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Electrical and pyroelectric properties of in-plane polarized lead lanthanum titanate thin film

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$Pb_{0.9}La_{0.1}Ti_{0.975}O_3$ (PLT10) thin films were deposited on SiO_2/Si(100) substrates coated with a ZrO_2 buffer layer. Studies by x-ray diffraction and scanning electron microscopy reveal that the ZrO_2 film consists of both tetragonal and monoclinic phases, with the tetragonal phase being the dominant one. The PLT10 film has a perovskite structure and the grains in the film have a rather uniform size of about 50 nm. By using interdigital transducer (IDT) electrodes the in-plane electrical properties, hysteresis loop, and pyroelectric coefficient of the PLT10 film were measured. The dielectric constant and loss factor vary only slightly with frequency in the range 10^3-10^6 Hz, with the loss factor being less than 0.01 over the entire range. The leakage current density is lower than 2×10^{-8} A/cm^2 at a bias field of 5 kV/cm. The remnant polarization and coercive field are 12.6 μC/cm^2 and 9.93 kV/cm, respectively. The film exhibits a reasonably high pyroelectric coefficient (95 μC/m^2 K) after it has been poled by applying 120 V ac at 0.1 Hz across the IDT electrodes. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1387265]

Lanthanum-modified lead titanate [$Pb_{1-x}La_xTi_{1-x/4}O_3$, PLTX] thin films have attracted considerable attention because of their good pyroelectric and piezoelectric properties.[1–4] These films have potential applications in a variety of devices including nonvolatile memories, optical switches, and infrared detectors.[5,6]

Lead zirconate titanate (PZT) films were successfully deposited on ZrO_2-passivated silicon substrates and were poled parallel to the film surface to give in-plane polarization.[7] Micromachined ultrasound arrays based on in-plane polarized PZT films showed a 30 dB improvement in sensitivity.[8] In this work, PLT10 thin films were deposited on silicon substrates coated with ZrO_2 buffer layers. We investigated the in-plane electrical and pyroelectric properties of the PLT10 thin films by using interdigital transducer (IDT) electrodes. The films were found to exhibit good dielectric, ferroelectric, and pyroelectric properties in this in-plane configuration.

The ZrO_2 buffer layer and PLT10 thin film were prepared by the metal–organic decomposition (MOD) method. A precise control of the solution concentration was important to produce high-quality, smooth, and crack-free films. To prepare the ZrO_2 solution, zirconium *n*-propoxide was added to distilled 2-methoxyethanol; the mixture was stirred at 120 °C for 1 hr until the associated water was removed. After cooling to room temperature, the solution was filtered and a suitable amount of 2-methoxyethanol was added so as to give a concentration of 0.3 M. The raw materials for preparing PLT10 thin films were lead acetate trihydrate, lanthanum nitrate, and titanium isopropoxide. 2-methoxyethanol was used as the solvent. The preparation procedure of the metal-alkoxide precursor solution has been described in detail elsewhere.[9,10]

The substrate was a (100)-oriented *n*-type silicon wafer coated with a 5.46-μm-thick SiO_2 layer. ZrO_2 layers were deposited on the substrate by spin coating at 2500 rpm for 25 s. Each layer was pyrolyzed in O_2 at 600 °C for 10 min. After depositing 20 layers of ZrO_2, the resulting film was annealed in O_2 at 600 °C for 1 hr. Another 20 layers of PLT10 were then spin coated and annealed in the same way as the ZrO_2 layers except that the annealing temperature was set at 650 °C.

