Applied Physics Letters

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Citation: Appl. Phys. Lett. **90**, 262902 (2007); doi: 10.1063/1.2751580
View online: http://dx.doi.org/10.1063/1.2751580
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v90/i26
Published by the American Institute of Physics.

APPLIED PHYSICS LETTERS **90**, 262902 (2007)

Enhancement of field-induced strain by La substitution in epitaxial $Pb(Zr,Ti)O_3$ films grown by metal organic chemical vapor deposition

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(Received 24 March 2007; accepted 30 May 2007; published online 25 June 2007)

High-quality epitaxial La-substituted $Pb(Zr_{0.65}Ti_{0.35})O_3$ films were grown on $(100)_c SrRuO_3 \| (100)_c SrTiO_3$ substrates at 600 °C using metal organic chemical vapor deposition. Single-phase perovskite was obtained for La/(Pb+La) ratios ranging from 0 to 33%; La ions were selectively substituted at the Pb sites when the La/(Pb+La) ratio was 6% or less and were substituted at both *A* and *B* sites when it was greater than 6%. Both the remanent polarization and coercive field monotonically decreased with the La/(Pb+La) ratio, and the maximum field-induced strain was around 6%. This means that La substitution enhances the field-induced strain. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2751580]

Lanthanum (La)-substituted $Pb(Zr,Ti)O_3$ has received a lot of attention for use as an electro-optical device. This is due to its high electro-optical coefficients and good transparency, even in a sintered body.[1] For sintered bodies, the largest field-induced strain and the largest electro-optical coefficient are found in La-substituted $Pb(Zr,Ti)O_3$,[2] not in $Pb(Zr,Ti)O_3$.

We grew high-quality epitaxial La-substituted $Pb(Zr,Ti)O_3$ films with various La/(Pb+La) ratios and investigated the effect of La substitution on the crystal structure, ferroelectricity, and elastic field-induced strain of the films. As a result, the increase in field-induced strain due to La substitution in $Pb(Zr,Ti)O_3$ films was ascertained.

We prepared $(Pb,La)(Zr_{0.65}Ti_{0.35})O_3$, PLZT, films on $(100)_c SrRuO_3 \| (100)_c SrTiO_3$ substrates.[3,4] The La/(Pb+La) ratio in the film was controlled between 0 and 33% at a fixed Zr/(Zr+Ti) ratio of 0.65.

The crystal structure and film orientation were determined using x-ray diffraction (XRD). Raman spectroscopy was used for the crystal symmetry analysis and to determine the site occupancy of La ions. The film composition was estimated using an x-ray fluorescence spectrometer calibrated using standard samples. The electric-field induced strain and ferroelectric properties of the films were measured simultaneously using a scanning probe microscope (SPM) with the apparatus connected to a ferroelectric test system.

Transparent crack-free PLZT films having a thickness of 2.0–2.7 μm and a smooth surface (average roughness R_a of 2.0–2.7 nm) were obtained irrespective of the La/(Pb+La) ratio.

Figure 1 shows the XRD patterns for the five La/(Pb+La) ratios used. Irrespective of the ratio, single-phase, epitaxially grown, perovskite films with (100) orientation were obtained: $(100)PLZT \| (100)_c SrRuO_3 \| (100)_c SrTiO_3$. The full width at half maximum of the PLZT (200) peak was less than 0.4° for all films. The peak position of PLZT (200)

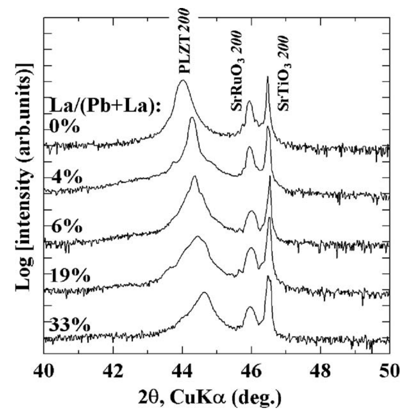

FIG. 1. XRD patterns for five La/(Pb+La) ratios.

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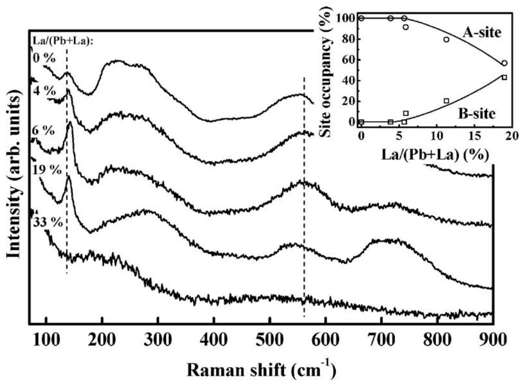

FIG. 2. Raman spectra of PLZT film for five La/(Pb+La) ratios. Inset shows calculated site occupancy of La ions in PLZT film.

shifted to a higher angle as the ratio was increased, indicating that the surface-normal lattice parameter decreased.

The Raman spectra of the films are shown in Fig. 2. The spectrum for the 0% ratio exhibited intense phonon modes at ~135, 200–275, ~560, and 680–725 cm^{-1}, which is typical for a rhombohedral system PLZT.[5] The crystal symmetry retained a rhombohedral system for the ratios up to 19%. The peaks were broader and weaker at the 33% ratio, indicating the crystal symmetry change from rhombohedral to cubic.

