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Electrical properties of PLZT thin films formed by photochemical metal-organic deposition with various Zr/Ti ratios

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Abstract Lanthanum-doped lead zirconate titanate (PLZT) films formed by photochemical metal-organic deposition using photosensitive starting precursors were characterized. The substitution of La for Pb was found to induce the improved ferroelectric properties, especially fatigue property through the reduction of oxygen vacancies with excess electrons. But remnant polarization was reduced, because the doping of La gives the same effect as shift of composition of Zr/Ti ratio in PLZT film from morphotropic phase boundary composition of PZT(Zr/Ti ratio of 56/44). The measurement results of polarization-electric field and capacitance-voltage indicate that the composition of maximum ferroelectric properties of PLZT film shifts toward Ti-rich side between 52/48 and 48/52 of Zr/Ti ratio. A decrease in Zr/Ti ratio induced an improvement in I-V and fatigue properties due to the low defect concentration such as Pb or O vacancies and the intergrain depletion of grain boundary limited conduction.

Keywords PLZT · MPB composition · Direct-patterning · Photochemical reaction · UV exposure

Introduction

For the application of a film to an electronic device, various thin film deposition techniques such as chemical vapor deposition, sputtering, and sol-gel process etc. have been investigated [1]. After deposition, a patterning process should be carried out. Ion etching and ion milling are presently the most widely applied processes for fine patterning of ferroelectric films. However those processes tend to degrade the properties of the film [2]. So, a new patterning of the film, which does not induce the degradation of the properties of the film, has been required.

Recently, there has been an increasing interest in photochemical metal-organic deposition (PMOD) of a thin film [3]. PMOD lithographically produces a patterned structure without using either photoresist or dry etching because of the photosensitive nature of starting precursors. That is, after exposure to UV, image development can be accomplished directly by removing the unexposed area by rinsing in a solvent.

A number of papers have reported on the effects of doping on the electrical properties of PZT films [4]. One of alternatives to improve the electrical properties is doping with A (Pb)-site donors like La^{3+}. However, a structure-composition relation of PLZT film at morphotropic phase boundary (MPB) composition is modified due to the doping with La. The MPB composition of PLZT film continues to draw considerable attention for the application of microelectromechanical system because PLZT films show their maximum dielectric and ferroelectric properties, especially in the composition at the MPB [5]. Therefore, it is important for PLZT film to find the MPB composition exhibiting the maximum ferroelectric properties. The electrical properties of PLZT films by PMOD with various Zr/Ti ratios are still unknown near the MPB composition.

In this work, a direct patterning method for the lithographic deposition of PLZT films with various Zr/Ti ratios was introduced by using PMOD. The ferroelectric and electrical properties of direct-patternable PLZT films with

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UV-irradiation process were investigated near MPB composition through the variation of Zr/Ti ratio.

Experimental procedure

The precursors used for the photochemical production of PZT or PLZT films were lead(II) 2-ethylhexanoate, lanthanum(III) 2-ethylhexanoate, zirconyl(IV) 2-ethylhexanoate, and titanium(IV) isopropoxide. The composition ratio of Zr/Ti was varied from 56/44 to 44/56 with fixed La concentration of 3 mol%. Also, 10% of extra Pb was added for the compensation of Pb-loss during high temperature anneal [6]. PZT or PLZT precursors dissolved in hexane were spin-coated at 2000 rpm for 30 s on two different kinds of substrate. One was chemically cleaned Pt(111)/Ti/SiO_2/Si(100) for monitoring of ferroelectric properties and the other was a p-Si(100) wafer, to show a generality of direct-patterning process. 350 nm thick PLZT film by PMOD was prepared after both a spin-coating of PLZT precursor film and UV exposure once in order to demonstrate a possibility of direct-patterning.

The precursor films for lithography were exposed for 30 min with 1000 W of mercury arc lamp passed through a chromium mask. The latent image was developed by rinsing with hexane to reveal a negative pattern. The patterned film was annealed for 10 min at 400°C. This process was repeated for each layer. Following the formation of direct-patterned structure, the patterned films were annealed at 650°C for 30 min. A 150 nm thick Pt top electrode with a 200 μm diameter was sputter-deposited and then annealed at 650°C for 10 min under O_2 ambient.