The crystalline structure of the ZrO_2 and PLT10 films was characterized by x-ray diffraction (XRD). The surface and cross section of the PLT10 film was examined by scanning electron microscopy [(SEM), Leica Stereoscan 440]. The film roughness was determined by an alpha-step profiler (Tencor P-10). The capacitance and dielectric loss factor were measured using a computer controlled impedance analyzer (HP 4192A). The polarization–electric–field ($P-E$) hysteresis loop was obtained using a Sawyer–Tower circuit. The leakage current was measured using a Keithley model 237 electrometer. The pyroelectric coefficient was measured by a dynamic technique.[11,12]

Figure 1(a) shows the XRD spectrum of a ZrO_2 film annealed at 600 °C for 1 hr. It is evident that tetragonal and monoclinic phases coexist in the film, but the tetragonal phase is the dominant one. Figure 1(b) shows that the PLT10 film has a well-formed perovskite structure. The relevant intensities of the peaks are similar to those found for PLT10 ceramics,[13] indicating that the crystallites in the film are randomly oriented. SEM micrographs of the surface and cross section of the film are shown in Fig. 2. Figure 2(a) shows that the PLT10 film is dense and crack free, and the grains in the film have a rather uniform size ($\sim$50 nm). The average surface roughness is 8.8 nm. In Fig. 2(b), three layers—amorphous SiO_2, ZrO_2 with columnar structure and PLT10

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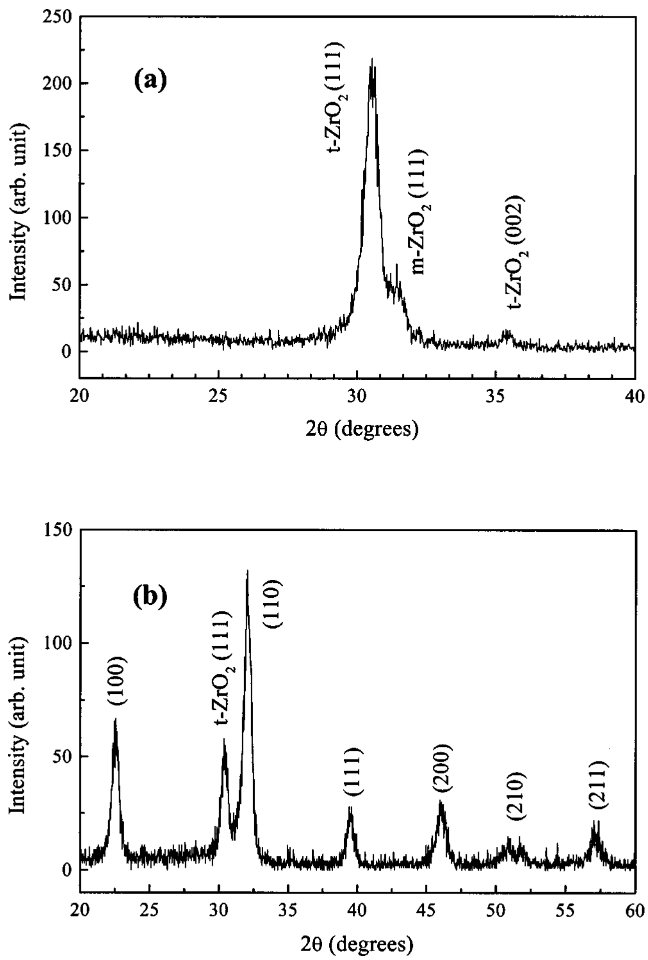


FIG. 1. X-ray diffraction pattern of (a) ZrO_2 thin film and (b) PLT10 thin film.

