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Electric Properties of $Bi_{4-x}Pr_xTi_3O_{12}$ Lead-Free Piezoelectric Thick Films with *a*-/*b*-Mixed Domain Configuration

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Pr-substituted $Bi_4Ti_3O_{12}$ (BPT, $Bi_{4-x}Pr_xTi_3O_{12}$, x=0.1-0.3) polycrystalline thick films with *a*-/*b*-axes orientations and thickness of 2 μm were grown on sputter-grown IrO_2 layers by solution route and orientation behaviors and electric properties were investigated upon Pr-substitution. The degree of *a*-axis orientation (volume fraction of *a*-domain against *b*-domain) f_a increased with increasing x. This behavior was led by that differential thermal strain between BPT thick film of ferroelectric phase and Si substrate was reduced with the increase of x because of the decrease of Curie temperature T_C upon Pr-substitution. The values of remanent polarization contributed from the *a*-domain P_r/f_a and T_C exhibited simple power low $P_{sat} \propto (T_C - T)^{\gamma}$ with a single value of critical exponent $\gamma=0.45$ in the range of x=0.1-0.3 indicating that Pr-substitution diluted spontaneous polarization along the polar *a*-axis $P_{s\|a}$ of pure $Bi_4Ti_3O_{12}$ (BIT). Electric-field-induced strain measurements were performed by double-beam laser displacement meter and longitudinal strain of $S=0.25$ % under 400 kV/cm and piezoelectric coefficient $d_{33}=63$ pm/V at 10 Hz were observed in BPT thick film of x=0.1 with *a*-/*b*-axes mixed orientations. The value of S closely related to $P_{s\|a}$ through the forced alignment of off-center ionic displacements by applying external electric field and monotonously decreased with increasing x.

Key words: Bi-layer ferroelectric film, ferroelectric polarization, field-induced strain, chemical solution deposition

1. INTRODUCTION

In the last decade, interest in ferroelelctric films in mechanical-electric micro systems (MEMS) has rapidly been grown by the advanced technologies developed in ferroelectric memory devices [1]. Because of the overall excellent ferro- and piezoelectric properties, $Pb(Zr,Ti)O_3$ (PZT) solid solution system and lead-oxide-based compounds are the most important materials for bulk and film microdevice applications. Lead-free ferroelectric materials have also attracted interest due to the recent environmental concern [2]. High temperature stability of electric properties is also an important issue in searching for alternative materials due to the relatively low phase transition temperatures in lead-oxide-based materials [3]. Good ferroelectric properties and fatigue endurance in $Bi_4Ti_3O_{12}$ (BIT) thin film with lanthanum substitution [4] have created intense interest in BIT as one of the most competitive candidates in lead-free ferroelectric film applications. The pseudo-orthorhombic BIT lattice unit is constructed by alternate stacking of triple perovskite-like blocks and Bi_2O_2 layers in the *c*-axis direction [5]. BIT single crystal exhibited spontaneous polarizations P_s=50 and 4 μC/cm^2 along the *a*-axis and *c*-axis [6,7] with a relatively high Curie temperature of T_C=675 ºC. The anisotropy of crystallographic lattice emphasized the importance of the orientation engineering of the polar axis with utilizing lattice matching between oxide stacking layers [8]. In addition, recently reported growth of BIT-type structures with *a*- or *a*-/*b*-axes orientations on conducting oxide layers [9,10] and on oxidized layers of Ir [11] demonstrated the crucial role of polar-axis orientation.

Precise evaluation of electric-field-induced strain in ferroelectric films [12-14] is also important for designing piezoelectric MEMS devices, *e.g.* actuators, sensors, transducers, ultrasonic motors, and pumps. In our present study, we report the electric-field-induced strain in Pr-substituted BIT (BPT) thick films with *a*-/*b*-axes orientations grown on $IrO_2(101)/SiO_2/Si$ substrates by chemical solution deposition (CSD). Pr substituent for Bi was selected by the aim to replace volatile Bi for reducing defect density [15] while to maintain the anisotropy of BIT lattice as well; Pr^{3+} possesses most similar ionic radius to that of Bi^{3+} among the trivalent lanthanide ions [16].