Phase formation and crystallization were monitored using X-ray diffraction (XRD). For the measurement of electrical properties, 300 nm thick film was prepared by repeated coating. The current-voltage (I-V) characteristics were obtained using HP4145B (Hewlett Packard). The ferroelectric hysteresis loop and polarization fatigue were measured using a RT66A (Radiant Technology) ferroelectric tester.

Results and discussion

XRD patterns of PLZT films coated on Pt(111)/Ti/SiO_2/Si substrate are given in Fig. 1. PLZT films with various Zr/Ti ratios were fully crystallized after anneal treatment at 650°C for 30 min under O_2 ambient. The diffraction peaks were indexed only with perovskite structure with preferred orientation of (111). The highly preferred orientation means that the nucleation of PLZT films was strongly affected from Pt substrate due to the lattice matching between Pt and PLZT [7]. According to the decrease with Zr/Ti ratio, relative intensities of (111) diffraction increased. Due to smaller size of

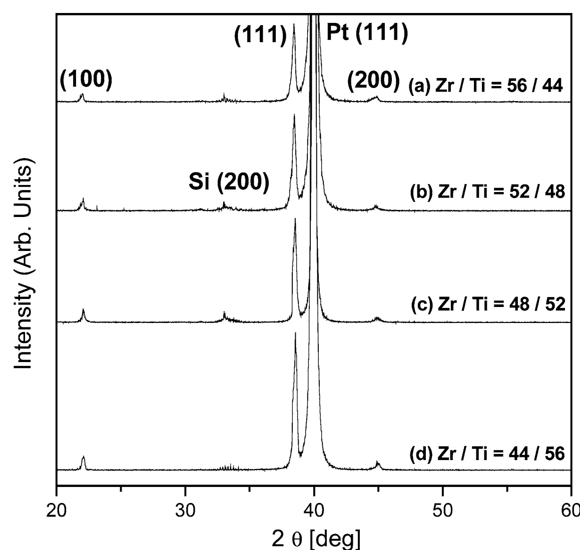

Fig. 1 XRD patterns of PLZT films annealed at 650°C as a function of Zr/Ti ratio

La compared with Pb, average size of A site cation decreases (ionic radii of Pb^{2+} and La^{3+} are 1.21 Å and 1.15 Å, respectively [8]) and in this case, PLZT film with ABO_3 structure shows higher lattice matching with Pt (111) substrate when B site cation size decreases. For example, because ionic radius of Ti^{4+} is smaller than that of Zr^{4+}, PLZT film with Zr/Ti ratio of 44/56 showed the most intensified (111) diffraction in Fig. 1.

P-E hysteresis loops of PZT and PLZT films as a function of Zr/Ti ratio with 15 voltages are given in Fig. 2. The measured remnant polarization (P_r) values of PZT films with Zr/Ti ratio of 60/40, 56/44, 52/48, 48/52, and 44/56 were 26, 32, 29, 27, and 24 $\mu C/cm^2$, respectively. Maximum P_r value was obtained with Zr/Ti ratio of 56/44, which relates to MPB composition. However, PZT bulk ceramics show maximum P_r value of the vicinity of Zr/Ti ratio of 52/48 [9]. The MPB composition of PZT films tends to move toward rhombohedral phase field, Zr-rich side, under the influence of in-plane film stress, regardless of whether it is tensile or compressive [10]. In case of PLZT films, the measured P_r values with Zr/Ti ratio of 56/44, 52/48, 48/52, and 44/56 were 19, 24, 26, and 20 $\mu C/cm^2$, respectively. MPB composition of PLZT thin film could be assigned between 52/48 and 48/52 of Zr/Ti ratio when considering a symmetric slope change in remnant polarization (P_r) values with Zr/Ti ratio. This result is contrary to the observation of G.H. Haertling that the MPB compositions of PLZT ceramics shift to more Zr-rich side than that of PZT ceramic [11]. However Y. Honda found that the MPB composition of PLZT films was expanded in Zr/Ti ratio (for example, in case of 5% of La/(Pb + La) ratio, coexistence region of tetragonal and rhombohedral phases was found as 50/50–65/35 of Zr/Ti ratio), different with that of PLZT bulk ceramics [12]. This might be due to the variation

