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Composition dependence of electrooptic property of epitaxial $(Pb,La)(Zr,Ti)O_3$ films

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The Zr/Ti ratio dependence of refractive index and electrooptic coefficient of epitaxial $(Pb,La)(Zr,Ti)O_3$ (PLZT) films were investigated. PLZT films were fabricated on La-doped $SrTiO_3$ (La-STO) substrates by a chemical solution deposition (CSD) method. Optical properties in TE- and TM-modes were measured individually using a prism coupling method. The refractive indexes both in TE- and TM-modes were as large as that of the polycrystalline film, and increased with increasing Ti/(Zr + Ti) ratio. The refractive index in TE-mode was larger than that in TM-mode because the PLZT films received compressive stress from the La-STO substrates due to lattice mismatch. The refractive index in TM-mode almost linearly decreased with increasing applied an electric field while that in TE-mode slightly increased and saturated around at 200 kV/cm. The Pockels coefficient in TM-mode r_{33} showed large change for compositions, while that in TE-mode r_{13} showed little change. The maximum Pockels coefficient r_c of 156 pm/V was obtained for the epitaxial PLZT film with Ti/(Zr + Ti) ratio of 50%.

Key-words : Electrooptic effect, Epitaxial film, PLZT, Composition dependence, Zr/Ti

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1. Introduction

Ferroelectric materials have unique optical properties such as electrooptic effect and nonlinear optical effect, and have already been applied in bulk form to stand-alone optical devices such as an optical shutter, a second-harmonic generator and an optical associative memory. If ferroelectric materials were embedded in film form with semiconductor integrated circuits, novel optical devices such as a spatial light modulator of the electrooptic type (EO-SLM),[1] an integrated optical waveguide[2] and a tunable photonic crystal[3] would be realized. $(Pb,La)(Zr,Ti)O_3$ (PLZT) is a potential material for future integrated optical devices because of having a high electrooptic coefficient. We previously reported that the PLZT film with La content of 2 at.%, not 8–9 at.%, and Ti/(Zr + Ti) ratio of 40% is an optimum composition for getting high electrooptic coefficient and smooth surface in polycrystalline films by investigating La content and Zi/Ti ratio dependences of electrooptic properties.[4),5)] On the other hand, Ishii et al. reported that the highest electrooptic coefficient was obtained in the epitaxial PLZT film with La content of 9 at.%.[6)] These results show that the La contents dependence of electrooptic properties has different trend between polycrystalline films and epitaxial films, and suggest that the Zr/Ti ratio dependence may also have different trend. Therefore, in this study, the Zr/Ti ratio dependence of refractive index and electrooptic property of epitaxial PLZT films were investigated.

2. Experimental procedure

PLZT films were formed by a chemical solution deposition (CSD) method. A precursor solution for the CSD was prepared from trihydrated lead acetate (99.5%, Nakalai Tesque), hydrated lanthanum acetylacetonate (97%, Aldrich), titanium isopropoxide (99.999%, Aldrich) and zirconium *n*-propoxide (70% in propanol, Gelst) with a solvent of 2-methoxyethanol (99.7%, Aldrich). Ti/(Zr + Ti) ratios were varied from 35 to 50%, and each precursor solution contained 20 at.% excess Pb. La content was fixed to be 2 at.% in this study. Therefore, the nominal compositions of the precursor solutions were indicated as $(Pb_{1.18},La_{0.02})(Zr_{1-x},Ti_x)O_3$ ($x = 0.35$–0.5). The concentration of the precursor solution was controlled to be 0.2 M. (111)-oriented $SrTiO_3$ single crystal plates with lanthanum doping of 0.75 wt% (La-STO) were used as substrates and simultaneously bottom electrodes. The precursor solutions were spin-coated on the La-STO substrates. The spin-coated films were dried at 150°C for 1 min and pyrolized at 500°C for 3 min in air. After the process from spin-coating to pyrolysis was repeated 5 times, the films were fired at 700°C for 5 min in air by a rapid thermal annealing system (RTA). This sequence was repeated 4 times. Finally, an ultrathin Pt electrode layer with a thickness of up to 10 nm was sputtered onto the surface of the PLZT films as a top electrode.