2. EXPERIMENTAL

Coating solutions were prepared from Bi acetate, Ti isopropoxide, and Pr acetate hydrate dissolved in anhydrous 2-methoxyethanol with the nominal composition of $Bi_{3.9-x}Pr_xTi_3O_{12}$ (BPT, x=0.1, 0.2, 0.3). (101)-oriented IrO_2 bottom electrode layer was deposited on thermally oxidized SiO_2/Si(001) substrate by reactive RF sputtering. The solutions were spin-cast on the substrates, subsequently dried and crystallized on a hot plate. After repeating these procedures for several times, rapid thermal annealing was performed for grain growth. The film thickness of 2.0-3.0 μm was measured by field-emission scanning electron microscope (FE-SEM, S-5000, Hitachi). The crystal structure and orientation characteristics of BPT thick films were studied by x-ray diffraction [(XRD), X'Pert Pro, PANalytical] of Cu-*K*α radiation. Pt top electrode layer was deposited by RF sputtering with the thickness of 200 nm. The top electrodes were fabricated with the diameters of Φ_{TE}=200, 300, 500, and 700 μm through metal mask. Electric-field-induced strain and ferroelectric polarization were simultaneously measured by laser Doppler vibrometer [MLD-102 and MLD-821, Neoark] and ferroelectric tester (FCE-1, Toyo Corporation). Disk-shape BPT microstructures on IrO_2 layer with Pt top electrode layer of Φ_{TE}=100, 200, 300, and 500 μm were fabricated from BPT thick films by reactive ion etching [(RIE), Plasmalab, Oxford] to study the process conditions of lead-free piezoelectric microdevice fabrication.

3. RESULTS AND DISCUSSION

Figure 1 shows an XRD profile of BPT thick film of x=0.1 with the thickness of 2.0 μm. Single-phase formation of BIT-type structure was confirmed with preferred *a*-/*b*-axes orientations. Similar orientation behavior was revealed in x=0.2 and 0.3 but optimizations of deposition processes have been performed for the individual compositions.

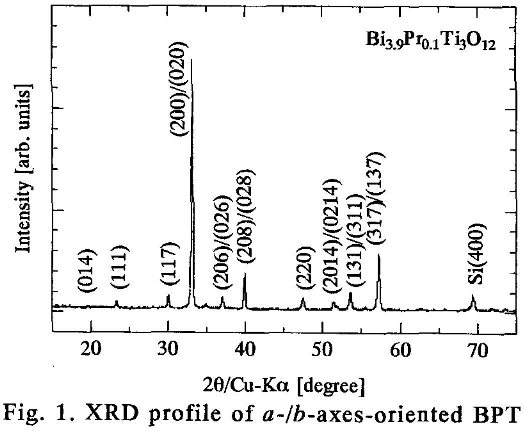

Fig. 1. XRD profile of *a*-/*b*-axes-oriented BPT thick film of x=0.1 with the thickness of 2.0 μm. Similar orientation was revealed in the range of x=0.1-0.3.

The volume fraction of *a*-domain against non-polar *b*-domain (f_a) was estimated by decomposing (200)/(020) peaks in XRD profiles with pseudo-Voigt fitting and calculating as $f_a=I_a/(I_a+I_b)$, where I_a and I_b were the diffraction intensities of (200) and (020) peaks, respectively. As shown in Fig. 2, the estimated value of f_a slightly increased with increasing x. This behavior may indicate that increase of x leads to reduce the lateral tensile stress introduced by differential thermal strain during cooling process of films.

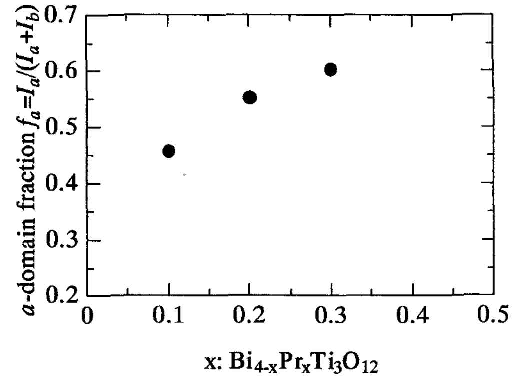

Fig. 2. The variation of volume fraction of *a*-domain against *b*-domain (f_a) estimated by profile fitting of (200)/(020) diffraction peak intensity.

Figure 3 shows leakage current density and electric field (*J*-*E*) characteristics in 2.0-μm-thick BPT film (x=0.1). Reflecting good insulating quality and high breakdown endurance, *J*=1.5 × 10^{-7} A/cm^2 was observed with the application of DC electric field of *E*=400 kV/cm (=2.7E_c, [19]). This quality ensures our films are free from the overvaluations of ferro- and piezoelectric properties.

