

Effect of composition on ferroelectric properties of sol-gel derived lead bismuth titanate ($\text{PbBi}_4\text{Ti}_4\text{O}_{15}$) thin films

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Bismuth layer-structured ferroelectric $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ (PBT) thin films were fabricated on Pt/Ti/SiO₂/Si substrates by sol-gel spin coating and the effect of lead and bismuth concentration on phase transition, microstructure and ferroelectric property was investigated. Especially, the effect of non-stoichiometric compositions, that is, deficient concentration of Pb and excess concentration of Bi with respect to the stoichiometric composition, was examined. With an increase of lead and bismuth concentration, the pyrochlore phase was suppressed and PBT phase was developed. Large increases of $2P_r$ and $2E_c$ were also observed as lead and bismuth concentration increased. An improved ferroelectric property could be obtained by inserting a Bi-rich buffer layer between Pt electrode and Pb-rich PBT film. The PBT thin films with Bi-rich buffer layer showed homogeneous grain size distribution, good fatigue endurance up to 1×10^9 switching cycles, low relative permittivity of 270 and sufficient $2P_r$ values of $15.7 \mu\text{C}/\text{cm}^2$.

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1. Introduction

Research and development activities are strongly increasing worldwide on devices based upon ferroelectric thin films for nonvolatile memory (NvRAM) applications. However, ferroelectric thin films such as PbTiO_3 , PZT or PLZT, deposited on metal electrode such as Pt, have several problems in their polarization fatigue properties that afford only a limited number of switching cycles to the ferroelectric memory cells [1–6]. Recently, Bi-layer structured ferroelectric oxide films such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) [7–10], $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) [11–13] and $\text{SrBi}_2\text{Nb}_2\text{O}_9$ [14] that show little or no fatigue have been developed. Among them, SBT films have especially high potential for NvRAM device application. However, the SBT films also have some technical problems concerning reliability and processing, i.e., a low remnant polarization and a high heat-treatment temperature.

Therefore, study on other Bi-layer structured materials is needed for NvRAM application. However, many reports have been concentrated on a limited numbers

of materials represented by SBT, and few studies have been reported up to the present time on the film processing and ferroelectric properties of other Bi-layer structured ferroelectric oxide thin films. Therefore, it is interesting to investigate the film processing and the ferroelectric properties of other unknown materials belong to this Bi-layer structured ferroelectric family.

We have investigated the fabrication and ferroelectric properties of $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ (PBT) thin films as one of the efforts to enlarge the study field of NvRAM materials.

PBT is one of the bismuth layer-structured ferroelectric compounds that has the general formula: $(\text{Bi}_2\text{O}_2)^{2+}(\text{M}_{m-1}\text{R}_m\text{O}_{3m+1})^{2-}$, where M represents mono- to trivalent ions as Na, K, Ca, Ba, Sr, Pb, Bi, etc., R represents tri- to hexavalent ions as Ti, Nb, Ta, W, Fe, V etc. and the number of the oxygen octahedra, m , is 1–5 [15]. The crystal structures of PBT is composed of three pseudo-perovskite blocks, $(\text{PbBi}_2\text{Ti}_4\text{O}_{13})^{2-}$, interleaved with bismuth oxide layers $(\text{Bi}_2\text{O}_2)^{2+}$ along the pseudo-tetragonal c-axis as shown in Fig. 1 [16, 17]. PBT corresponds to the compound with $m = 4$ in the

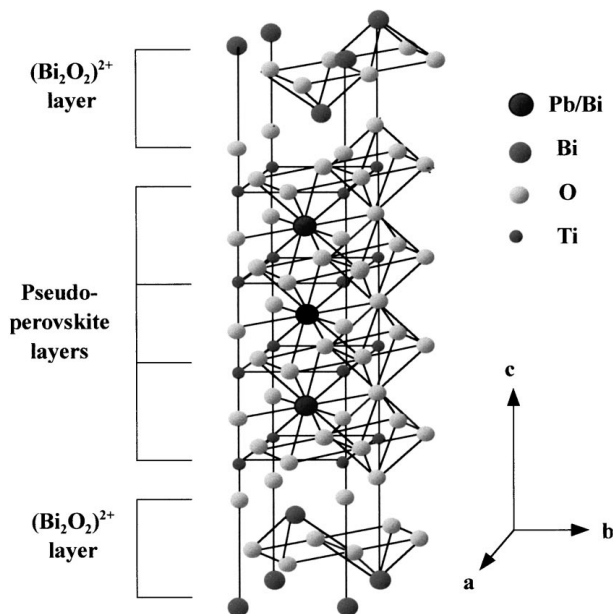


Figure 1 Schematic diagram of one half unit cell of $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$.

general formula and has a block with four TiO_6 octahedra in its perovskite layers between two nearest $(\text{Bi}_2\text{O}_2)^{2+}$ layers. The reported bulk PBT ceramics have a high Curie point of 570°C compared with 335°C of SBT and 385°C of PZT(52/48), allowing poled polycrystals to maintain a remnant polarization state up to at least 300°C with an average temperature coefficient for permittivity of $+1200\text{ppm}/^\circ\text{C}$. As for other bismuth layer-structured ferroelectrics, $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ shows anisotropy in ferroelectricity, that is, a large dielectric constant and large reversible polarization along the a(b)-axis and a small dielectric constant and a small polarization along the c-axis of orthorhombic structure [18].

PBT was chosen in this study because of the reported beneficial properties of bulk PBT ceramics as follows [16–19];

(i) having the most large number of same family compounds ($m = 4, 5, 6, 7$) that is very interesting for future studies on the crystal structure and its effect on ferroelectric properties in Bi-layer structured ferroelectric thin films,

(ii) its large polarization value ($+11 \mu\text{C}/\text{cm}^2$ along a(b)-axis in polycrystal at R.T., $+8 \mu\text{C}/\text{cm}^2$ along a(b)-axis and $+0.2 \mu\text{C}/\text{cm}^2$ along c-axis in single crystal (not saturated, measured at 200°C , at $\pm 34 \text{ kV}$),

(iii) small dielectric constant of 250 at 25°C ,

(iv) relatively low sintering temperature of 1050°C – 1100°C compared to the high sintering temperature over 1200°C for SBT bulk ceramics.