The peak at ~135 cm^{-1} corresponds to the Pb-site (*A* site in a perovskite structure, ABO_3)-based lattice mode,[6] while that at ~560 cm^{-1} corresponds to the Zr/Ti–O (*B* site-O) stretching mode.[7] The site occupancy of La ions at the *A* and *B* sites are shown in the insert in Fig. 2. The La ions were selectively substituted at *A* sites below 6% and were substituted at both *A* and *B* sites over 6%. This shows that the solid solubility limit of La ion substitution at *A* sites was 6% in the present study.

Figure 3 shows typical polarization (P)-electric field (E) hysteresis loops measured up to 100 kV/cm and 5 Hz. Well-saturated hysteresis loops were observed for all compositions and became slim as the ratio was increased. The remanent polarization (P_r) and the coercive field (E_c) monotonically decreased from 56 to 0 $\mu C/cm^2$ and 35 to 0 kV/cm, respectively, as the ratio was increased.

The field-induced strain measured at 5 Hz in bipolar (a) and unipolar (b) electric fields is shown in Fig. 4. Both increased with the ratio up to about 6%, and then decreased. This La/(Pb+La) ratio of 6% agrees with the solid solubility limit of La ion substitution at *A* sites. This result shows that PLZT with a La/(Pb+La) ratio of about 6% has a larger field-induced strain than nondoped $Pb(Zr_{0.65}Ti_{0.35})O_3$ and suggests the possibility of a close correlation between the

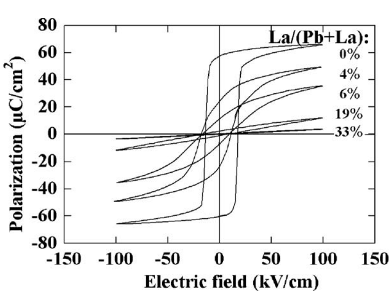

FIG. 3. Hysteresis loops for five La/(Pb+La) ratios for Zr/(Zr+Ti)=65% at 5 Hz.

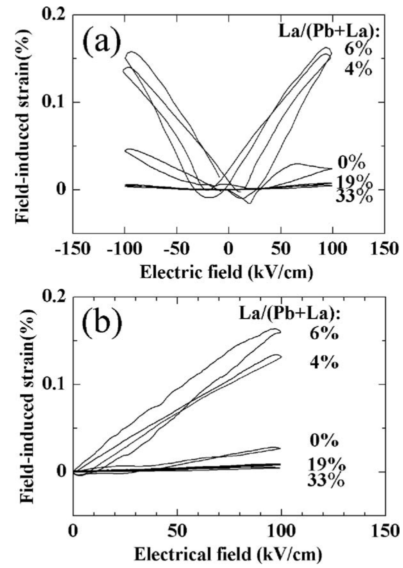

FIG. 4. La/(Pb+La) ratio dependency of field-induced strain in bipolar (a) and unipolar (b) electric fields measured at 5 Hz.

substitution sites of La ions and the amount of field-induced strain in the PLZT film.

The improvement in the piezoelectricity by La substitution was also reported in the sintered body[1] and it was not limited to the film form. These are consisted of two factors, the intrinsic and the extrinsic ones.[8,9] Since the largest nonlinear *C-V* characteristic was obtained at La content of 6% (not shown here), the extrinsic factor is considered to be the major in this study.[10] We are under measure *in situ* XRD in order to reveal the origin of large piezoelectric property.

The strain in ferroelectric materials is given by $x=QP^2$, and the field-induced strain observed by SPM in a unipolar electric field from zero to the maximum electric field is given by $\Delta x_{SPM}=Q_{SPM}(P_{max}^2-P_r^2)$, where Q_{SPM} is the electrostatic constant and P_r and P_{max} are the polarization for an electrical field of zero and the maximum value.

Figure 5 shows the field-induced strain and $[P_{max}^2-P_r^2]$ as a function of the La/(Pb+La) ratio. The strain took a

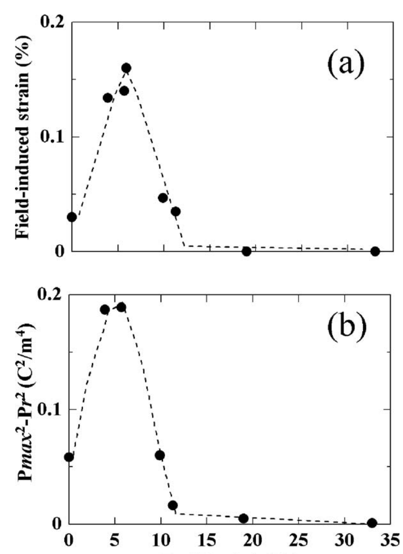

FIG. 5. La/(Pb+La) ratio dependency of field-induced strain and $[P_{max}^2-P_r^2]$.

maximum at a ratio of 6% and was in good agreement with the estimation from the polarization property. This result clearly indicates that PLZT film, which has a large field-induced strain, is a suitable candidate for microelectromechanical system applications.

In summary, high-quality epitaxial (Pb,La)$(Zr_{0.65}Ti_{0.35})O_3$ films were grown on $(100)_c SrRuO_3 \| (100)_c SrTiO_3$ substrates at 600 °C using metal organic chemical vapor deposition. Both P_r and E_c monotonically decreased with the La/(Pb+La) ratio. The field-induced strain showed a maximum at around 6%, where La ions were selectively substituted at the *A* sites of PLZT film. This indicates that PLZT is a candidate piezoelectric material with a large field-induced strain.

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