Effect of bottom electrodes on polarization switching and energy storage properties in Pb$_{0.97}$La$_{0.02}$(Zr$_{0.95}$Ti$_{0.05}$)O$_3$ antiferroelectric thin films

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**Abstract**

Polarization switching and energy storage properties of a series of Pb$_{0.97}$La$_{0.02}$(Zr$_{0.95}$Ti$_{0.05}$)O$_3$ (PLZT) thin films deposited on (100)-textured LaNiO$_3$ (LNO)-buffered Si substrates and (111)-textured Pt/Ti/SiO$_2$/Si substrates were investigated. It was revealed that the PLZT films deposited on the (100)-textured LNO-buffered Si substrates prefer the (100) textured structure, while the orientation of the films deposited on the (111)-textured Pt-coated Si substrates is random. With respect to the films on the Pt-coated Si substrates, the (100) textured PLZT films have bigger compressive residual stress, larger electrical polarization, better dielectric properties, and better energy storage performances. For the (100)-oriented PLZT films, the energy density ($W$) and efficiency ($\eta$) measured at room temperature are about 15.3 J/cm$^3$ and 56% respectively. Moreover, the better frequency stability in the range from 20 Hz to 10 kHz, and temperature stability in the range from 25 to 270 °C are demonstrated in the (100)-oriented PLZT films. These results indicate that the PLZT films with LNO bottom electrode could be potential candidate for applications in high energy storage density capacitors.

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**1. Introduction**

Antiferroelectric (AFE) materials with the electric field induced antiferroelectric-to-ferroelectric phase switching have received considerable attentions due to the promising candidates for future high-energy and fast-speed storage capacitors [1–3]. Among this family, the lead lanthanum zirconate titanate (PLZT) materials exhibiting high dielectric constant and low energy loss have been extensively studied. The AFE PLZT is the solid solution with La substitution at Pb site of lead zirconate titanate (PZT) ferroelectric (FE) materials. Depending on the compositions, various phases, typically including orthorhombic antiferroelectric (AFE), rhombohedral or tetragonal FE, and paraelectric (PE), can be obtained in PLZT solid solutions [4,5]. Currently, many research groups have reported the energy storage performances of PLZT dielectrics by modifying compositions, [6,7] and using different substrates, buffered layers, [8] and top/bottom electrodes [9,10]. For example, Hao et al. [11] reported a high recoverable energy density of $\sim$28.7 J/cm$^2$ (under maximal electric field $E_{\text{max}}$ $\sim$ 2 MV/cm) and an energy efficiency of $\sim$ 60% in (Pb$_{0.92}$La$_{0.08}$)(Zr$_{0.65}$Ti$_{0.35}$)O$_3$ films deposited on Pt coated Si substrates. Tong et al. [8] studied (Pb$_{0.92}$La$_{0.08}$)(Zr$_{0.55}$Ti$_{0.48}$)O$_3$ ceramic films grown on LaNiO$_3$ buffered Ni substrates, and reported a high recoverable electric energy ($\sim$ 22 J/cm$^2$ at $E_{\text{max}}$ $\sim$ 2 MV/cm) and an energy efficiency of $\sim$ 77%. In these works, one key factor affecting the polarization and energy storage performances is the bottom electrode, which chemically interacts with the AFE PLZT [12]. Generally, Pt bottom electrode is adopted in most of the previous studies on the antiferroelectric films. However, Pt layer as the bottom electrode could deteriorate ferroelectric properties by the interdiffusion with the interposed adhesion layer of Ti on the substrate [13]. LaNiO$_3$ conductive oxide layers as electrodes were the excellent alternatives for solving this problem because it has an acceptable resistivity and the same perovskite structure as many ferroelectric and antiferroelectric materials with small lattice mismatch so that it can be suitable for an effective interface layer for the growth of highly textured and smooth thin films [9]. Furthermore, temperature and frequency responses of polarization switching are also important for the device applications. Currently, study on the temperature and frequency dependent energy storage properties is still limited.

Under this motivation, we adopted Pb$_{0.97}$La$_{0.02}$(Zr$_{0.95}$Ti$_{0.05}$)O$_3$ with 2 mol% La-doping since La concentration of 2 mol%...
destabilizes the original FE state of PLZT and favors an incommensurate AFE state [14]. The conductive LaNiO$_2$ and Pt films were chosen as the bottom electrodes and coated on Si substrates. In this study, the effects of the bottom electrodes on orientation, microstructure, polarization, and dielectric properties of the PLZT thin films are reported. Finally, we place special emphasis on the frequency- and temperature-dependent polarization, dielectric, and energy storage properties of the PLZT thin films.