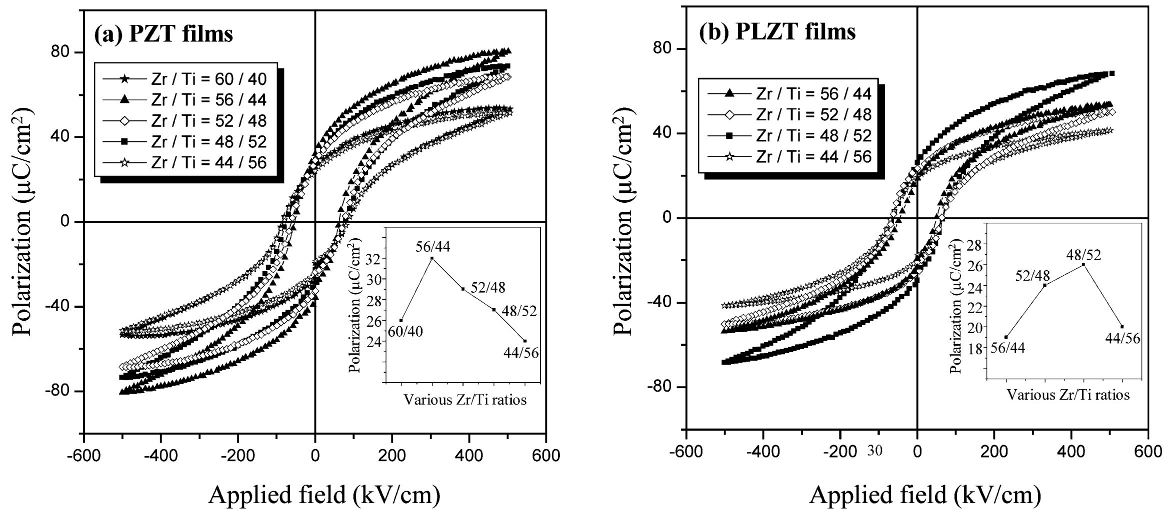

Fig. 2 P-E hysteresis loops of (a) PZT and (b) PLZT films annealed at 650°C with various Zr/Ti ratios

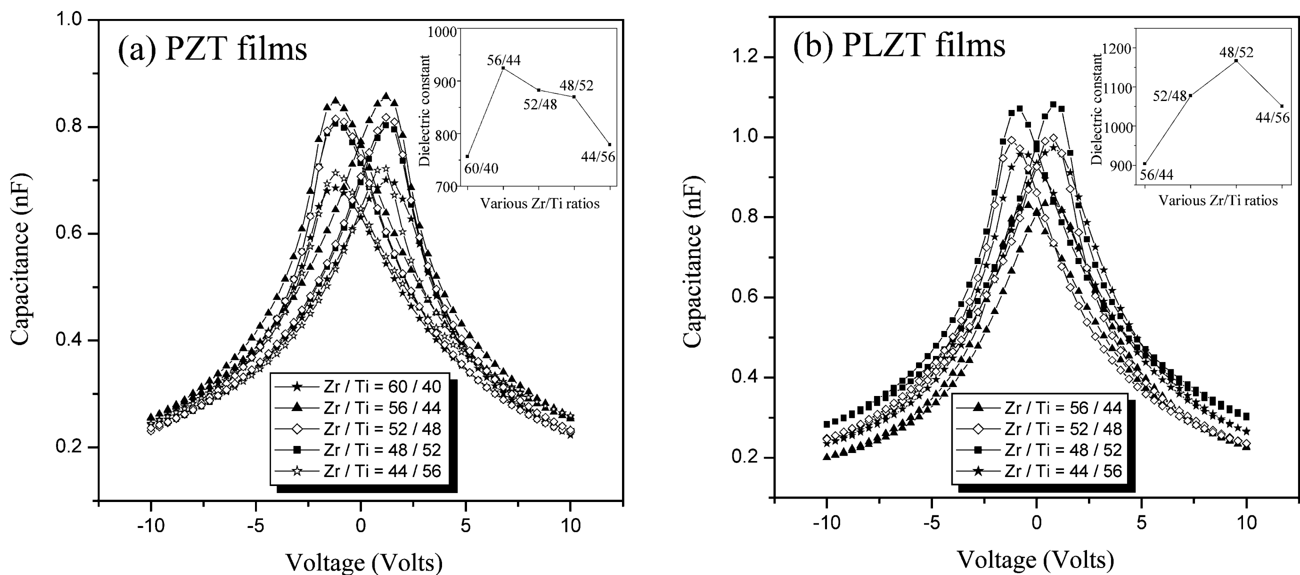

Fig. 3 C-V characteristics of (a) PZT and (b) PLZT films annealed at 650°C as a function of Zr/Ti ratio