The crystal structure and the orientation of the PLZT films were investigated with an X-ray diffractometer (XRD; PANalytical, X'pert PRO MPD). An atomic force microscopy (AFM) probing system (Toyo Corporation, Nano-R) with a conductive cantilever was connected to a ferroelectric test system (Toyo Corporation, FCE-PZ) to simultaneously measure *P–E* hysteresis curves and longitudinal displacement-electric field curves. Details of the measurement method were described elsewhere.[7)] Optical properties were evaluated by a prism coupling method as shown in **Fig. 1**. Laser light with a wavelength of 1550 nm was coupled to the PLZT films through a silicon prism, and reflection intensity and the incident angle were then measured. The TE- and TM-modes were defined as the propagations modes in which an electric vector of light was parallel and perpendicular to the substrate surface, respectively,

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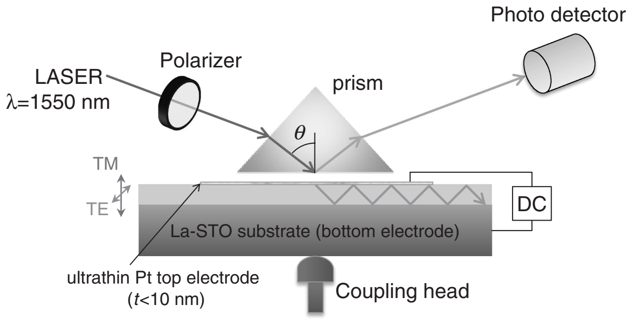

Fig. 1. Schematic illustration of refractive index and electrooptic property measurements by a prism coupling method.

as shown in Fig. 1. Refractive index change was measured by applying DC bias voltage between the top and the bottom electrodes. When we measured the electric and the electrooptic properties, driving voltage was applied to the bottom electrode.

3. Results and discussion

3.1 Crystal structure and electrical properties

Approximately 650-nm-thick PLZT films with 2 at.% La and various Zr/Ti ratios were successfully formed on La-STO substrates. From the XRD measurement, it is confirmed that all the PLZT films were crystallized into a single perovskite phase with a rhombohedral or a pseudo cubic structure and epitaxially grown as [111] axis was perpendicular to the substrate surface. It was also found that the PLZT films had the same symmetry, threefold rotation, with the La-STO substrates.

The longitudinal displacement-applied electric field curves of the PLZT films simultaneously measured with *P–E* hysteresis loops are shown in **Fig. 2**. Although the *P–E* hysteresis loops and displacement curves had asymmetry shapes because of the generation of depletion layers under positive bias field, it seems that spontaneous polarization was fully switched by applying an electric field of 500 kV/cm.

3.2 Refractive index

It is confirmed by a rotating spectroscopic ellipsometer (J. A. Woollam Co. Inc., M-2000) that the extinction coefficients of all the epitaxial PLZT films were lower than 1.2×10^{-4} at the wavelengths larger than 600 nm.

Figure 3 shows the refractive indexes of the epitaxial PLZT films at a wavelength of 1550 nm as a function of Ti/(Zr + Ti) ratio measured by a prism coupling method. The refractive index of a polycrystalline PLZT film[5] is also plotted in the figure for comparison. The refractive indexes both in TE- and TM-modes were as large as that of the polycrystalline film, and increased with increasing Ti/(Zr + Ti) ratio.

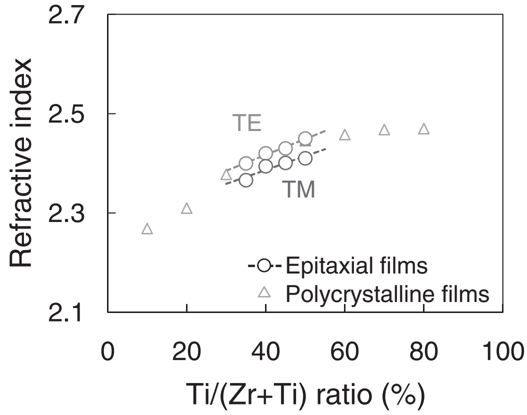

Fig. 3. Refractive index of the epitaxial PLZT films, and for comparison, refractive index of the polycrystalline PLZT films[5] as a function of Ti/(Zr + Ti) ratio.