These dielectric properties and the inherent structure of $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ are very attractive for memory applications, because small non-switching linear response (ϵE), and faster switching speed, high retention and high endurance are expected as in other Bi-layer structured ferroelectrics.

Otherwise, it has been reported that 20%–30% Sr-deficient and 10–20% Bi-excess sol-gel films yield

high P_r values than the films with stoichiometric Sr/Ta atomic ratio in SBT thin films heat-treated at 700°C – 800°C [20–22]. However, the reason why P_r value increases in SBT is not clear yet. Therefore, it is also interesting to examine the non-stoichiometric composition effect on ferroelectric property of PBT thin films, and it is expected to find a clue for explanation on the relationship between composition and ferroelectric property in Bi-layer structured ferroelectric thin films including SBT.

In this paper, the effect of lead and bismuth concentration on phase transition, microstructure and ferroelectric property was mainly investigated.

2. Experimental procedure

The procedure for preparation of PBT precursor solutions is illustrated in Fig. 2. Bismuth acetate ($\text{Bi}(\text{OCH}_2\text{COO})_2$), in an amount of 0.01–0.014 mol and lead acetate trihydrate ($\text{Pb}(\text{OCH}_2\text{COO})_2 \cdot 3\text{H}_2\text{O}$) in an amount of 0.002–0.00275 mol were initially dissolved and distilled in glacial acetic acid. Two times of distillation-dilution process was repeatedly carried out using a vacuum evaporating system (R-114RE, Buchi) at 60°C until the volume of the solution reached one-third of its initial state. A stoichiometric amount of titanium isopropoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$), was added to this mixture with constant stirring and then diethanolamine (DEA, $\text{HN}(\text{C}_2\text{H}_5\text{OH})_2$) was added as a chelating agent to stabilize hydrolysis and condensation reaction and to enhance the solubility of the acetates [23]. 0.002 mol of H_2O was added to the solution for hydrolysis reaction. The solutions in which DEA was not added were extremely unstable and precipitated within 1 h. The solution that has DEA/Ti molar ratio of 10 showed a lifetime of over 1 month and good adhesion properties. The obtained DEA-complexed PBT solutions were distilled again and diluted with acetic acid to evaporate by-products. The coating solutions were filtered

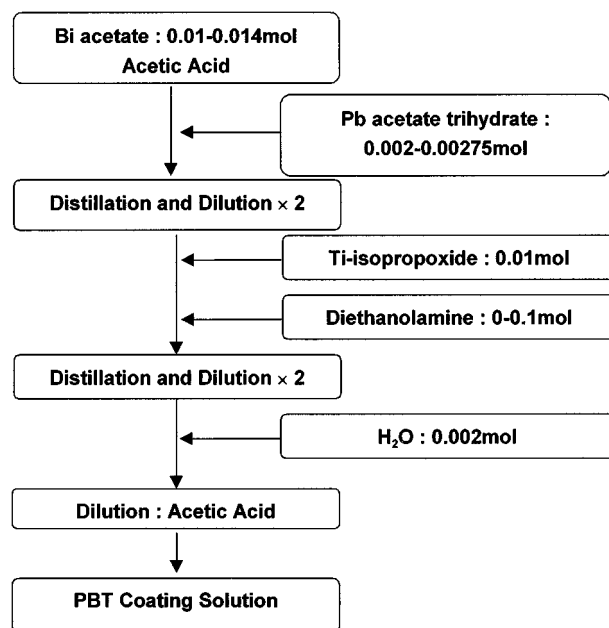


Figure 2 Flow diagram for the preparation of PBT coating solutions.

TABLE I Samples prepared for this study

Composition (Pb/Bi/Ti)	Buffer layer (Pb/Bi/Ti)	Heat treatment (°C/30 min)	Thickness (nm)	$2P_r$ ($\mu\text{C}/\text{cm}^2$)	$2E_c$ (kV/cm)
1/4/4	—	700	288	12.6	199
1/4.8/4	—	700	332	6.2	204
1/5.2/4	—	700	297	1.6	110
1/5.6/4	—	700	325	1.4	100
0.8/4/4	—	700	299	7.2	90
0.9/4/4	—	700	310	10.8	102
1.0/4/4	—	700	304	12.3	204
1.1/4/4	—	700	328	13.1	191
1.1/4/4	1/5.6/4	700	334	15.7	122
1.1/4/4	1/5.6/4	700	508	7.5	98
1.1/4/4	1/5.6/4	700	685	6.3	99
1.1/4/4	1/5.6/4	600	350	—	—
1.1/4/4	1/5.6/4	750	305	—	—
1.1/4/4	1/5.6/4	800	285	—	—

through a 0.2 μm PTFE membrane and deposited onto Pt/Ti/SiO₂/Si(100) and Pt/Ti/Si(100) substrates (Pt = 200 nm, Ti = 50 nm (SiO₂ = 500 nm)) by spin coating at 3000 rpm for 30 sec, and were dried at 450–500°C for 1 min. Coating-drying process was repeated until the desired film thickness was obtained. The thickness of each spin-coated layer after final sintering was about 20 nm. Final sintering was conducted at 600–800°C for 30 min at a heating rate of 35°C/min in an electric furnace with flowing O₂ gas at a speed of 40 ml/min. Pt upper electrode of 300 μm diameter was formed by sputtering and then heat-treated at 600°C for 10 min. All the samples prepared for this study were summarized in Table I.

Phase development and film orientation were determined by X-ray diffractometer (Philips) using Cu K α radiation at room temperature. Film thickness was determined using alpha step (model 200, Tencor Instruments). Field-emission scanning electron microscope (FE-SEM S4100, Hitachi) was used to observe the film microstructure. Relative permittivity and dissipation factor were measured using an impedance analyzer (YHP4192A, Yokogawa Hewlett Packard) at 1 MHz at room temperature. Ferroelectric properties were determined by RT6000HVS (Radiant Technologies).

