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# Fatigue-free La-modified $PbTiO_3$ thin films prepared by pulsed-laser deposition on $Pt/Ti/SiO_2/Si$ substrates

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Fatigue-free 14 mol % La-modified $PbTiO_3$ (PLT) thin films were grown on $Pt/Ti/SiO_2/Si$ substrates using pulsed-laser deposition and crystallized by furnace annealing at 600 °C. The 220-nm-thick PLT film capacitors with a Pt top electrode showed excellent ferroelectric properties. The remanent polarization ($2P_r$) and the coercive field ($2E_c$) were about 20 $\mu C/cm^2$ and 70 kV/cm, respectively, and the PLT capacitors did not show any noticeable fatigue up to $3\times10^9$ read/write switching cycles at a frequency of 1 MHz and switching voltage of 5 V. By comparing the microstructures, electric, and dielectric properties with those of pure $PbTiO_3$ thin films, the suppression of oxygen vacancies and/or charged defects, and the coral-like microstructures developed in PLT films were attributed to its fatigue-free feature.  [DOI: 10.1063/1.1556559]

Ferroelectric thin films have attracted much attention in recent years for nonvolative random-access memory (NvRAM) applications and microelectromechanical systems devices. For practical applications, it is important that the films have a low crystalline temperature, low coercive field, high remanent polarization, and are fatigue free. $Pb(Zr,Ti)O_3$ (PZT) with perovskite structure, $SrBi_2Ta_2O_9$ (SBT) and $Bi_{4-x}La_xTi_3O_{12}$ (BLT) with bilayered perovskite structure, have been recently studied for NvRAM applications. PZT has the advantages of low crystalline temperature (~650 °C) and large polarization value ($2P_r \sim 60$ $\mu C/cm^2$), but has the drawbacks of poor fatigue endurance with a conventional Pt electrode and high coercive field ($2E_c \sim 120$ kV/cm).[1] While SBT has good fatigue endurance and low coercive field ($2E_c \sim 70$ kV/cm), it generally has high crystallization temperature (750–800 °C) and small polarization ($2P_r \sim 20$ $\mu C/cm^2$).[2] However, low-temperature (near 600 °C) process for SBT was demonstrated in recent literature.[3,4] BLT has low crystalline temperature (650–700 °C), good fatigue endurance, reasonable polarization value ($2P_r \sim 20$ $\mu C/cm^2$), but high coercive field ($2E_c \sim 100$ kV/cm).[5]

Recently, La-modified lead titanate $(Pb_{1-x}La_x)Ti_{1-x/4}O_3$ (PLT) solid solution has received considerable attention both in bulk and thin-film forms. By changing the La doping content in PLT, interesting dielectric, ferroelectric, pyroelectric, piezoelectric, and nonlinear electro-optic properties can be achieved.[6–11] Since PLT thin film has reasonable coercive fields and remanent polarizations if the doping concentration of La does not exceed certain level, and can be crystallized at low temperature (below 650 °C) to be compatible with Si-based integrated-circuit technology, it may serve as an alternative material to PZT in NvRAM applications. However, up to date, little effort has been attempted to study the fatigue properties of PLT thin films. The aim of this work is to investigate the fatigue behavior and ferroelectric properties of PLT films. La content in our study is selected as 14 mol % [PLT(14)]. Pure PT and PLT(28) thin films have also been fabricated and measured for comparison.

The 220-nm-thick film samples on $Pt/Ti/SiO_2/Si(100)$ substrates were made by pulsed-laser deposition.[12] A 10-mol % excess PbO was added in the powder mixture during the preparation of PLT targets in order to compensate for the Pb loss. The atmosphere pressure was first lowered to 0.01 Pa, and the substrate was then heated up to 450 °C while the air pressure was further pumped down to $2\times10^{-4}$ Pa. Afterwards, pure oxygen was introduced to make the depositing ambient equal to 2 Pa. In our experiment, the pulsed-laser energy and the focused-beam area on the target are kept at 200 mJ and 0.028 $cm^2$, respectively. After the film deposition, Pt electrodes with a diameter of 0.25 mm were deposited onto the top surface of the films at room temperature through a shadow mask by rf sputtering. Consequently, the films were subjected to 600 °C annealing for crystallization under 1 atm flowing oxygen ambient in a tube furnace for half an hour, which can also eliminate the interface stress between the electrode and film.

