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Relaxor behavior and energy storage performance of ferroelectric PLZT thin films with different Zr/Ti ratios ☆

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Abstract

Ferroelectric lead lanthanum zirconate titanate (PLZT) films with 8 mol% lanthanum and different Zr/Ti ratios (70/30, 65/35, 58/42, 52/48, 45/55, and 40/60) have been grown on platinized silicon substrates by chemical solution deposition. The effects of the Zr/Ti ratios on the dielectric and ferroelectric properties were investigated for high-power energy storage applications. These films exhibited relaxor behavior and slim polarization–electric field hysteresis loops, and the degree of phase transition diffuseness decreased with increasing Ti. The PLZT films with Zr/Ti = 52/48 had a high spontaneous polarization of ≈51.2 μC/cm^2, a low remanent polarization of ≈9.1 μC/cm^2, and a low coercive electric field of ≈25.9 kV/cm, leading to a recoverable energy density of ≈30 J/cm^3 and a charge–discharge efficiency of ≈78% at room temperature. The high energy density and high efficiency indicate that relaxor PLZT with La/Zr/Ti = 8/52/48 is a promising candidate for high-power film capacitors.

Keywords: A. Sol–gel processes; C. Ferroelectric properties; D. PLZT; E. Capacitors

1. Introduction

Ceramic film capacitors have recently attracted considerable interest for short-term energy storage in renewable energy systems such as wind turbines and electric vehicles, due to their high dielectric constant and reliability compared to polymer and electrolyte capacitors [1–6]. The ceramic materials used for capacitors can be paraelectric (linear dielectric), normal ferroelectric, antiferroelectric, or relaxor ferroelectric [3–8]. In a capacitor, when the electric field E increases from zero to the maximum E_m, the polarization P increases to P_m, and electric energy is stored in the capacitor. The energy stored per unit volume is defined by $U_{st} = \int_0^{P_m} E\,dP$. As the electric field decreases from E_m to zero, the stored energy is released on discharge from P_m to remanent polarization P_r. The recoverable electric energy density U_{re} is then represented as $U_{re} = \int_{P_r}^{P_m} E\,dP$. The charge–discharge efficiency η can then be calculated by $\eta = (U_{re}/U_{st}) \times 100\%$. To minimize the size and weight of capacitors, ceramic films with high U_{re} and high η are required. From the polarization–electric field (P–E) hysteresis loops of ceramic materials, it is clear that lower P_r and higher P_m lead to higher recoverable energy density at fixed E_m. One can also conclude that linear dielectrics exhibit the highest efficiency for energy storage because of their low energy loss ($U_{st} \approx U_{re}$); however, the low P_m in linear dielectrics depresses the energy density [9–11]. Normal ferroelectrics exhibit relatively high P_r and large coercive electric field (E_c), leading to low energy density and efficiency [10]. Antiferroelectrics have low P_r and E_c but also wide hysteresis loops, contributing to large energy loss [12–16]. In contrast, relaxor ferroelectrics exhibit slim P–E hysteresis loops with high P_m and low P_r and E_c, implying higher energy storage density and better energy conversion efficiency [8].

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Lead lanthanum zirconate titanate (PLZT) films are considered as one of the most promising candidates for high-power energy storage [12]. Generally, when PLZT has a high concentration of lanthanum (≥7 mol%), the c/a ratio of the unit cell decreases to near unity, approaching a pseudocubic structure. This condition leads to relaxor behavior and slim *P–E* hysteresis loops [7,8]. Several research groups have reported investigations on PLZT-based relaxor ferroelectrics for energy storage applications [17–21]. Sigman et al. reported a recoverable energy density of ≈22 J/cm^3 in PLZT (12/70/30) thin films deposited on platinized silicon (PtSi) [19]. Kim et al. observed a high capacitance density of ≈2.4 μF/cm^2 in PLZT (7/62/38) thin films deposited on nickel with a lanthanum nickel oxide buffer (LNO/Ni) [20]. Hao et al. studied PLZT (9/65/35) films on PtSi and reported a high recoverable energy density of ≈28.7 J/cm^3 and an energy efficiency of ≈60% [21]. Recently, PLZT (8/52/48) films have received increasing interest due to their excellent ferroelectric and dielectric properties and high Curie temperature [6,13,22]. Energy-storage densities of ≈13 and 45 J/cm^3 have been reported in PLZT (8/52/48) films deposited on PtSi and LNO/Ni, respectively [10,13]. These reports demonstrated the possibility of using PLZT relaxor ferroelectrics for high-power energy storage. However, the relationship between the composition and the energy storage capability has not been studied in relaxor PLZT. In this work, we systematically investigated the effects of the Zr/Ti ratio on the relaxor behavior and energy storage performance of PLZT film capacitors grown on PtSi.