3. Results and discussion

3.1. Effect of Bi and Pb concentrations on phase growth and ferroelectric property

Main peaks in the XRD patterns of PBT(Pb/Bi/Ti = 1/4y/4; y = 1.0–1.4) films on Pt/Ti/SiO₂/Si, and remnant polarization ($2P_r$) and coercive field ($2E_c$) as a function of Bi concentration are shown in Fig. 3. The peak intensity of pyrochlore Bi₂Ti₂O₇ decreases and those of (0014)(119) and (200) peaks of PBT increases with increasing Bi concentration from 4 (y = 1.0) to 5.6 (y = 1.4). Volatilization of Bi [7] and diffusion of Bi atoms into the substrate is attributed to co-existence of pyrochlore and PBT phases in the film prepared with stoichiometric PBT composition (Pb/Bi/Ti = 1/4/4). Notwithstanding large amount of excess Bi content,

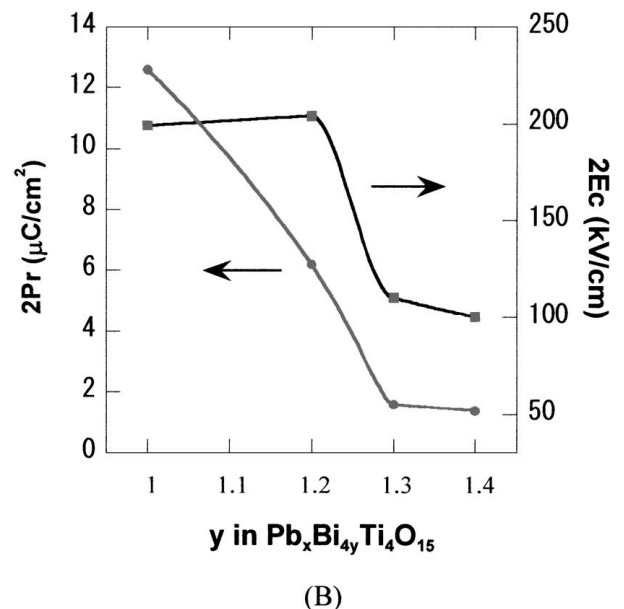
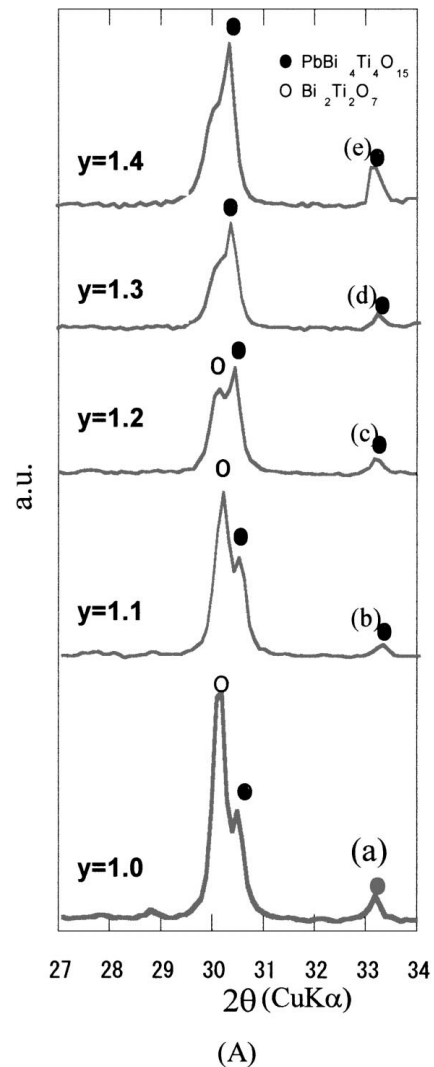


Figure 3 (A) XRD patterns of Pb_xBi_{4-y}Ti₄O₁₅ thin films; (a) x = 1.0, y = 1.0, (b) x = 1.0, y = 1.1, (c) x = 1.0, y = 1.2, (d) x = 1.0, y = 1.3 and (e) x = 1.0, y = 1.4, and (B) $2P_r$ and $2E_c$ as a function of Bi concentration, y.

some extent of remained pyrochlore phase were observed at y = 1.4 composition. Even though pyrochlore phase decreases and PBT phase increases with an increase of Bi concentration, $2P_r$ and $2E_c$ extremely

decreases. This result implies that excess Bi may reside in the grain boundaries of the PBT(1/5.6/4) thin film in amorphous bismuth oxide form. Reported drastic increase of P_r as Bi concentration increases in SBT films (x from 1.0 to 1.2 in $\text{SrBi}_{2x}\text{Ta}_2\text{O}_9$) was not observed in PBT film.

Fig. 4 shows the main peaks in the XRD patterns of the PBT($\text{Pb}/\text{Bi}/\text{Ti} = x/4/4$; $x = 0.8\text{--}1.1$) films and $2P_r$ and $2E_c$ as a function of Pb concentration. With an increase of Pb concentration from 0.8 to 1.1, a decrease of pyrochlore phase and an increase of PBT phase were observed. Large increases of $2P_r$ and $2E_c$ observed in the Pb concentration range of $x = 0.8\text{--}1.1$ are explained as a result of the PBT phase growth. This result is also very different with the tendency of increasing P_r with decreasing Sr concentration in SBT. An increase of $2P_r$ and $2E_c$ in the range of $x = 0.8\text{--}1.1$ is rather resemble PZT thin films, and may be due to a compensation effect for Pb vacancies produced by Pb volatilization, that has been reported previously in the studies on Pb-based perovskite structured thin films, i.e. PbTiO_3 or PZT [4].

Drastic increase of ferroelectric property at non-stoichiometric composition (deficient Pb and excess Bi in PBT) that has been reported in SBT at reduced concentration of centered-cation in perovskite block (Sr) and excess concentration of Bi, could not be observed in this study. Large Pb volatilization and high m value of PBT structure ($m = 4$ for PBT, $m = 2$ for SBT in the general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{M}_{m-1}\text{R}_m\text{O}_{3m+1})^{2-}$) resulting in more narrow tolerance factor region for perovskite blocks (0.85 to 0.89 for $m = 4$) [17], compared to large tolerance factor region in SBT (0.81 to 0.93 for $m = 2$) that is enough even for formation of inter-growth layers [24–26] in SBT may be the reason for this difference between PBT and SBT.

3.2. Effect of Bi-rich buffer layer on phase growth and ferroelectric property

In order to clarify the main reason for the changes in phase and ferroelectric property by Bi concentration change, a PBT film with Bi-rich buffer layer ($\text{Pb}/\text{Bi}/\text{Ti} = 1.0/5.6/4$) was fabricated by a two-step coating process. To prepare the film with Bi-rich buffer layer, only the first spin layer was deposited with $\text{Pb}/\text{Bi}/\text{Ti} = 1/5.6/4$ composition solution, and then $\text{Pb}/\text{Bi}/\text{Ti} = 1.1/4/4$ composition solution was repeatedly spin-coated onto the substrate until the desired thickness was achieved. (hereafter called PBT film with buffer layer).