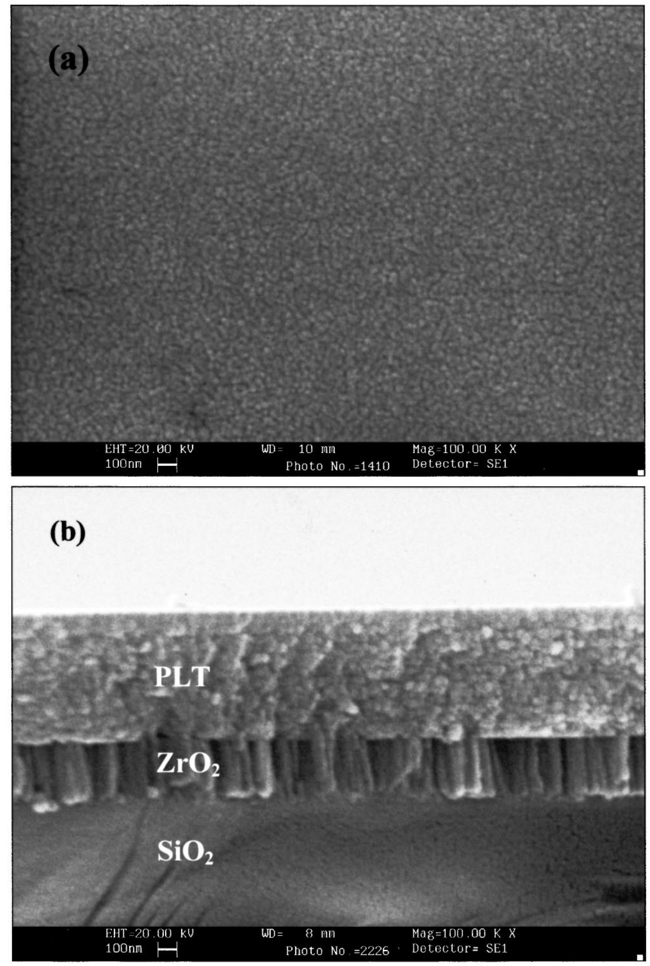


FIG. 2. SEM micrograph of the (a) surface and (b) cross section of PLT10 film.

with spherical grains— can be clearly seen. The thickness of the PLT10 and ZrO_2 layers are about 670 and 350 nm, respectively.

In order to measure the electrical properties of the film under a transverse electric field, IDT electrodes were patterned by conventional photolithography. A 100-nm-thick Cr/Au layer was deposited on the surface of the PLT10 by magnetron sputtering. The electrodes were formed after a standard lift-off process. The IDT had 22 pairs of electrodes with a finger width of 30 μm and a gap of 20 μm. The overlapping length was 620 μm.

The typical leakage current density was found to be $1-2\times10^{-8}$ A/cm^2 at 10 V dc bias (transverse electric field $\sim$5 kV/cm). The dielectric constant of the PLT10 film was calculated from the measured capacitance based on established methods.[5,14,15] The dielectric constant ϵ and loss factor $\tan\delta$ versus frequency are shown in Fig. 3. It can be seen that ϵ and $\tan\delta$ vary only slightly with frequency. The values of ϵ and $\tan\delta$ of the film at 1 kHz are 206 and 0.0033, which are lower than the corresponding values ($\epsilon=576$, $\tan\delta=0.023$) for bulk PLT10 ceramics.[13] A depression in ϵ is commonly observed in thin films and is attributed mainly to microstructural inhomogeneity and poor crystalline quality.[16]

The hysteresis loop of the PLT10 film was measured using a modified Sawer–Tower circuit at a frequency of 200 Hz. It was assumed that the volume in which the dipoles were switched was the product of the film thickness, the overlapping length of the electrodes, and the gap distance between adjacent electrodes. The electric field was assumed to be uniform across the gaps. Figure 4(a) shows the $P-E$ loop obtained using a maximum field of 75 kV/cm. The remnant polarization P_r and coercive field E_c are 12.6 μC/cm^2 and 9.93 kV/cm, respectively. Figure 4(b) show P_r and E_c as functions of the maximum applied field.

A dynamic method was used to measure the pyroelectric coefficient p at room temperature.[11,12] Controlled by a Peltier heater, the sample temperature was modulated sinusoidally