2. Experimental procedure

The Pb$_{0.97}$La$_{0.02}$(Zr$_{0.95}$Ti$_{0.05}$)O$_3$ (PLZT) AFE thin films were deposited on (100)-textured LaNiO$_3$ (LNO)-buffered Si substrates and (111)-textured Pt/Ti/SiO$_2$/Si substrates via a chemical solution deposition method. The conductive LNO-buffered layers with thickness of 150 nm were coated on Si substrate by a simple sol-gel method. The detailed deposition conditions can be found elsewhere [15]. PLZT precursor solutions with excess Pb-acetate 10 mol% were prepared by dissolving appropriate amount of lead acetate trihydrate [Pb(CH$_3$COO)$_2$·3H$_2$O], lanthanum acetate [La(CH$_3$COO)$_3$·H$_2$O], zirconium propoxide [Zr(OCH(CH$_3$)$_2$)$_4$], titanium iso-propoxide [Ti(OCH(CH$_3$)$_2$)$_4$] into 2-methoxyethanol (all agents from Aladdin). After that the solution was passed through a filter and spin-coated on the LNO- and Pt-buffered Si substrates at 4000 rpm for 30 s to ensure the film uniformity. For each coating cycle, the sample was pyrolyzed at 450 °C for 10 min in air. This process was repeated several times to reach the expected film thickness of ~200 nm. Finally, the as-prepared thin films were introduced to a rapid thermal annealing process at ~700 °C for 10 min at oxygen atmosphere to crystallize into perovskite structure.

For electric measurements, top Au electrodes with a 200 μm in diameter were deposited by a rf-sputtering (Model: SBC-12, China) through a shadow mask. The crystallization characteristics of the PLZT films were characterized by an X-ray diffractometer (XRD) with CuKα radiation (PANalytical X’Pert PRO). Surface microstructures of the films were observed using an atomic force microscope (AFM) (Cypher, Asylum Research). Temperature-dependent dielectric properties of the films were examined by an Agilent 4980A LCR analyzer with the ac drive amplitude of 100 mV at 1 kHz. To evaluate energy storage performances of the films, temperature- and frequency-dependent electric field-induced polarization (P–E) hysteresis loops of the films were measured using a Radiant ferroelectric testing system (Multiferroics, Radiant Company). The temperature was changed from room temperature to 463 K with the ac applied electric field of 1 MV/cm at 1 kHz, and the frequency was altered from 1 Hz to 100 kHz at 1 MV/cm.

3. Results and discussion

Fig. 1 shows the XRD patterns of the two representative PLZT films deposited on LaNiO$_3$ (LNO)-buffered and Pt-coated Si substrates respectively. All the peaks of the two films are indexed according to the pseudo-cubic structure, indicating that the PLZT films are pure perovskite phase without any second peaks such as parasitic pyrochlore phase. It is noted that the PLZT/LNO films exhibit a (100)-textured structure because the two strongest peaks are (100) and (200). Actually, the textured property can be determined by comparing the relative intensities of the family of planes (100) with the cumulative intensities of all the peaks in the PLZT films. The ratio in the PLZT/LNO films is up to 83.3%, while it is only 62.1% in PLZT/Pt films. The (100) texture in the PLZT/LNO films can be explained by two reasons. One is that the LNO-buffered Si substrate itself presents a preferential (100) texture to some extent [not shown here]. Other is that the oxide LNO bottom electrode exhibiting a perovskite structure provides good compatibility in structure and lattice matching with the PLZT films than the metal Pt bottom electrode [16,17].

When comparing with the XRD patterns of the two films, the peaks of (100)/(200) and (110) in PLZT/LNO films show slight shift towards lower 20 angle related to that of PLZT/Pt films. Note that an expansion of d-spacing in the out-of-plane direction appears, which is a result of compressive strain in-plane direction that is parallel to the substrate surface [18]. Consider that the two PLZT films are deposited using the same deposited conditions, the intrinsic and transformation stress can be treated as the same for all samples [19]. Therefore, the compressive stress exhibited in PLZT/LNO films could be originated from the lattice mismatch between LNO (3.81 Å [20]) and PLZT (4.078 Å [5] in a pseudo-cubic).

The surface morphologies of the two PLZT films observed from AFM imaging are shown in Fig. 2. Clearly, the PLZT film with the Pt bottom electrode exhibits homogeneous surface morphology, while the surface of PLZT film with the LNO bottom electrode represents microstructure consisting of small grains and coarse grains. Such a non-uniform texture in PLZT/LNO films can be ascribed to the non-uniform LNO layer, as reported in previous published papers [17]. The average grain size in PLZT/LNO films is ~25 nm which is slightly smaller than that with the Pt bottom electrode (~30 nm).