Fig. 5 shows XRD patterns for PBT thin films with and without PBT buffer layer. The pyrochlore phase observed in the XRD pattern for PBT(1.1/4/4) film decreased in the XRD pattern for PBT film with buffer layer. This suggests that formation of pyrochlore phase and low ferroelectric property in the film prepared with stoichiometric composition ($\text{Pb}/\text{Bi}/\text{Ti} = 1/4/4$) is due to insufficient Bi concentration in the first coated layer (about 20 nm thick) caused by the diffusion of Bi into the substrate.

FE-SEM images of PBT thin films with and without Bi-rich buffer layer are shown in Fig. 6. The grain size

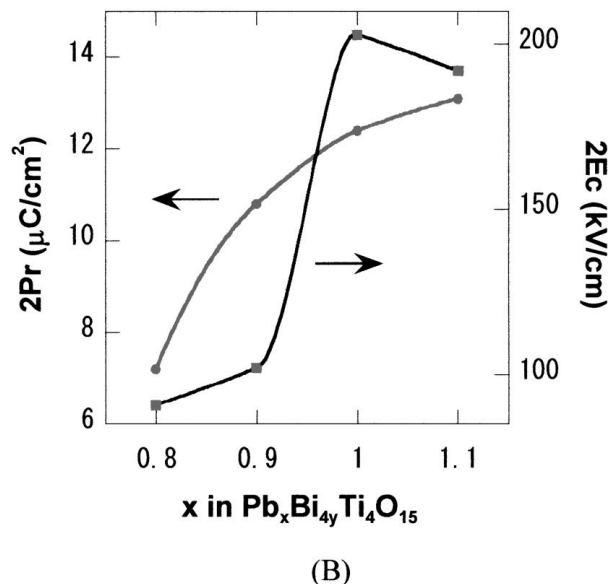
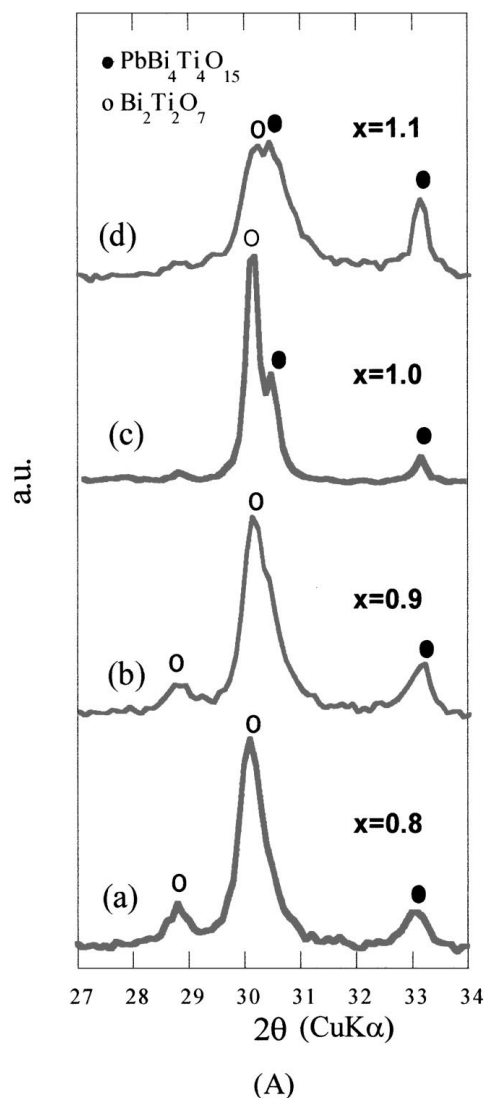


Figure 4 (A) XRD patterns of $\text{Pb}_x\text{Bi}_{4-y}\text{Ti}_4\text{O}_{15}$ thin films; (a) $x = 0.8$, $y = 1.0$, (b) $x = 0.9$, $y = 1.0$, (c) $x = 1.0$, $y = 1.0$, (d) $x = 1.1$, $y = 1.0$, and (B) $2P_r$ and $2E_c$ as a function of Bi concentration, x .

distribution of the PBT film without buffer layer is very random compared to the PBT film with buffer layer that shows a uniform grain size distribution. In order to observe the diffusion of bismuth into the substrate

through Pt electrode layer, a substrate without SiO₂ layer was used. The XRD pattern of the PBT(1/4/4) film with buffer layer deposited onto Pt/Ti/Si substrate is shown in Fig. 7. A large peak of Bi₂SiO₅ around 2θ of 29° was detected and this strongly supports the possibility of Bi diffusion into the substrates. How-

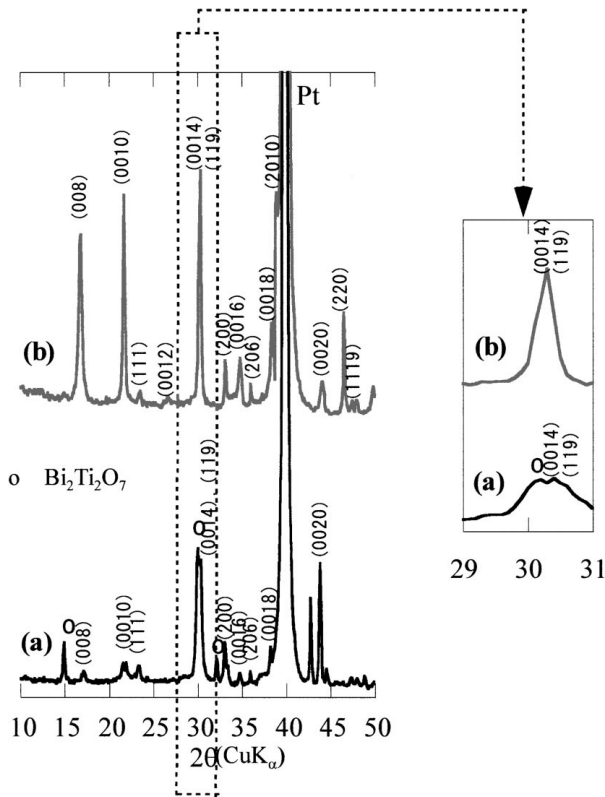


Figure 5 XRD patterns of PBT (1.1/4/4) thin films (a) without and (b) with buffer layer.

ever, single PBT phase could not be obtained even in this film with buffer layer (see Fig. 10a). In addition to Bi-diffusion into substrate, Bi-volatilization also seems to be effective for development of pyrochlore phase.

