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Journal of the European Ceramic Society 24 (2004) 993–997

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Stoichiometry and crystal orientation of YAG-PLD derived ferroelectric PZT thin film

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Abstract

$PbZr_{0.53}Ti_{0.47}O_3$ (PZT) thin films were synthesized by the pulsed laser deposition (PLD) technique using the fourth harmonic generated light source ($\lambda = 266$ nm) of Nd^{3+}:$Y_3Al_5O_{12}$ (YAG) laser beam. The film crystallinity and stoichiometry were examined as a function of the partial oxygen pressure (P_{O_2}) in the range 1–10 Pa during the PLD process. With increasing P_{O_2}, the major crystalline phase of the thin film was changed from pyrochlore to perovskite. This variation was correlated with the volatile property of Pb element during the deposition process. At P_{O_2} of 5 Pa, perovskite formation and its (111) crystallographic orientation were maximized in the thin film when Pt/Ti/SiO_2/Si substrates were used. Additionally, the control of the preferred crystallographic orientation of the PZT thin film was performed using PZT(sol-gel-seed)Pt/Ti/SiO_2/Si and $LaSr_{0.5}Co_{0.5}O_3$/SiO_2/Si substrates. A laser-Doppler-interferometer measured the electric-field-induced displacement of 1-μm-thick PZT films with different growth conditions in order to investigate the effect of stoichiometry and crystal orientation on the piezoelectric property.

Keywords: Actuators; Films; Piezoelectric properties; PZT; X-ray methods

1. Introduction

The number of reports on the preparation of ferroelectric thin films by pulsed laser deposition (PLD) using excimer laser source, in particular, has remarkably increased in recent years.[1–3] One of the most important advantages of employing the PLD to synthesize oxide thin films is the fact that the film deposition can be carried out under an ambient of the desired pressure, even in oxidative atmosphere, since there is no energy source in the deposition chamber but short-wavelength pulsed laser is focused onto the target material through a chamber window from external laser generator. Compared with excimer laser, such as KrF ($\lambda = 248$ nm) and XeCl ($\lambda = 308$ nm), Nd^{3+}:$Y_3Al_5O_{12}$ (YAG) laser has superior advantages in running cost, easy maintenance and safety. Nd^{3+}:YAG laser ($\lambda = 1064$ nm) can generate a shorter wavelength of $\lambda = 266$ nm (the forth harmonic generation, FHG) using nonlinear optical crystals (KH_2PO_4, KDP), which is expected to have a higher average power transmission close to KrF excimer laser. While there are enough reports on the synthesis of ferroelectric thin films using the excimer laser, only limited work has been reported for the preparation of ferroelectric thin films using the FHG- Nd^{3+}:YAG laser as a light source for the PLD.

In the present study, the PLD technique using FHG-Nd^{3+}:YAG was applied for the preparation of $PbZr_{1-x}Ti_xO_3$ (PZT) thin films with the composition corresponding to a morphotropic phase boundary (MPB) around $x = 0.47$ which separate a tetragonal Ti-rich crystallographic phase from a rhombohedral Zr-rich phase. This paper gives data on film crystallinity and composition as a function of the partial oxygen pressure (P_{O_2}) during the YAG-PLD processing to confirm a proper condition of P_{O_2}. The ferroelectric and piezoelectric properties of the derived thin films are also reported. Additionally, we prepared PZT thin films with different crystal orientations in the MPB region by selecting sub-

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doi:10.1016/S0955-2219(03)00456-4

strate materials to study the dependence of the film texture on the piezoelectric properties.

2. Experimental

A FHG–Nd^{3+}:YAG laser beam with a wavelength $\lambda = 266$ nm and a repetition rate of 10 Hz was focused onto a rotating, sintered PZT bulk target. The fluence of the incident laser beam was 1.5 J/cm^2 and the base pressure of the vacuum chamber was 10^{-5} Pa. The vaporized material was deposited on Pt(111)/Ti/SiO_2/Si substrate heated at 700 °C under oxygen partial pressure (P_{O_2}) ambient in the range 1–10 Pa. The distance between the bulk target and the substrate was 46 mm. After the film formation, the specimen was cooled to room temperature (5 °C/min) in 0.1 MPa of oxygen. Further two kinds of substrates, (1) a Pt/Ti/SiO_2/Si substrate coated with a sol-gel-derived PZT seed layer and (2) a SiO_2/Si substrate coated with a PLD-derived $LaSr_{0.5}Co_{0.5}O_3$ (LSCO) bottom-electrode/seed layer, were used for controlling the preferred crystallographic orientation of deposited PZT (Zr/Ti = 53/47) thin films. Detailed sample preparation procedure is described elsewhere.[4,5]