In the TE- and TM-modes, the electric vectors of light were parallel to $[\bar{1}1\bar{1}]$ and [111], respectively. Therefore, the refractive indexes in both modes should be ideally almost the same values because of the symmetry. However, the refractive index in the TE-mode was larger than that in the TM-mode. We suggested that in this study, the *d*-space of (111) was longer than that of $(\bar{1}1\bar{1})$ because the PLZT films received compressive stress from the La-STO substrates due to lattice mismatch and the difference in the thermal expansion coefficient between PLZT (around $6 \times 10^{-6}\,K^{-1}$) and La-STO ($9 \times 10^{-6}\,K^{-1}$) substrate.[8] It seems that this distortion caused the index ellipsoid which had an oval shape with the minor axis was perpendicular to the substrate surface as shown in **Fig. 4**a).

3.3 Electrooptic properties

Figure 5 shows the refractive index change Δn of the PLZT films with various Ti/(Zr + Ti) ratios by applying an electric field. The curves were asymmetry due to the generation of depletion layers in positive bias field. In this configuration, applying negative bias field is appropriate for device applications because a larger index change is obtained by a lower applied field. **Figure 6** shows the backward refractive index changes of the PLZT films in negative bias field. The refractive index in TM-mode almost linearly decreased with increasing applied an electric field while that in TE-mode slightly increased and saturated around at 200 kV/cm. The index ellipsoid was deformed as shown in Fig. 4b). These results indicate that the

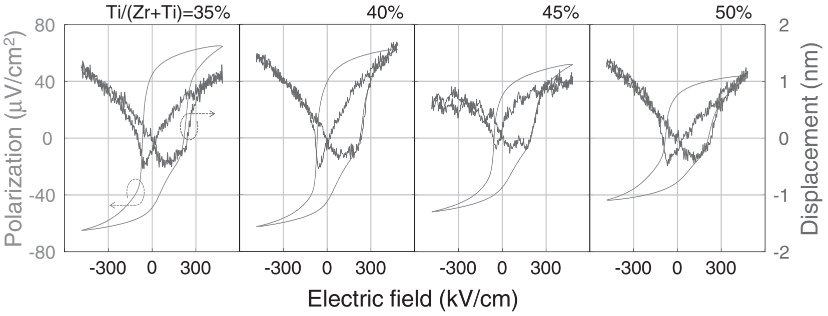

Fig. 2. Longitudinal displacement-applied electric field curves of the PLZT films with various Zr/Ti ratios simultaneously measured with *P–E* hysteresis loops.

susceptivity of electron clouds in the TM-mode was strongly affected by a coulomb's force caused by applying an electric field. The susceptivity in TE-mode slightly increased because the *d*-space of $(\bar{1}1\bar{1})$ was decreased by piezoelectric response.

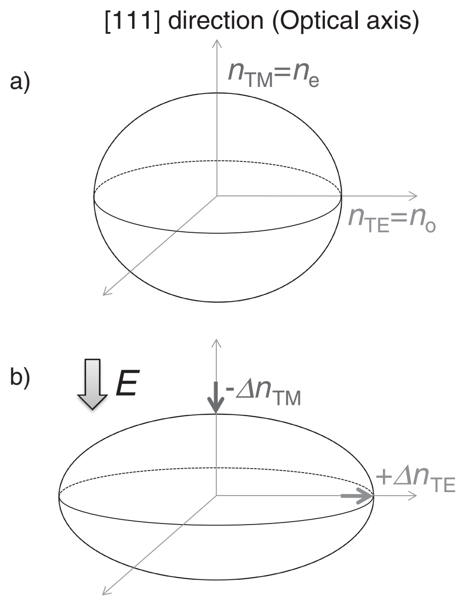

Fig. 4. a) Index ellipsoid of the epitaxial PLZT film and b) its deformation behavior by applying an electric field.

After negative poling, spontaneous polarization was aligned to the direction from top to bottom electrodes. Generally, it is optically defined that n_o and n_e are the refractive indexes in the cases of polarization vectors of light are perpendicular (ordinary) and parallel (extraordinary) to an optical axis, respectively. Therefore, the refractive index in TE- and TM-modes are correspond to n_o and n_e, respectively.