Fig. 8 shows P-E hysteresis loops for PBT thin films with and without the buffer layer. $2P_r$ of the film with buffer layer increased from 13.1 $\mu\text{C}/\text{cm}^2$ for the film without buffer layer to 15.7 $\mu\text{C}/\text{cm}^2$. Homogeneous microstructure and suppression of pyrochlore phase is responsible for a large increase of ferroelectric property in PBT films.

3.3. Effect of thickness on film orientation and ferroelectric properties

XRD patterns for the PBT films (Pb/Bi/Ti = 1.1/4/4) with different film thickness are shown in Fig. 9. Only the main (444) peak of pyrochlore Bi₂Ti₂O₇ phase could be detected near PBT (0041/119) peak around 2θ of 30° in all patterns as shown in the enlarged image. Among the observed two peaks in the curve-fitted XRD peak patterns (using Lorentz function), one peak at 2θ of 29.989° is Bi₂Ti₂O₇ (444) peak and the other at 2θ of 30.456° is PBT (0014/119) peak (Fig. 10a).

Intensity fraction for Bi₂Ti₂O₇ (444) peak to PBT (0014/119) peak was calculated by the following equation;

$$\Psi = I_{\text{BTO}} / (I_{\text{PBT}} + I_{\text{BTO}})$$

where, I_{BTO} = peak intensity for Bi₂Ti₂O₇ (444) peak, I_{PBT} = peak intensity for PBT (0014/119) peak, Ψ = intensity fraction.

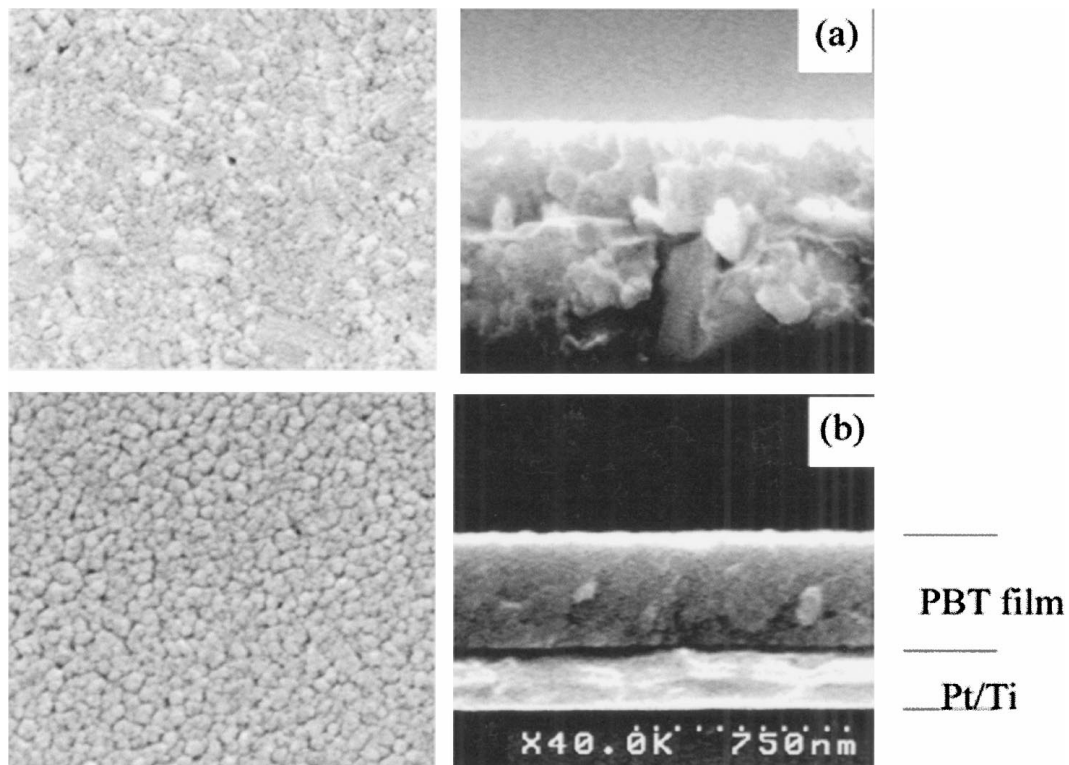


Figure 6 FE-SEM images of the surface and cross section of PBT(1.1/4/4) thin films (a) without and (b) with buffer layer.

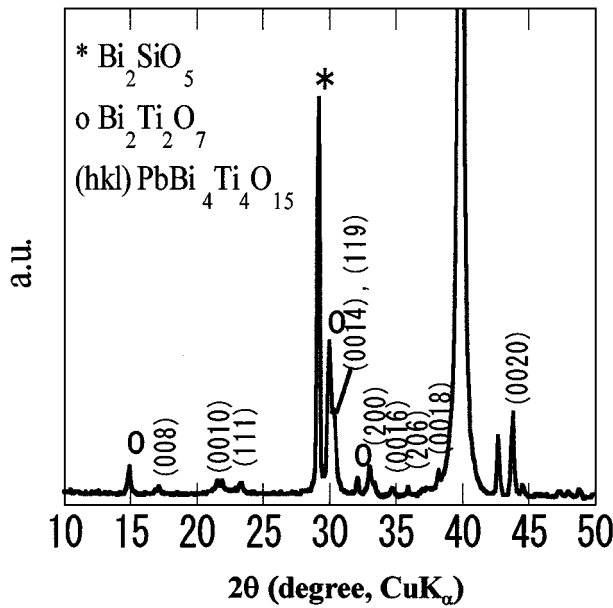


Figure 7 XRD pattern of the PBT (1.1/4/4) film deposited on Pt/Ti/Si substrate.