X-ray diffraction (XRD) was carried out in a Rigaku D/MAX 3c diffractometer using Cu K$\alpha$ radiation at 40 kV. A RT6000S ferroelectric test system (RADIANT Technologies, Inc.), working in the virtual ground mode, was used to plot the hysteresis loops of polarization–electric-field relationships and also for the fatigue measurements. The dielectric properties were measured using a HP4294A impedance analyzer. The $I-V$ data were acquired using a Keithley 6517A

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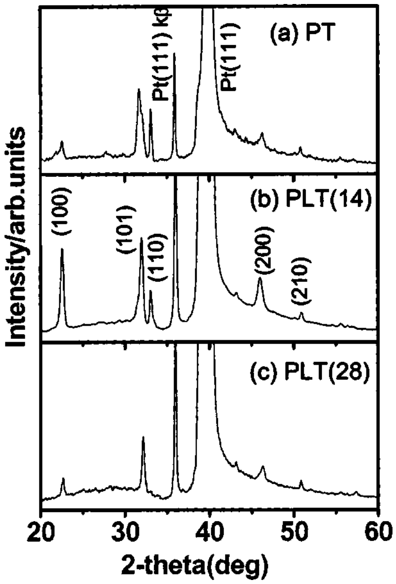


FIG. 1. XRD patterns of the PLT thin films with various La content.

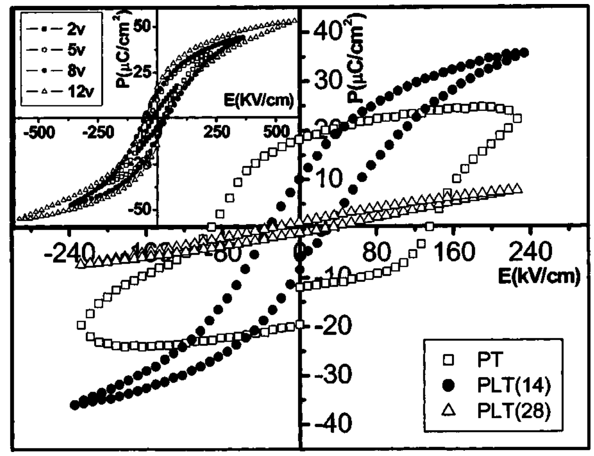


FIG. 2. ($P-E$) hysteresis loops of PLT thin film capacitors with various La content. The inset is the $P-E$ hysteresis loops of PLT(14) thin film capacitors at different applied voltages.

electrometer as the voltage source and a picoampere meter. The surface morphology was examined by field-emission scanning-electron microscopy (FESEM) (JEOL JSM6335F), and the film thickness was determined by an ET350 Talysurf profilometer (Kosaka Laboratory Ltd.).

Typical XRD patterns (Fig. 1) show that the PLT films grown on Pt/Ti/$SiO_2$/Si substrates were polycrystalline with perovskite structure. The obvious splitting of (101) and (110) diffraction peaks of PT and PLT(14) films indicates that the film is in tetragonal phase. When the La content is increased to 28 mol %, the splitting of this peak disappears. According to the (100) and (101) peaks, the lattice constant $c/a$ ratios were calculated as: 1.025, 1.010, and 1.003 for PT, PLT(14), and PLT(28) films, respectively. This tetragonality decrease indicates that the crystal structure transforms from tetragonal to cubic when the La concentration increases from 0 to 28 mol %.[9]