Electrooptic coefficients, r_{33}, r_{13}, and r_c are defined by the following equations:

$$\Delta n_e = -\frac{1}{2} n_e{}^3 r_{33} E_3, \quad (1)$$

$$\Delta n_o = -\frac{1}{2} n_o{}^3 r_{13} E_3, \quad (2)$$

$$r_c = r_{33} - \left(\frac{n_o}{n_e}\right)^3 r_{13}, \quad (3)$$

where E_3 is an electric field toward the optical axis, Δn_o and Δn_e are the refractive index changes, r_{13} and r_{33} are the Pockels coefficients in TE- and TM-modes, and r_c is the Pockels coefficient of light propagation in a vertical direction of applying an electric field, respectively. **Figure 7** shows the Pockels coefficients of the PLZT films with various Ti/(Zr + Ti) ratios estimated from Fig. 6. The r_{13} showed little change, while the r_{33} and r_c showed large change for compositions. The maximum r_c of 156 pm/V was obtained for the epitaxial PLZT film with Ti/(Zr + Ti) ratio of 50%, and this value increased 1.5-fold compared to that of the polycrystalline film with Ti/(Zr + Ti) ratio of 40% which showed maximum Pockels coefficient of

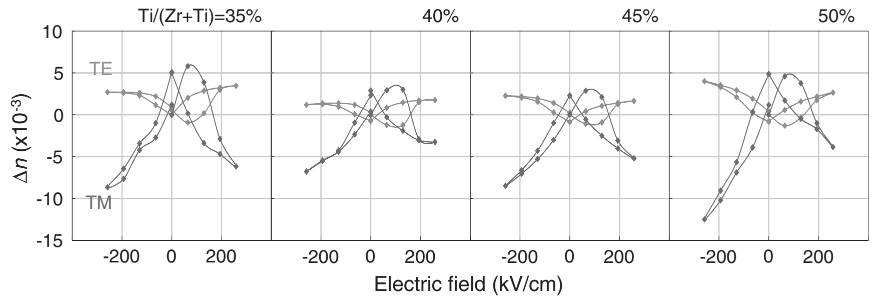

Fig. 5. Refractive index change of the epitaxial PLZT films with various Ti/(Zr + Ti) ratios by applying an electric field.

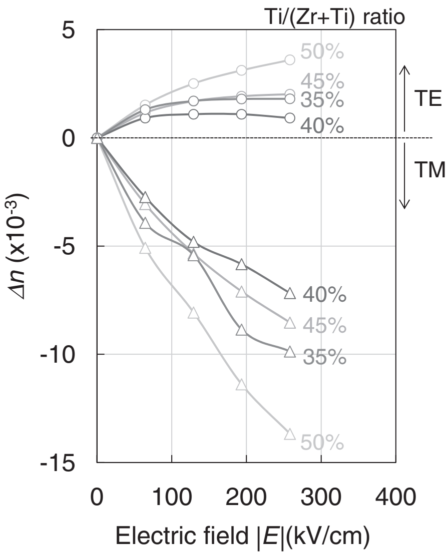

Fig. 6. Backward refractive index changes of the epitaxial PLZT films in negative bias field.

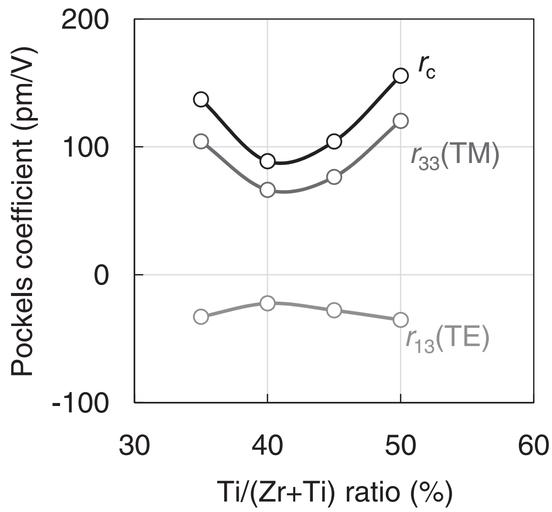

Fig. 7. Electrooptic coefficients of the epitaxial PLZT films as a function of Ti/(Zr + Ti) ratio.