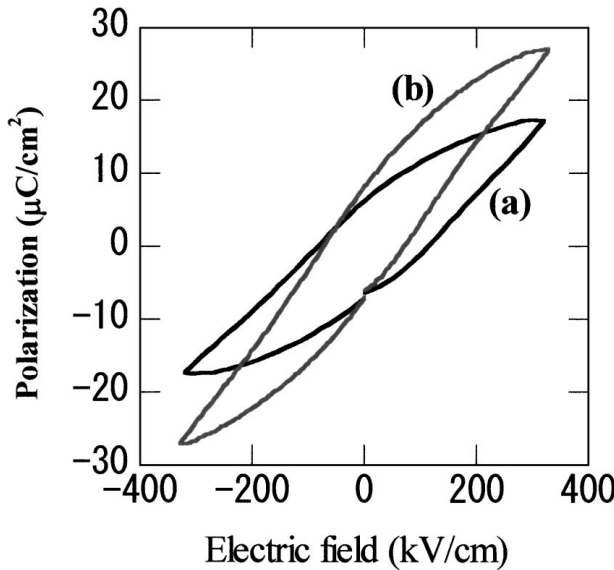


Figure 8 P-E hysteresis loops of PBT(1.1/4/4) thin films (a) without and (b) with buffer layer.

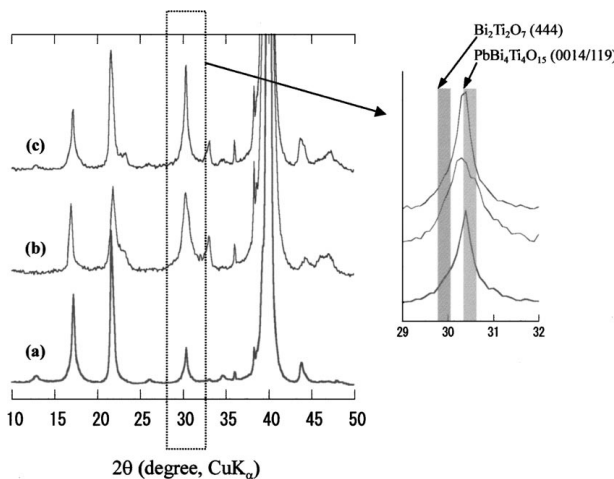


Figure 9 XRD patterns for the PBT films with different film thickness; (a) 334 nm, (b) 508 nm, and (c) 685 nm.

The calculated Ψ value shows almost no change in spite of a large increase of film thickness (Fig. 10b). Ψ slightly increases from 0.226 to 0.249 as film thickness increases from 334 nm to 508 nm, and then decreases to 0.233 at 685 nm. This pyrochlore phase developed in these films is attributable to cation deficiency, especially Bi-deficiency formed by volatilization.

The orientation factors for the films, F , were calculated by the following equations from the XRD indices in the range of $10 \leq 2\theta \leq 35^\circ$ to avoid overlapped PBT crystalline peaks by platinum peak at high 2θ angles.

$$F = (f - f_0)/(1 - f_0)$$

$$f = \Sigma I(00l)/\Sigma I(hkl)$$

where, I = peak intensity

f_0 = f of PBT polycrystal

F = c-axis orientation factor.

The calculated F values for PBT (1.1/5.6-4/4) films were 0.77 for 320 nm-thick, 0.45 for 508 nm-thick and 0.40 for 685 nm-thick films, respectively, showing a decrease of orientation with increasing film thickness (Fig. 10c).

It has been reported that P_r value of Bi-layer structured ferroelectric oxides along a(b)-axis is larger than that along c-axis. Although the polarization value along the c-axis is small, the low coercive field makes it possible to reach saturated polarization state more easily in a low electric field. Therefore, the decreasing P_r of PBT films with increasing film thickness is attributed to the decreasing c-axis orientation as thickness increases (Fig. 11).

The pyrochlore phase developed in PBT films as shown in Fig. 10a and 10b, is also regarded as one of back-drawings of P_r increase.

With the obtained Ψ and F values, effect factor η was calculated by the following equation;

$$\eta = \Psi/F = \{I_{\text{BTO}}/(I_{\text{PBT}} + I_{\text{BTO}})\}/\{(f - f_0)/(1 - f_0)\}$$

Calculated η as a function of the film thickness is shown in Fig. 10b. η shows a decrease with increasing film thickness.

In Fig. 11, P-E hysteresis loops and the measured P_r and E_c at different film thickness are shown. $2P_r$ and $2E_c$ decreased with increasing film thickness, and η -thickness plot (Fig. 10b) shows a good coincidence with the obtained P_r -thickness plot (Fig. 11b).

Therefore, a proportional expression can be made as follows;

$$P_r \propto \eta$$

It was found that c-axis orientation and second phase strongly affect on ferroelectric property in PBT thin film.

Since the used composition (Pb concentration $x = 1.1$ and Bi concentration $y = 1.0$ in $\text{Pb}/\text{Bi}/\text{Ti} = x/4y/4$) was found not to be optimum, more Bi and Pb concentration will be needed for a single PBT phase and a better ferroelectric property.