2. Experimental procedures

PLZT precursor solutions (0.5 M) with various Zr/Ti ratios (Zr/Ti=70/30, 65/35, 58/42, 52/48, 45/55, and 40/60) were prepared by a modified 2-methoxyethanol synthesis route. In the solutions, 8 mol% lanthanum was added to enhance the relaxor behavior and insulating property [2]. The starting chemicals were lead acetate trihydrate, lanthanum nitrate hexahydrate, zirconium propoxide, and titanium isopropoxide. Excess lead (20 mol%) was used to compensate for the lead loss during the high temperature crystallization. Detailed solution synthesis conditions can be found in our prior report [6]. The PLZT films were grown by spin coating the solution on PtSi substrates at 3000 rpm for 30 s. Each layer was pyrolyzed at 450 °C for 10 min before being annealed at 650 °C for 5 min. An additional annealing at 650 °C for 5 min was applied after every three layers of coating. A final crystallization anneal was performed at 650 °C for 15 min. The thickness of the PLZT films with six layers of coating was ≈690 nm, resulting in a per-coating thickness of ≈115 nm. Platinum top electrodes with a diameter of 250 μm and a thickness of 100 nm were deposited on the prepared samples through a shadow mask by electron-beam evaporation.

Phase identification was carried out by analysis using a Bruker D8 AXS diffractometer with General Area Detector Diffraction System. A Signatone QuieTemp® probe station with heatable vacuum chuck (Lucas Signatone Corp., Gilroy, CA) was used for electrical characterization. Dielectric permittivity and loss were measured as a function of temperature (25–300 °C), frequency (1–1000 kHz), and bias field with an Agilent E4980A LCR meter using an oscillation signal of 0.1 V. Ferroelectric hysteresis loops were measured by a Precision Premier II ferroelectric test system (Radiant Technologies).

3. Results and discussion

X-ray diffraction (XRD) patterns of the PLZT films are shown in Fig. 1. All the diffraction patterns show only well-crystallized polycrystalline perovskite phases, together with PtSi substrate, and can be well indexed by a pseudocubic structure. No other phases were detected, suggesting that neither pyrochlore phases nor interfacial reactions affected the structure. The peak position shifted toward higher angle with increasing Ti, as shown in Fig. 1(b), implying a gradual lattice distortion within the pseudocubic structure due to the variation of Zr/Ti ratios. Fig. 1(c) shows that the lattice parameter *a* decreases with increasing Ti, similar to that of bulk PLZT [23]. In the phase diagram of bulk PLZT, the

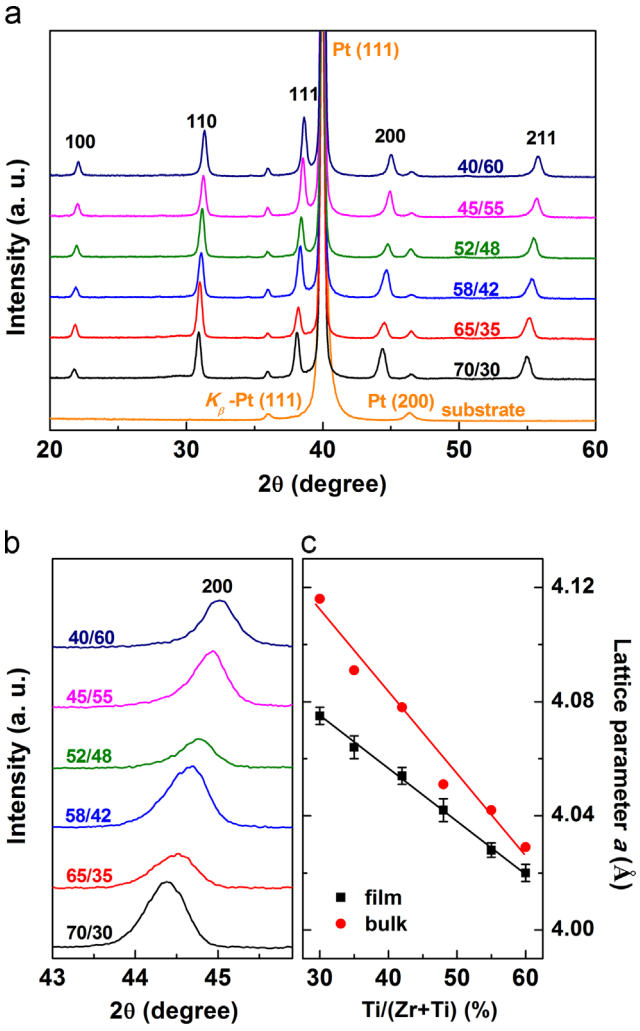

Fig. 1. (a) XRD pattern of PLZT films with different Zr/Ti ratios; (b) magnified XRD patterns in the vicinity of $2\theta=44°$; and (c) lattice parameter *a* of PLZT films calculated from the diffraction patterns as a function of Ti content (bulk values are from Ref. [23]).