The plots in Fig. 2 are the polarization of these PLT films as a function of electric field. A voltage of $\pm 5$ V was used for the tests, and the inset picture in Fig. 2 shows a family of hysteresis loops of PLT(14) film at different applied voltages. Under the applied voltage of $\pm 5$ V, the PT and PLT(14) films possessed remanent polarizations ($2P_r$) of about 38 and 20 $\mu C/cm^2$, respectively, while the PLT(28) was almost paraelectric without $P_r$. The result is attributed to the phase transformation from the ferroelectric to paraelectric phase by the addition of La to the PT, which is consistent with the XRD results mentioned earlier. It can be noted that the hysteresis loop of PLT(14) is more symmetric with a coercive field $2E_c$ (near 70 kV/cm) about one-fourth that of pure PT (near 250 kV/cm). During the tests of hysteresis loop, we found that the La-doped films can bear higher voltage than the PT films fabricated under similar conditions. The PLT(14) and PLT(28) films can withstand 12 V, whereas the PT films can not withstand voltages greater than 6 V. When the applied voltage of $\pm 12$ V was used, the maximum polarization of 55 $\mu C/cm^2$ was obtained in the PLT(14) film and its remanent polarization was about 36 $\mu C/cm^2$ with a coercive field of 90 kV/cm, as shown in the inset of Fig. 2.

Ferroelectric fatigue characteristics were evaluated using a switching voltage of $\pm 5$ V and a measuring voltage of $\pm 5$ V under a bipolar pulse of 1 MHz in frequency. Figure 3(a) shows the polarization–electric-field curves for PLT(14) thin film before and after being subjected to $3\times 10^9$ read/write cycles, the two shapes do not show obvious changes. The inset picture shows the curves for PT thin film. It can be noted that the hysteresis loops change dramatically, and are distorted after being subjected to $3\times 10^9$ read/write cycles. Figure 3(b) illustrates the polarization of ($P^* - P^\wedge$) as a function of polarization switching cycles acquired from PLT(14) and PT thin films. Apparently, the value of ($P^* - P^\wedge$) of PLT(14) remained nearly constant after being subjected to $3\times 10^9$ read/write repetitive cycles, suggesting that the PLT(14) film had a fatigue-free character. In contrast, the PT thin films exhibited large polarization degradation under the

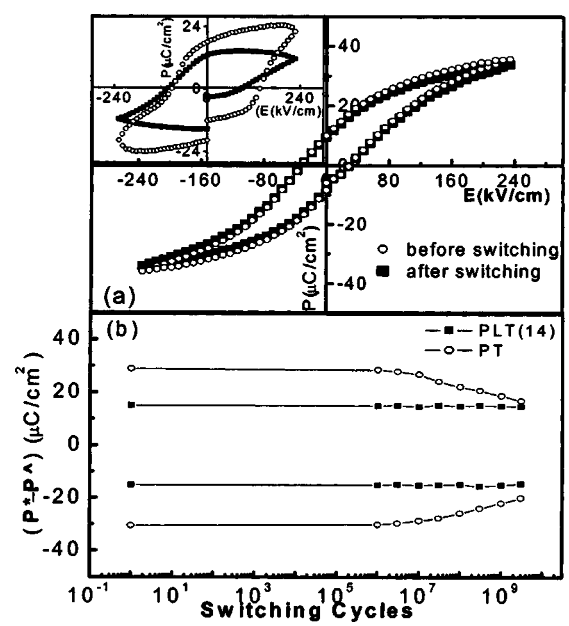


FIG. 3. Polarization fatigue characteristics of the PT and PLT(14) thin film capacitors. (a) $P-E$ hysteresis loops for PLT(14) (the inset is for PT) thin film capacitors measured at an applied voltage of $\pm 5$ V before and after being subjected to $3\times 10^9$ read/write switching cycles at a frequency of 1 MHz. (b) Fatigue test results using a switching voltage of $\pm 5$ V and a measuring voltage of $\pm 5$ V at a frequency of 1 MHz.

