2 films and Pt(111)/Ti/SiO_2/Si substrates [9]. The proposed nucleation mechanism of Pb-based (111)-oriented thin films prepared by the sol–gel process on Pt/Ti/SiO_2/Si substrates was the formation of a (111)-oriented transient intermetallic phase Pt_3Pb. This transient intermetallic phase took the role of a seed layer and decreased the activation energy for crystallization of the PLZST 2/85/13/2 films. Thereafter the antiferroelectric thin films were induced to grow along the (111) direction during the heat-treatment process and a strong (111) texture developed. The random orientation PLZST 2/85/13/2 films on LNO/SiO_2/Si substrates were closely connected to the orientation of the LNO layer. It can be found that the strongest peaks (100), (110) and (200) of PLZST 2/85/13/2 films correspond to the only three peak appearing in the LNO films.