in the residual stress, internal microstructure, growth orientation affected by substrate, and so on. Furthermore in case of PSZT ceramics, PZT-modified by Sr (smaller ionic size than Pb, same as La), MPB composition is changed from Zr-rich side to Ti-rich side according to incorporated amount of Sr [13]. As a result, the shift in the MPB composition toward Ti-rich region in our PLZT film comparing with PLZT bulk ceramics could be explained by the reduction in residual stress due to the incorporation of La and high {111} growth orientation relation with Pt substrate.

Figure 3 shows capacitance-voltage plots of PZT and PLZT films with applied voltage ranging from -10 to 10 V as a function of a Zr/Ti ratio. A dielectric constant variation was given as the inset of the figure. In case of PZT film, maximum dielectric constant was obtained with the film of Zr/Ti ratio of 56/44. The composition is identical with that obtained from the P-E measurement. The dielectric constants of PLZT films with Zr/Ti ratios of 56/44, 52/48, 48/52, and 44/56 were 904, 1078, 1167, and 1051 as given at the inset of Fig. 3(b). Measured maximum dielectric constant, 1167 was obtained with PLZT film of Zr/Ti ratio of 48/52. However, considering the positive and negative slopes of dielectric constant values according to Zr/Ti ratio, the Zr/Ti ratio for real maximum dielectric constant could be assigned between 52/48 and 48/52. This is well agreed with the observation through P-E measurements.

I–V characteristics of 300 nm thick PLZT films annealed at 650°C for 30 min are shown in Fig. 4(a). According to the decrease with Zr/Ti ratio, I–V characteristics of PLZT films were enhanced. The major leakage current source of

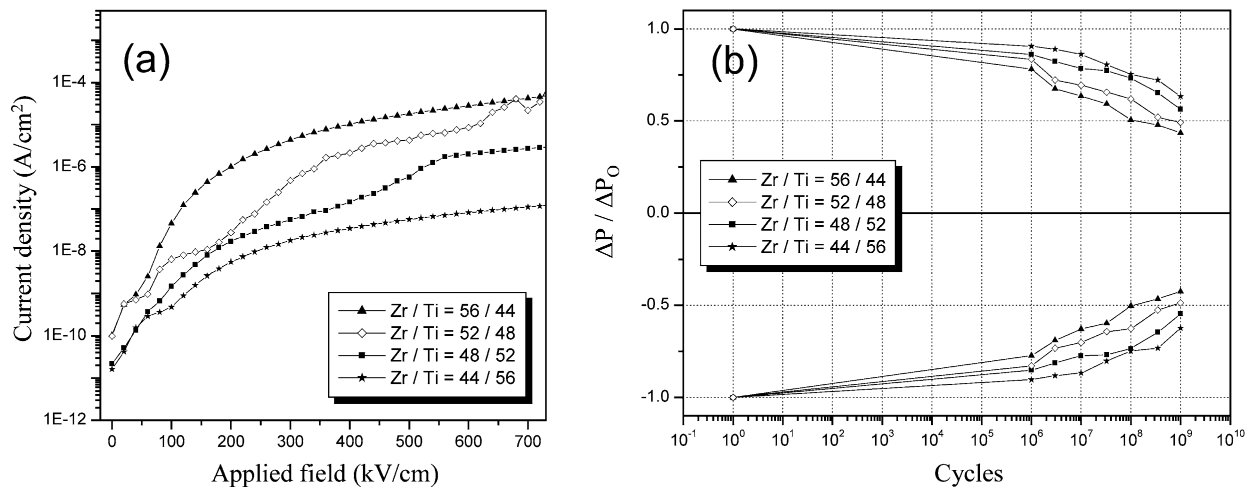

Fig. 4 (a) I-V and (b) fatigue characteristics of PLZT films annealed at 650°C with various Zr/Ti ratios