The polarization–electric field (P–E) curves of the PLZT films on the two substrates measured at 1 MV/cm and 1 kHz are given in Fig. 3. The double loops and nearly zero remnant polarization demonstrate the antiferroelectric nature of PLZT films. Moreover, the electric field-induced switching between the AFE and FE states is clear for the two films. The forward (AFE-to-FE) phase switching field ($E_F$) and backward (FE-to-AFE) phase switching field ($E_A$) can be determined by a drastic increase and decrease in polarization, respectively. The values of $E_F$ and $E_A$, respectively, are 566 kV/cm and 365 kV/cm for the PLZT with the LNO bottom electrode, which are larger than those with the Pt bottom electrode (410 kV/cm and 230 kV/cm, respectively). Interestingly, the saturation polarization $P_s$ of PLZT/LNO films is ~44.8 μC/cm$^2$ (measured at 1 MV/cm), which is much larger than that of PLZT/Pt films (~31.6 μC/cm$^2$). Oppositely, the remnant polarization $P_r$ of the former is smaller than that of the latter. Lee et al. revealed that the saturation polarizations increase with an increase in the in-plane compressive stress, which is beneficial to dipole alignment along the out-of-plane direction that is parallel to the applied field [21]. Therefore, the significantly enhanced ferroelectric polarization in the PLZT/LNO films can be attributed to the higher compressive stress, textured structure and better interface.
To clarify the effect of bottom electrode on the observed macroscopic dielectric behavior, we measured the dielectric properties at different temperatures. Fig. 4 displays the dielectric permittivity ($\varepsilon_r$) and loss tangent ($\tan \delta$) of the two PLZT films deposited on the LNO and Pt bottom electrodes. In the PLZT/LNO films, the $\varepsilon_r$ value is calculated by the numerical integration of the area $\delta$ value is calculated according to the formula: $\eta = W_s/(W_s + W_{loss})$. Where $W_{loss}$ is the energy loss density calculated by the numerical integration of closed area of the hysteresis loops. Note that $W_s$ of PLZT films in most reported works is greatly dependent upon the operating electric field [10]. Our results in Fig. 5 are calculated at 1 MV/cm, and the valuated value of $W_s$ at room temperature is about 15.3 J/cm$^3$ for PLZT/LNO films, which is larger than that of PLZT/Pt films ($\sim$ 6.8 J/cm$^3$). With increasing temperature, the $W_s$ value for the PLZT/LNO films decreases gradually to $\sim$ 8.7 J/cm$^3$ at 463 K, but is always larger than that of PLZT/Pt films over the whole temperature range. Moreover, the $\eta$ in the PLZT/LNO films is almost constant ($\sim$ 56%) from 298 K to 443 K. In contrast, the $\eta$ in PLZT/Pt film is relatively low ($\sim$ 42%). It is worth noting that some sudden jumps of energy storage performances in the higher temperature may be owing to the leakage affiliated with the switching current, as the gap between the start and end point of the P-E loops decreases with increasing temperature. It can be concluded from our results that the PLZT films deposited on the LNO bottom electrodes possess higher energy storage performances and better temperature stability in $\eta$. 

**Fig. 2.** AFM images of PLZT films on (a) LNO-, and (b) Pt-buffered Si substrates.

**Fig. 3.** Room temperature polarization–electric field ($P$–$E$) hysteresis loops measured at 1 kHz for PLZT thin films deposited on the LNO and Pt bottom electrodes.

**Fig. 4.** Dielectric constant ($\varepsilon_r$) and loss tangent ($\tan \delta$) as functions of temperature for PLZT films. Insets show the representative $P$–$E$ loops at selected temperatures. In the $P$–$E$ loop insets, x-axis units are in kV/cm, and y-axis units are in $\mu$C/cm$^2$. 

As to temperature-dependent energy storage performances, we measured $P$–$E$ loops of the two PLZT films at 1 MV/cm and at different temperatures. The insets in Fig. 4 show several representative $P$–$E$ loops at selected temperatures. With increasing temperature, the measured $E_p$ and $E_A$ values gradually decrease, implying that the AFE domain energy recedes and its state becomes more and more unstable. At higher temperature, electric dipoles with a certain degree of freedom overcome the disorder state due to the thermal motion and turn to the uniform direction. Thus, the double hysteresis behavior becomes less pronounced with increasing temperature and eventually transforms into a similar ferroelectric hysteresis loop.
within the time scale of $10^{-4}$ s, and the low domain switching speed may be attributed to the pinning effect of the electric dipoles in the films [27].

4. Conclusions

In summary, we have grown (100)-textured and nearly random oriented PLZT films on LaNiO$_3$/Si and Pt/Ti/Si$_3$O$_3$/Si substrates respectively by sol–gel processing. It was observed that the (100)-textured PLZT films have a large compressive residual stress and exhibit enhanced critical electric fields $E_c$ and $E_a$, as well as electrical polarization, in comparison with those on Pt-coated Si substrates. An energy storage density of 15.3 J/cm$^3$ and an efficiency of 56% were achieved in the (100)-textured PLZT films. Moreover, the (100)-textured PLZT films also showed better energy storage stability in the temperature range from 25 to 270 $^\circ$C and in the frequency range from 20 Hz to 10 kHz. These results suggest that the PLZT AFE films with LNO bottom electrode have a potential for application in pulsed power electronic systems.

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