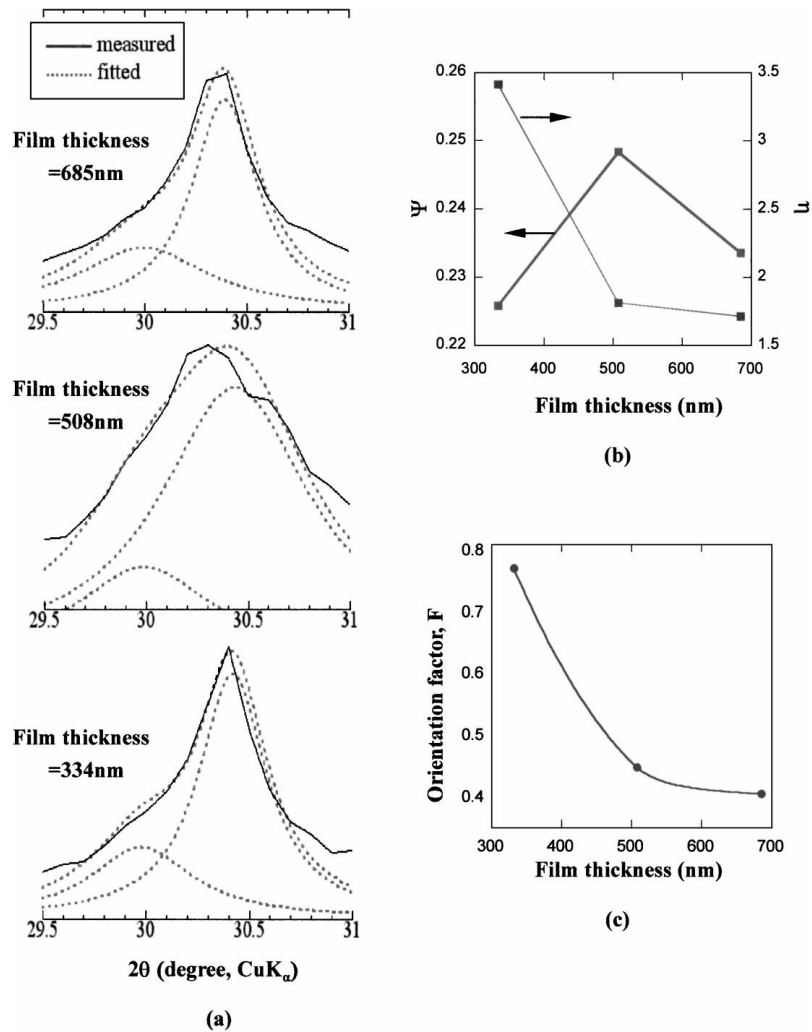


Figure 10 (a) Curve-fitted XRD patterns around 2θ of 30° , (b) orientation factor, F , at different film thickness, and (c) intensity fraction Ψ for Bi₂Ti₂O₇ and effect factor η at different film thickness.

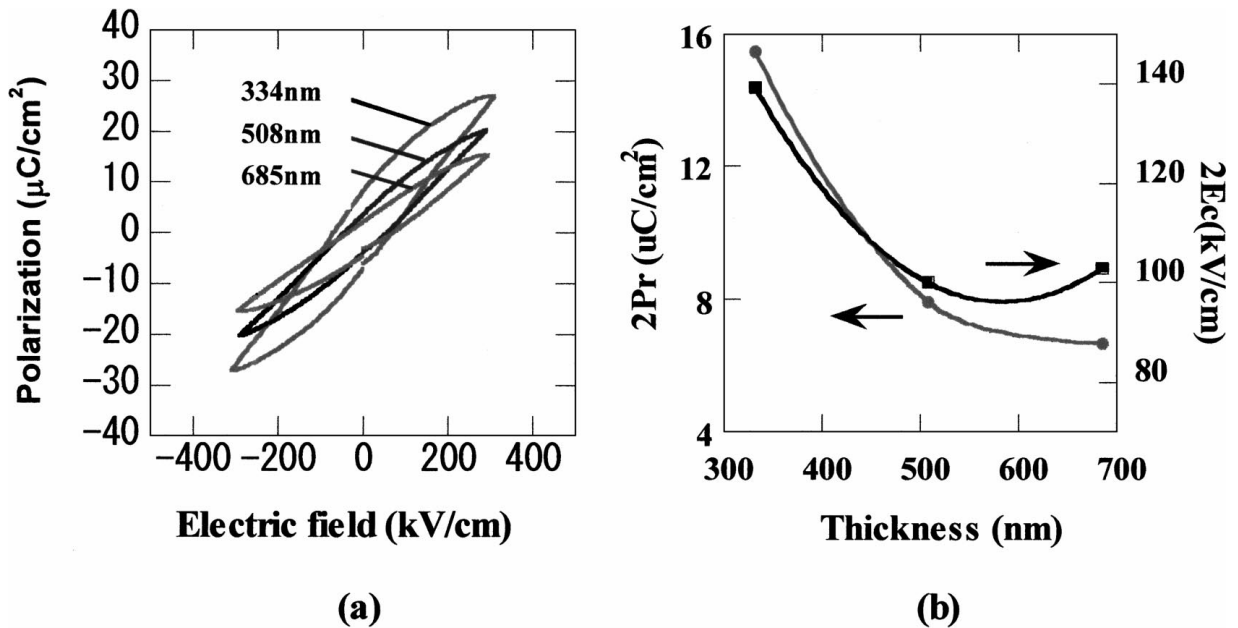


Figure 11 (a) P-E hysteresis loops and (b) $2P_r$ and $2E_c$ as a function of film thickness.

3.4. Ferroelectric and fatigue properties of PBT films with buffer layer

Fig. 12 shows P-E hysteresis loops of the 334 nm-thick PBT (Pb/Bi/Ti = 1.1/4/4) film with buffer layer at different electric fields. The PBT film with buffer

layer showed non-linear ferroelectric P-E hysteresis loops. However, the well-saturated hysteresis loops could not be obtained. This may be due to; (1) relatively high coercive field of PBT [19] compared to PZT or SBT [11–13] and (2) high leakage current and

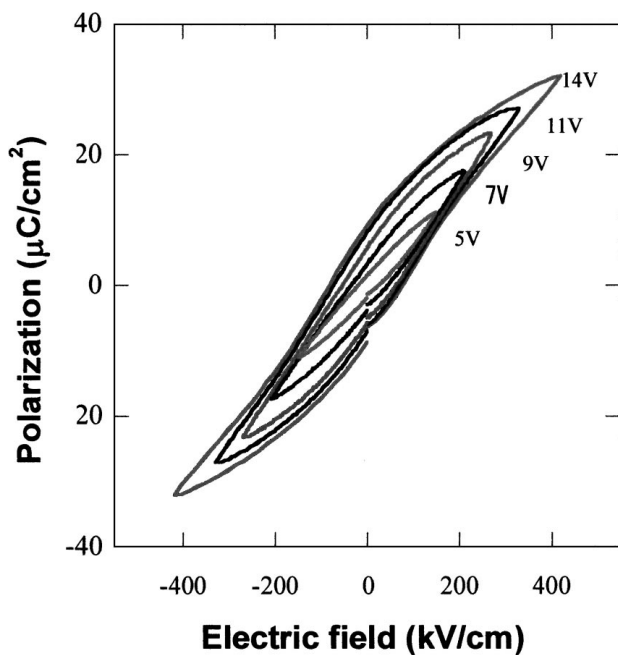


Figure 12 P-E hysteresis loops of the PBT(1.1/4/4) thin film (thickness = 334 nm) with buffer layer at different applied voltage.