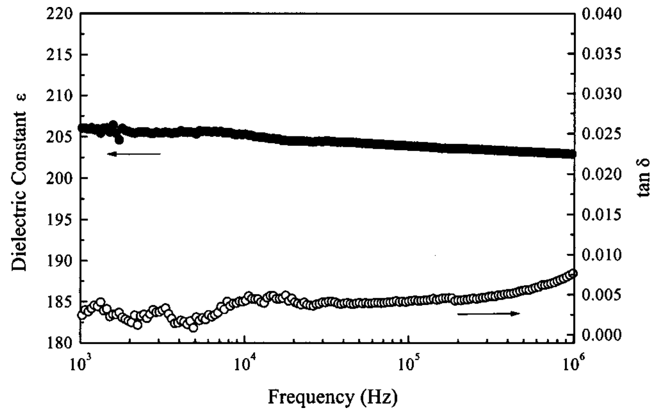
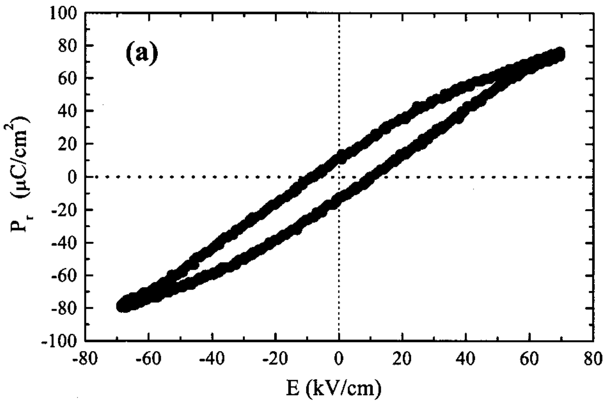


FIG. 3. Frequency dependence of the dielectric constant and loss tangent of PLT10 film.



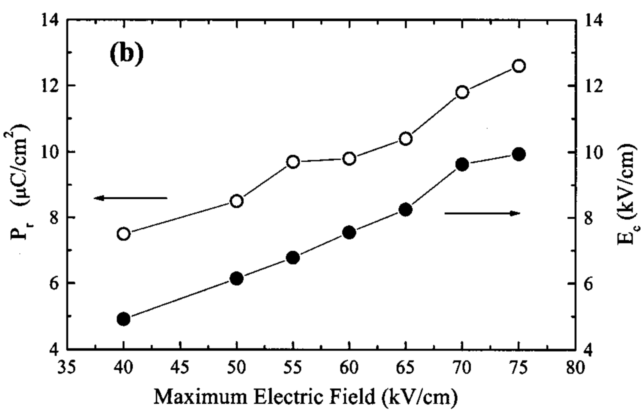


FIG. 4. (a) Polarization–electric-field hysteresis loop of PLT10 film at a maximum applied electric field of 75 kV/cm. (b) P_r and E_c as functions of the maximum applied field.

by ± 1 °C at a frequency of 5 mHz. The pyroelectric current was amplified by an electrometer and the 90° out-of-phase component of the current with respect to the temperature modulation was measured with a lock-in amplifier.[17] A PLT10 film was first poled at room temperature by applying an ac voltage of amplitude 120 V (equivalent to 6 times E_c) and frequency 0.1 Hz for 15 min and then short circuited overnight. The measured pyroelectric coefficient of the film is $95\,\mu C/m^2 K$, which is significantly lower than that of PLT10 bulk ceramics ($p = 234\,\mu C/m^2 K$).[12] However, improvement is possible because the poling conditions have not been optimized. The voltage responsivity, defined as $F_v = p/c\epsilon\epsilon_o$, where c is the heat capacity per unit volume and ϵ_o is the permittivity of free space, is $0.021\,m^2/C$.

In conclusion, a PLT10 film of 670 nm thickness was prepared on a ZrO_2-coated silicon substrate. The 350-nm-thick ZrO_2 film serves as an insulating layer as well as a buffer layer to inhibit diffusion between the PLT10 film and the silicon substrate. This helps the PLT10 thin film to develop uniform grains and smooth surface and leads to a reduction of the parasitic capacitance between the film and the substrate. We have demonstrated that a transverse electric field applied across IDT electrodes can effectively switch the domains to give a symmetric hysteresis loop and a reasonably high remnant polarization. The transversely polarized PLT10 film also exhibits quite a high pyroelectric coefficient. For in-plane polarized pyroelectric sensors with IDT electrodes, an electrode or a conductive layer at the bottom is not required. This will give an additional freedom in choosing buffer or seeding layers as well as substrates for the growth of ferroelectric films. Moreover, the sensor performance will not be affected by interlayer defects and stray capacitance in the normal direction of the film.

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