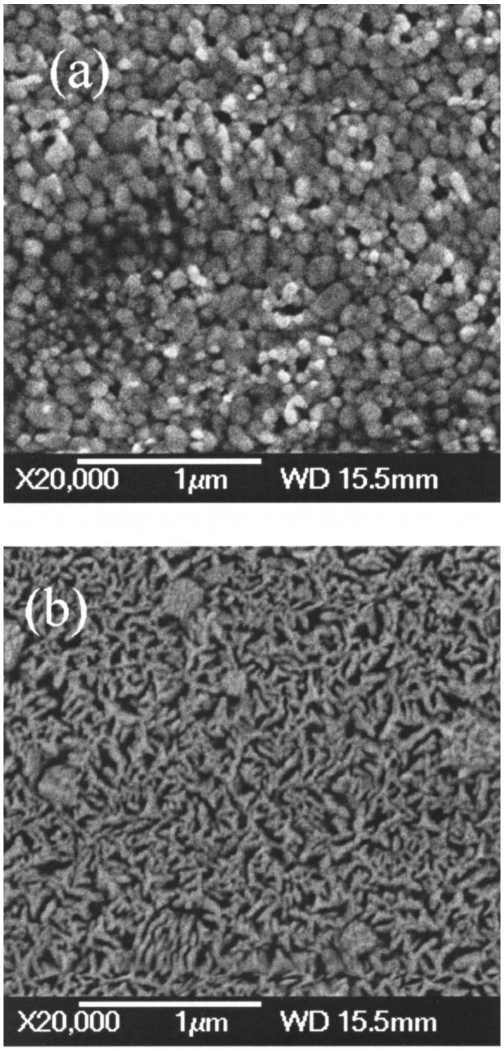


FIG. 4. FESEM surface morphology of the PT (a) and PLT(14) (b) thin films.

same test condition. As reported by others,[13,14] the fatigue properties are related to the switching voltage. It is found in our experiment that the PLT(14) thin film capacitors did not show any noticeable fatigue up to $10^{11}$ read/write switching cycles at a switching voltage of 3 V, which is generally used in the fatigue properties testing of BLT thin films with similar thickness.[15] The fatigue-free character of the PLT(14) thin films might be due mainly to two reasons:

(1) It has been widely accepted that polarization fatigue of the PT thin film originates mainly from the accumulation of oxygen vacancies, which can pin the domain walls. The deficiency of Pb content in PT film will induce many oxygen vacancies.[16] As the lanthanum is doped into the PT film, the generation and diffusion of the oxygen vacancies will be suppressed. More importantly, the carrier numbers in the film will decrease through defect compensation of the added La, as reported by others.[17]

Two aspects in our measurements can indirectly support this explanation. The first is the leakage current measurement. The leakage current of the PT film was $5.2\times10^{-6}$ A/cm$^2$, while a leakage current of $2.0\times10^{-7}$ A/cm$^2$ was observed in PLT(14) film at an electric field of 120 kV/cm. The second is the frequency dispersion of dielectric constant and loss measurement. Obvious low-frequency (between 100 Hz and 1 kHz) dispersion of the dielectric constant was observed in PT film, while PLT(14) thin film has a very flat dielectric-constant–frequency relation between 100 Hz and 1 MHz. The dielectric loss of PT films (0.04 at 10 kHz) is much higher than that of PLT(14) (0.014 at 10 kHz). These facts indicate that the PLT(14) thin film contains less oxygen vacancies or/and charged defects than does pure PT thin film.

(2) We found that doping lanthanum into the PT film changes the microstructure. Figure 4 shows the surface morphology of the PT and PLT(14) thin films by FESEM. One can see that the surface morphology of PLT(14) is totally different from that of PT thin films. The PT film shows a surface full of round particles with diameters ranging from 30 to 100 nm, while PLT(14) film shows coral-like structure, which may correspond to the preferred (100) orientation of XRD pattern shown in Fig. 1(b). We proposed that the peculiar microstructure and the preferred orientation in PLT(14) may reduce the strain during the polarization switching and thus be partially responsible for the fatigue-free character of PLT(14) thin film.

In conclusion, fatigue-free PLT(14) thin films 220-nm thick were grown on Pt/Ti/$SiO_2$/Si(100) substrates using pulsed-laser deposition. The PLT films were crystallized at 600 °C. At a testing voltage of $\pm5$ V, the remanent polarization ($2P_r$) and the coercive field ($2E_c$) were about 20 $\mu$C/cm$^2$ and 70 kV/cm, respectively. More importantly, the PLT capacitors did not show any significant fatigue up to $3\times10^9$ read/write switching cycles at a frequency of 1 MHz and a switching voltage of 5 V. Through comparing the microstructure, electric, and dielectric properties with pure $PbTiO_3$ thin films, we propose that the suppression of oxygen vacancies and/or charged defects, and the coral-like microstructure produced in PLT(14) films are responsible for its fatigue-free feature.

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