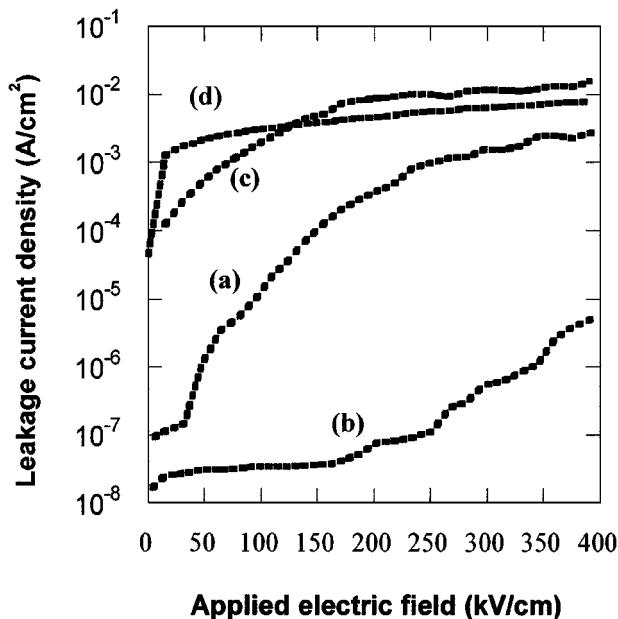


Figure 13 Leakage current density of the PBT(1.1/4/4) thin films heat-treated at (a) 600°C, (b) 700°C, (c) 750°C and (d) 800°C.

non-switching linear response due to space charge polarization [27] that is originated from pores reside in porous microstructure due to high organic content of starting solutions, and (3) paraelectric $\text{Bi}_2\text{Ti}_2\text{O}_7$ phase co-existing with PBT phase. Obtained $2P_r$ and $2E_c$ were $15.7 \mu\text{C}/\text{cm}^2$ and $122 \text{ kV}/\text{cm}$, respectively, at electric field of $\pm 410 \text{ kV}/\text{cm}$. In Fig. 13, measured leakage current density at different heat-treatment temperature is shown. The large leakage current density observed in the film heat-treated at 600°C may be due to high organic content that remained in film by insufficient burnout. Large amount of DEA (b.p. = 271°C) used for stabilization of solution may cause the large leakage current density in this case. Otherwise, films heat-treated at 750°C and at 800°C also showed large leakage

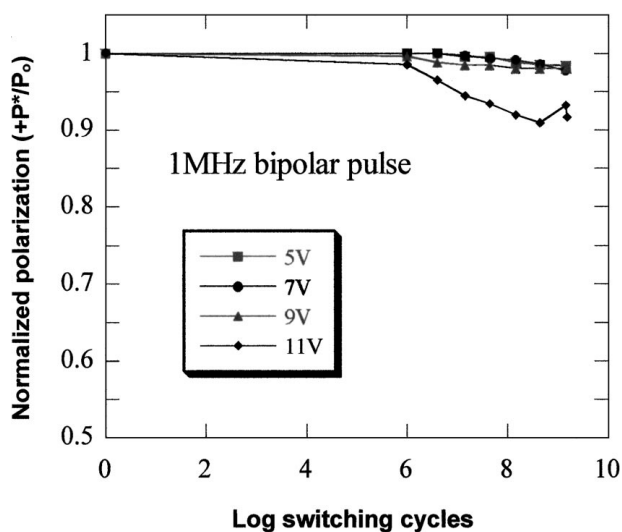


Figure 14 Fatigue property of the PBT(1.1/4/4) thin film with buffer layer at different applied voltage.

current density. Cation defects due to volatilization of Pb and Bi observed by phase analysis are attributable to this leakage current at high temperature. Even though the film heat-treated at 700°C shows relatively low leakage current density, the obtained leakage current is still large for saturation of dipoles and the accurate P_r and E_c values.

Fig. 14 shows fatigue properties of the 334 nm-thick PBT film with buffer layer at different applied voltage at 25°C . Fatigue tests were carried out using bipolar square waves of 5V–11V ($150\text{--}320 \text{ kV}/\text{cm}$) at 1 MHz. Almost no fatigue was observed in the fatigue tests performed using 5V–9V pulses up to 1×10^9 switching cycles. At switching pulses of 11V, about 9% of depolarization at 1×10^9 switching cycles and breakdown at 1×10^{10} switching cycles were observed. Measured relative permittivity of the PBT film with buffer layer was 270, that well matches with bulk ceramic values of about 250 [19].

It is interesting that PBT films show high fatigue endurance despite of its large Pb and Bi volatilization, while PZT films on Pt electrode have poor fatigue property over 40% of depolarization at 1×10^6 switching cycles. Therefore, inherent buffering reaction of Bi_2O_2 layers toward defects, that is general in Bi-layer structured ferroelectric family, seems to be valid in PBT films, too.

4. Summary

PBT thin films were successfully fabricated at 700°C by sol-gel spin coating and the composition effect on ferroelectric property was investigated.

The pyrochlore phase decreased and PBT phase increased with increasing Bi and Pb concentrations. This suggests that volatilization of these cations and diffusion of Bi atoms into the substrate is attributed to co-existence of pyrochlore and PBT phases in the film prepared with stoichiometric PBT composition (Pb/Bi/Ti = 1/4/4). Reported drastic increase of P_r in non-stoichiometric SBT films was not observed in this study.

The pyrochlore phase successfully suppressed by inserting a Bi-rich buffer layer between Pt electrode and

Pb-rich PBT films, to compensate Bi and Pb deficiency resulted from diffusion and volatilization. The fabricated Pb-rich PBT thin film with Bi-rich buffer layer showed homogeneous microstructure with low relative permittivity, and large $2P_r$ value of $15.7 \mu\text{C}/\text{cm}^2$. However, well-saturated P-E hysteresis loops could not be obtained in this study due to large leakage current and formation of second phase.

It was found that pyrochlore phase developed in the films with buffer layer is attributable to cation deficiency, especially Bi-deficiency formed by volatilization. The orientation factors for the films showed a decrease of c-axis orientation with increasing film thickness, and measured P_r also decreased with increasing film thickness.

PBT film with buffer layer also showed high fatigue endurance despite its large Pb and Bi volatilization.

Since the used composition (Pb concentration $x=1.1$ and Bi concentration $y=1.0$ in $\text{Pb}/\text{Bi}/\text{Ti} = x/4y/4$) was found not to be optimum, more Bi and Pb concentration will be needed for a single PBT phase and a better ferroelectric property.

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