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Enhancement of field-induced strain by La substitution in epitaxial Pb(Zr,Ti)O₃ films grown by metal organic chemical vapor deposition

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High-quality epitaxial La-substituted Pb(Zr_{0.65}Ti_{0.35})O₃ films were grown on (100)_cSrRuO₃||(100)_cSrTiO₃ 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)O₃ 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)O₃,² not in Pb(Zr,Ti)O₃.

We grew high-quality epitaxial La-substituted Pb(Zr,Ti)O₃ 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)O₃ films was ascertained.

We prepared (Pb,La)(Zr_{0.65}Ti_{0.35})O₃, PLZT, films on (100)_cSrRuO₃||(100)_cSrTiO₃ 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)_cSrRuO₃||(100)_cSrTiO₃. 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 $\sim 135 \text{ cm}^{-1}$ corresponds to the Pb-site (A site in a perovskite structure, ABO_3)-based lattice mode,⁶ while that at $\sim 560 \text{ cm}^{-1}$ 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 $\mu\text{C}/\text{cm}^2$ 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 $\text{Pb}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ and suggests the possibility of a close correlation between the

FIG. 3. Hysteresis loops for five La/(Pb+La) ratios for $\text{Zr}/(\text{Zr}+\text{Ti})=65\%$ 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 body¹ 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 non-linear 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 $\Delta x_{\text{SPM}} = Q_{\text{SPM}}(P_{\text{max}}^2 - P_r^2)$, 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 $[P_{\text{max}}^2 - P_r^2]$ 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 $[P_{\text{max}}^2 - P_r^2]$.

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})O₃ films were grown on (100)_cSrRuO₃||(100)_cSrTiO₃ 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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