The films were analyzed by X-ray diffractometry (XRD) using Cu*Ka* radiation, X-ray fluorescence spectroscopy (XRF), and atomic force microscopy (AFM). Polarization versus applied electric field (*P-E*) hysteresis loops were recorded using a modified Sawyer–Tower circuit. The electric-field-induced displacement at the center of the Au top electrode was measured using a laser-Doppler-displacement measuring system (Graphtec AT7211, Japan) under a bipolar drive up to 20 V_{p-p} at 1 kHz.

3. Results and discussion

Fig. 1 compares the XRD patterns of thin films deposited on the Pt(111)/Ti/SiO_2/Si substrate as a function of P_{O_2} in the PLD processing. In the low oxygen partial pressure up to 3 Pa, the pyrochlore (paraelectric $A_2B_2O_7$) phase forms mainly instead of perovskite (ferroelectric ABO_3) phase. With increasing P_{O_2}, the formation of the pyrochlore phase is suppressed and the perovskite phase becomes dominant. The formation of perovskite phase is maximized at P_{O_2} of 5 Pa (Fig. 2(a)). Above P_{O_2} of 5Pa, however, the deposition rate for film growth was slowed down with increasing P_{O_2}. Therefore, the diffraction intensity of perovskite phase is also weakened. Under the present PLD condition using the Pt(111)/Ti/SiO_2/Si substrate, (111)-preferred orientation is observed in the PZT thin film (Zr/Ti = 53/47). Such (111)-preferred orientation is most enhanced at P_{O_2} of 5 Pa which agrees well with a suitable P_{O_2} condition for

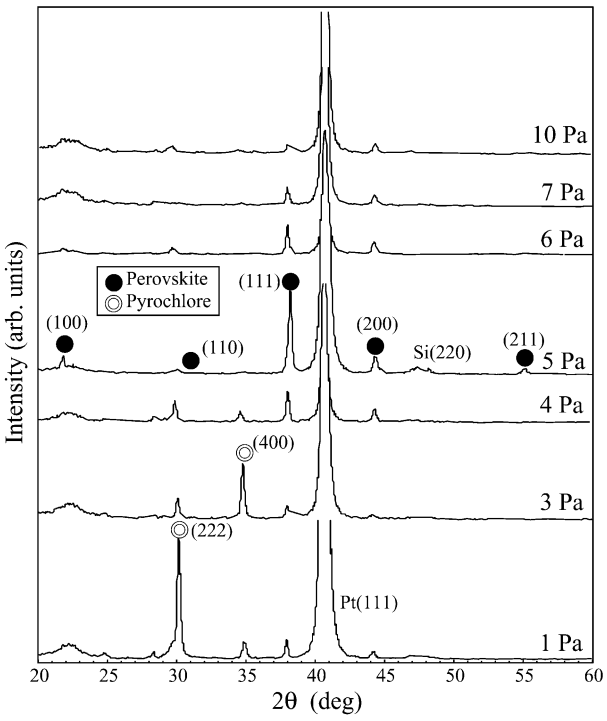

Fig. 1. XRD patterns of the thin films deposited on the Pt/Ti/SiO_2/Si substrates under various P_{O_2} in the PLD process.

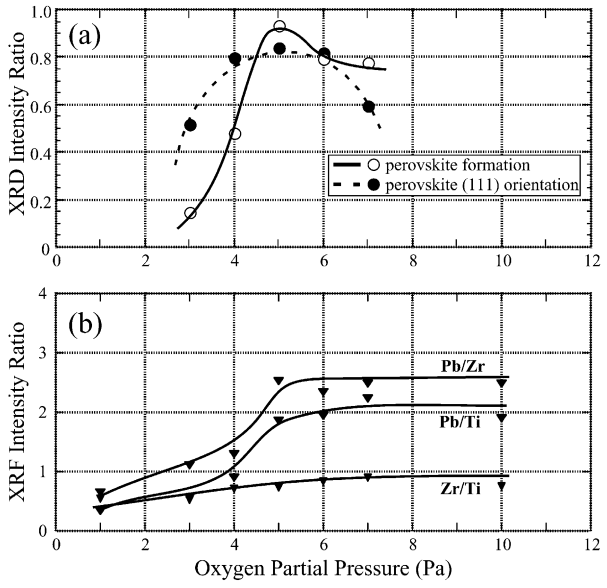

Fig. 2. (a) The degrees of perovskite formation and (111) orientation, and (b) XRF intensity ratios for the thin films synthesized by PLD at various P_{O_2}.