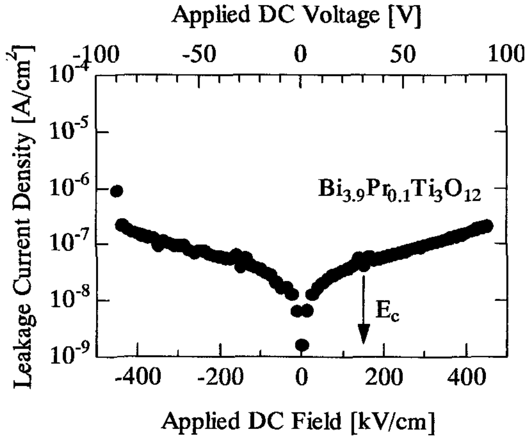

Fig. 3. Leakage current density *J* in BPT thick film of x=0.1 with the thickness of 2.0 μm.

Figure 4(a) and 4(b) respectively show ferroelectric polarization (*P*) electric field (*E*) hysteresis loops and saturation behaviors of remanent polarization (P_r) and coercive field (E_c) measured at room temperature with 10 Hz in BPT thick film of x=0.1 with the thickness of 2.0 μm. As suggested in *J-E* property (Fig. 3), good saturation characters were revealed.

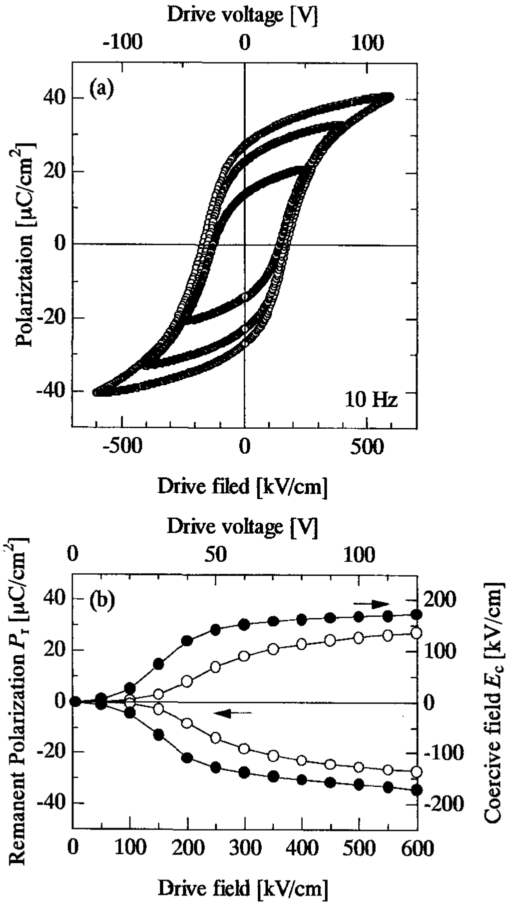

Fig. 4. Ferroelectric property of BPT thick film of x=0.1 with 2.0 μm in thickness measured at 10 Hz: (a) *P-E* hysteresis loops and (b) saturation behaviors of P_r and E_c. Solid lines assist viewing.

Saturated values of P_r were measured and polarization contribution from spontaneous polarization P_s in *a*-domain was evaluated by calculating P_r/f_a as a function of x (Fig. 5). The monotonous decrease of P_r/f_a with increasing x may be led by the decrease of P_s.

The values of P_r/f_a were described by phenomenological relation between spontaneous polarization P_s measured at temperature T and Curie temperature T_C ($P_s \propto (T_C\text{-}T)^\gamma$) with the critical exponent γ as shown in the inset of Fig. 5. T_C was estimated as temperature at which the lattice parameters *a* and *b* exhibited discontinuous change due to structural phase transition in the measurements of temperature dependence of XRD [11]. The calculated value of γ=0.45 agrees well with Landau theory (γ=0.5).

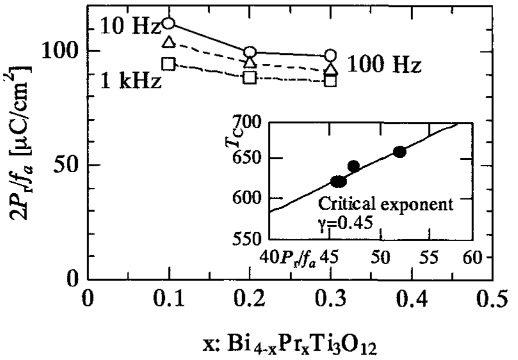

Fig. 5. Polarization contribution from P_s in *a*-domain was estimated by P_r/f_a. The thermodynamic behavior of P_r/f_a was described well by phenomenological Landau theory with a single value of γ=0.45.