crystalline PLZT has been known to be Pb or O vacancies created during high temperature anneal for crystallization [14]. With the decrease of Zr/Ti ratio in PLZT, perovskite phase formation temperature is lowered [15]. The defect concentration of Pb and O vacancies was decreased due to lowered temperature of perovskite phase formation, namely, Zr/Ti ratio of 44/56 showed the lowest leakage. Furthermore, the reduction of grain size with decreased Zr/Ti ratio was found from the changes in the diffraction peak width by using Scherrer relation [16]. The lower leakage current density of small-grained film might be due to the inter-grain depletion of grain boundary limited conduction [17–20]. Namely, local space charges near grain boundaries inhibit current flow and the overlapped depletion region of neighboring grain boundaries are substantial cause of low leakage current. Therefore, the leakage current density of PLZT film was improved due to the decrease with Zr/Ti ratio. The leakage current of PLZT film was enhanced by La-doping through the reduction of oxygen vacancies with excess electrons. Figure 4(b) illustrates the change of polarization of PLZT films as a function of Zr/Ti ratio with a number of switching cycle through a bipolar square wave of ± 10 V at a frequency of 500 kHz. After 10^9 cycles, the remaining remnant polarizations of Zr/Ti ratios of 56/44, 52/48, 48/52, and 44/56 were about 44, 50, 57, and 63%, respectively. The PLZT film with Zr/Ti ratio of 44/56 showed not-excellent but a somewhat improved fatigue resistance. This behavior is consistent with I-V characteristic. Namely, according to the decrease Zr/Ti ratio, I-V and fatigue characteristics were improved.

The possibility of direct-patterning of a PLZT film by removing the area unexposed to UV using hexane was examined and the result is given in Fig. 5. In the SEM micrograph, the dark-gray area corresponds to a PLZT film with Zr/Ti ratio of 48/52 and the gray area to the Si substrate. The direct-patterned lines are clearly visible with

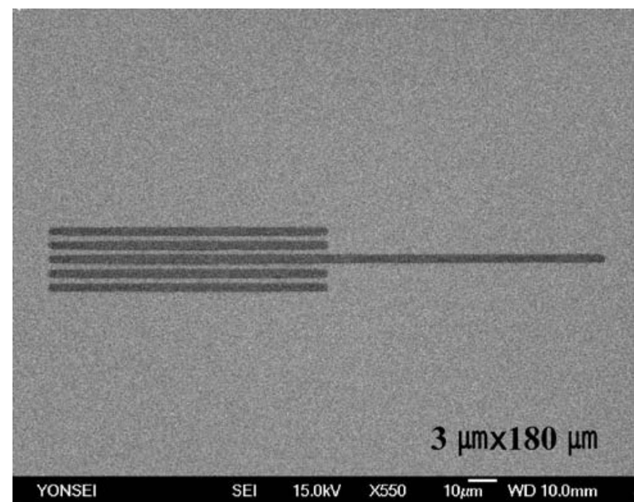

Fig. 5 SEM micrograph of UV-direct-patterned PLZT film with the Zr/Ti ratio of 48/52

$3\,\mu$m $\times$ $180\,\mu$m in size. This micrograph indicates that direct lithographic patterning of PLZT films could be accomplished by PMOD.

Conclusions

PZT or PLZT(3 mol% La) films as a function of Zr/Ti ratio were successfully characterized by using photosensitive starting precursors. Direct-patterning of PLZT films in several microns width by PMOD was accomplished by UV exposure and removal of the unexposed area of the film by rinsing with hexane. Due to high lattice matching between Ti-rich phase and Pt substrate, PLZT film with the lowest Zr/Ti ratio(in this experiment, 44/56) relatively showed the most intensified (111) diffraction. From P-E and C-V measurements, MPB composition of PLZT thin film could be

assigned between 52/48 and 48/52 of Zr/Ti ratio. In leakage current and fatigue measurements of PLZT films, a lowering of Zr/Ti ratio induced an improvement of leakage current and fatigue properties due to the lowered perovskite phase formation temperature.

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