perovskite formation. The orientation ratio reaches 84%, where the degree of (111) orientation was determined by the peak intensity fraction of (111)/[(100) + (110) + (111)] in the perovskite structure.

According to XRF measurement (Fig. 2(b)), both Pb/Zr and Pb/Ti intensity ratios remain at low values in

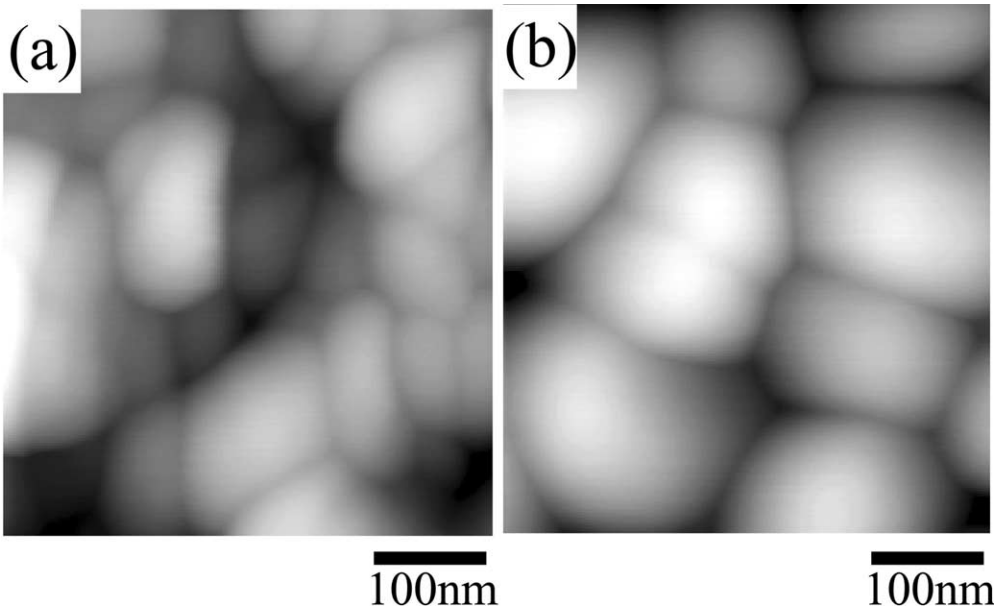

Fig. 3. AFM images of the surface of the thin films synthesized by PLD at P_{O_2} of (a) 3 Pa and (b) 5 Pa.

low P_{O_2} conditions and increase steeply in the vicinity where P_{O_2} exceeded 4 Pa to form PZT (Zr/Ti = 53/47), which indicates that the evaporation of Pb occurred actively under low P_{O_2} condition. As a result, pyrochlore phase is preferably formed at low P_{O_2}, since there is a quantitatively close relationship between Pb content and crystal structure in the PZT system.[6]

Fig. 3 presents the AFM images of the surface morphology of the PZT thin films prepared at different P_{O_2} of 3 and 5 Pa. Both films are composed of small grains, but the grain size and its packing density are different. The thin film grown at P_{O_2} of 5 Pa shows relatively dense morphology with a grain diameter of approximately 150 nm. On the other hand, it is apparent that the thin film grown at P_{O_2} of 3 Pa demonstrates somewhat smaller grains and less dense morphology. The morphology difference seems to have been affected by the degrees of crystallinity, stoichiometry and grain mobility (sinterability) on the heated substrate during the film deposition with different P_{O_2}.