Figure 6(a) shows longitudinal field-induced strain (*S*) in 2.0-μm-thick BPT film of x=0.1 measured at room temperature under maximum electric field of E=500 kV/cm at 10 Hz. Observed large strain S=0.25 % under E=400 kV/cm corresponded to the piezoelectric coefficient of d_{33}=63 pm/V, surpassing reported values of d_{33}=20 pm/V in bulk BIT [17] and of d_{33}=44 pm/V in single crystalline BIT [18]. This value agrees with d_{33} in atomic force microscopy (AFM) measurements [19] and the influence from elastic deformation of substrate was successfully eliminated by displacement measurements of

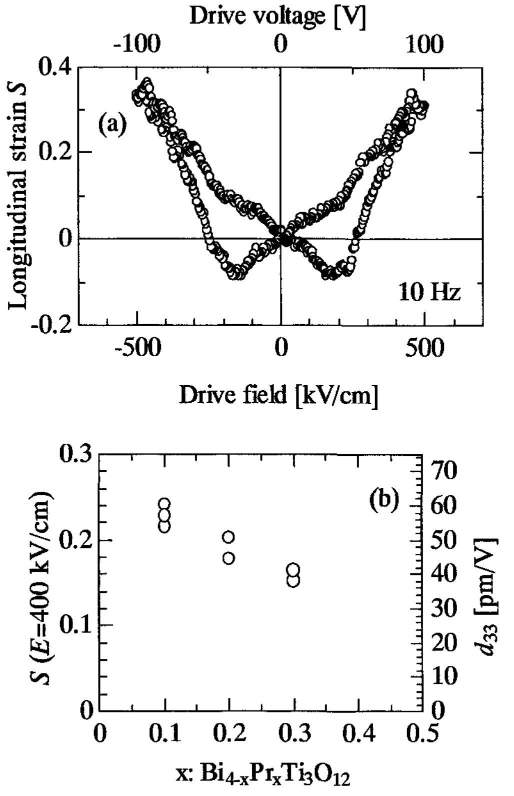

Fig. 6. Piezoelectric property of BPT thick film of x=0.1 with 2.0 μm in thickness measured at room temperature at 10 Hz: (a) hysteresis loop of electric-field-induced strain *S* and (b) x dependence of *S* at E=400 kV/cm and piezoelectric coefficient d_{33}.

double-beam configuration [20]. Both of S and d_{33} monotonously decreased with the increase of x; S=0.16 % and d_{33}=40 pm/V in x=0.3. (Fig. 6(b)).

As a displacive ferroelectric material, the large value of P_s in BIT is originated from the sum of off-center ionic displacements that form local electric dipoles and, therefore, we have expected that maximum strain associated with polarization alignment by the application of external electric field could be revealed by controlling the film orientation close to the polar *a*-axis [21]. The observed behavior of S on x in the present report supported our expectation. For the good performing piezoelectric film, in addition, x=0.1 is favored.

4. CONCLUSIONS

Polycrystalline, 2-μm-thick $Bi_{4-x}Pr_xTi_3O_{12}$ (BPT, x=0.1-0.3) films were grown by chemical solution deposition (CSD) method on (101)-oriented, sputter-grown IrO_2 electrode layer on SiO_2/Si substrates. The films possessed preferred *a*-/*b*-axes orientations.

The XRD (200)/(020) peaks were constituted by *a*- and *b*-domains and fraction of *a*-domain f_a increased with increasing Pr-substitution content x. This may suggest that lateral tensile stress was applied to BPT film during cooling process by differential thermal strain between film and Si substrate and the magnitude of stress was decreased with increasing x due to the decrease of Curie temperature T_C.

Quality of insulating property was carefully examined in leakage current density J measurements by applying DC electric field far above E_c. J=1.5×10^{-7} A/cm^2 was recorded with E_{DC}=400 kV/cm ensuring accurate measurement of ferro- and piezoelectric properties. Consideration of compositional dependence of f_a suggested monotonous decrease of P_s with the increase of x. P_s was well described with single value of critical exponent γ=0.45.

Field-induced strain S was measured by double beam laser configuration and exhibited close relation to P_s.

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