104 pm/V.[5] In this regard, we measured electrooptic properties of epitaxial films and polycrystalline films at the wavelengths of 1550 nm and 633 nm, respectively. Therefore, there is a possibility that the difference of the electrooptic coefficient become larger between epitaxial and polycrystalline films. Finally, we concluded that the Ti/(Zr + Ti) ratio of 50% is optimum to obtain the large electrooptic effect in (111)-oriented epitaxial PLZT films with La content of 2 at.%.

4. Conclusions

The (111)-oriented epitaxial PLZT films with Ti/(Zr + Ti) ratios ranging from 35 to 50% were fabricated on La-STO substrates using a CSD method, and the refractive index and the electrooptic property were investigated by a prism coupling method. It is confirmed that the extinction coefficients of all the epitaxial PLZT films were lower than 1.2×10^{-4} at the wavelengths larger than 600 nm. The refractive indexes both in TE- and TM-modes were as large as that of the polycrystalline film, and increased with increasing Ti/(Zr + Ti) ratio. The refractive index in TE-mode was larger than that in TM-mode. We suggested that in this study, the *d*-space of (111) was longer than that of $(\bar{1}1\bar{1})$ because the PLZT films received compressive stress from the La-STO substrates due to lattice mismatch and the difference in the thermal expansion coefficient between PLZT and La-STO. The refractive index change-applied electric field curves were asymmetry due to the generation of depletion layers in positive bias field. The refractive index in TM-mode almost linearly decreased with increasing applied an electric field while that in TE-mode slightly increased and saturated around at 200 kV/cm. These results indicate that the susceptivity of electron clouds in TM-mode was strongly affected by a coulomb's force caused by applying an electric field. The susceptivity in TE-mode slightly increased because the *d*-space of $(\bar{1}1\bar{1})$ was decreased by piezoelectric response. The Pockels coefficient in TM-mode r_{33} showed large change for compositions, while that in TE-mode r_{13} showed little change. The maximum Pockels coefficient r_c of 156 pm/V was obtained for the epitaxial PLZT film with Ti/(Zr + Ti) ratio of 50%, and this value increased 1.5-fold compared to that of the polycrystalline film with Ti/(Zr + Ti) ratio of 40% which showed maximum Pockels coefficient of 104 pm/V. These results indicated that the Zr/Ti ratio dependence of electrooptic property have different trend between in the epitaxial films and in the polycrystalline films. Finally, we concluded that the Ti/(Zr + Ti) ratio of 50% is optimum to obtain the large electrooptic effect in (111)-oriented epitaxial PLZT films with La content of 2 at.%. The research of other composition dependence of electrooptic property in the epitaxial PLZT films is a future work.

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References

1) T. Fujii, T. Suzuki, Y. Fujimori, T. Nakamura, M. Moriwake and H. Takasu, *Jpn. J. Appl. Phys.*, 45, 7520–7523 (2006).
2) A. L. Glebov, M. G. Lee, L. Huang, S. Aoki, K. Yokouchi, M. Ishii and M. Kato, *IEEE J. Sel. Top. Quantum Electron.*, 11, 422–430 (2005).
3) S. Okamura, Y. Mochiduki, H. Motohara and T. Shiosaki, *Integr. Ferroelectr.*, 69, 303–313 (2005).
4) H. Shima, H. Naganuma and S. Okamura, *Jpn. J. Appl. Phys.*, 45, 7279–7282 (2006).
5) H. Shima, T. Iijima, H. Funakubo, T. Nakajima, H. Naganuma and S. Okamura, *Jpn. J. Appl. Phys.*, 47, 7541–7544 (2008).
6) M. Ishii, K. Sato, M. Kato and K. Kurihara, *Key Eng. Mater.*, 269, 65–68 (2004).
7) T. Iijima, S. Ito and H. Matsuda, *Jpn. J. Appl. Phys.*, 41, 6735–6738 (2002).
8) M. Kondo, K. Saito, M. Ishii, N. Wakiya, K. Shinozaki and K. Kurihara, *Jpn. J. Appl. Phys.*, 45, 7516–7519 (2006).