Dependence of P_{O_2} during film deposition on the ferroelectricity of the PZT thin films was investigated by observing *P-E* hysteresis loops, as shown in Fig. 4. The thin film grown at P_{O_2} of 1 Pa showed no ferroelectric *P-E* hysteresis loop. In contrast, the thin films grown at P_{O_2} of 3 Pa or more demonstrated hysteresis loops, but an elliptical loop indicating the contribution of non-ferroelectric pyrochlore phase is observed for the thin film grown at P_{O_2} of 3 Pa. Such an elliptical loop is transferred into typical rhomboidal *P-E* hysteresis loop with increasing P_{O_2}. Larger remanent polarization (P_r) and smaller coercive field (E_c) are obtained for the thin film grown at P_{O_2} of 5 Pa than the thin film grown at P_{O_2} of 7 Pa, which seems to have correlation with the degrees in crystal orientation as well as PZT stoichiometry (Fig. 2).

As shown in Fig. 5, the electric-field-induced strain along the film thickness (1 μm) was monitored as displacement which arose from the bending vibration of the PZT film/substrate, i.e., the PZT film expanded or shrank in the horizontal direction, which led to the deflection of the film/substrate structure in the vertical direction as a clamp-free bimorph vibration.[7] Among the thin films deposited on the Pt(111)/Ti/SiO_2/Si substrate, the largest electric-field-induced displacement is observed for the thin film grown at P_{O_2} of 5 Pa, while nearly identical electric-field-induced strains are measured in the two films grown at P_{O_2} of 3 and 7 Pa. It is

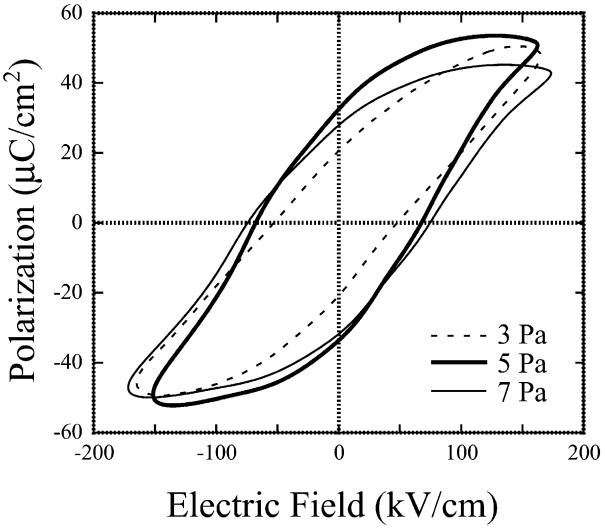

Fig. 4. *P-E* hysteresis loops of the thin films synthesized by PLD at various P_{O_2}.

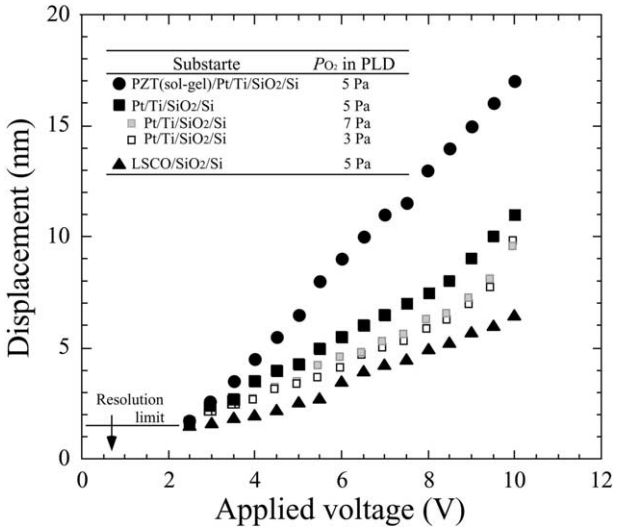

Fig. 5. Piezoelectric displacement of several kinds of PZT thin films with different conditions in the PLD process.

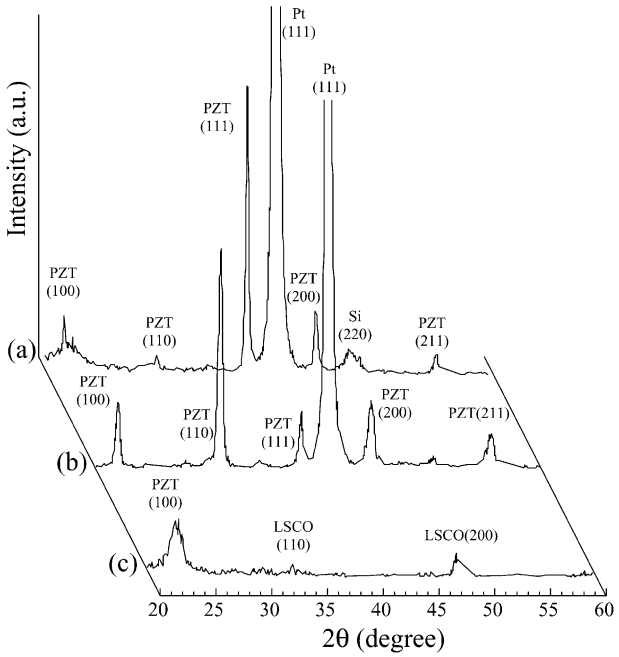

Fig. 6. XRD patterns of PZT (Zr/Ti = 53/47) thin films deposited on (a) $Pt/Ti/SiO_2/Si$, (b) PZT(sol–gel seed)/$Pt/Ti/SiO_2/Si$ and (c) LSCO/SiO_2/Si substrates.

apparent that the magnitude of the displacement is correlated with the degree of the crystal orientation rather than that of the stoichiometry, when one compares Fig. 2(a) with Fig. 5. It is therefore possible that film texture strongly affects the piezoelectric properties observed in the PZT thin film.

In order to study the dependence of the film texture on the piezoelectric properties, PZT (Zr/Ti = 53/47) thin films with different crystal orientations were synthesized at P_{O_2} of 5 Pa using YAG-PLD technique by selecting the appropriate substrate materials. As shown in Fig. 6, the PZT thin films demonstrated different preferred crystal orientations depending on the substrates. While the film deposited on the $Pt/Ti/SiO_2/Si$ substrate showed a strong (111) texture, the film deposited on the PZT(sol–gel seeds)/$Pt/Ti/SiO_2/Si$ substrate showed relatively random orientation with a major peak of (110) in the XRD pattern. In contrast, the film deposited on the $LSCO/SiO_2/Si$ substrate displayed (100)-oriented structure in the XRD pattern.

These films showed different electric-field-induced displacement depending on their crystallographic orientations, regardless of the same chemical composition (Zr/Ti = 53/47, MPB) and sample dimensions. Throughout this work, the displacement was calculated using the top amplitude of the time-dependent output wave recorded at elevated applied voltage under bipolar drive up to 20 V_{p-p} (−10/+10 V) which corresponds to the electric bias field of approximately 2 E_c for 1-μm-thick film. Therefore, the films were run through the butterfly strain curve caused by polarization reversal during the bipolar drive, indicating contribution of domain wall motion, such as non-180° domain walls, in this strain measurement. Additionally, MPB motion due to the coexistence of rhombohedral and tetragonal phases can also be attributed to such a domain wall motion. An almost linear increase and largest displacement are observed with increasing applied drive voltage for the PZT thin film deposited on the PZT(sol–gel seeds)/$Pt/Ti/SiO_2/Si$ substrate, while the other films show slightly non-linear curves with smaller displacements. This nonlinear behavior might have been related to the irreversible non-180° domain wall motions under the bipolar electric driving field.[8] It seems that the piezoelectric property of PZT thin films with MPB composition, where inherent effective polar axis directions have been remain unsettled, complicatedly relates to the degrees of crystallographic orientation and domain wall motion. Our study shows that the larger piezoelectric displacement with lower nonlinearity is observed in the randomly oriented PZT thin film than that in the other preferred texture films. This may be a consequence of the particular domain-wall structure for this orientation which correlates with the co-existence of the multiple polarization directions at the MPB composition.

4. Conclusion

The FHG–Nd^{3+}:YAG laser beam was utilized as a laser source for the PLD synthesis of $PbZr_{0.53}Ti_{0.47}O_3$ (PZT) thin films, since YAG laser has superior advantages especially in running cost, easy maintenance and safety to KrF excimer laser. YAG-PLD technique was successfully able to form PZT thin films with different preferred crystallographic orientation on various sub-

strate materials. During the PLD processing, the oxygen partial pressure (P_{O_2}) strongly affected the crystallinity and stoichiometry of the thin film. In particular, the preferred crystallographic orientation of the thin film contributed significantly to the piezoelectric response.

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