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Unusual 90° domain structure in (2/3)Bi(Zn_{1/2}Ti_{1/2})O₃-(1/3)BiFeO₃ epitaxial films with giant 22% tetragonal distortion

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Epitaxial films of tetragonal (001)/(100)-oriented (2/3)Bi(Zn_{1/2}Ti_{1/2})O₃-(1/3)BiFeO₃ were grown on (100)cSrRuO₃/(100)SrTiO₃ substrates by metalorganic chemical vapor deposition. 93% of the film is occupied by *c*-domain [(001) orientation], and the out-of-plane (*c*-axis) and in-plane (*a*-axis) lattice parameters are 0.465 nm and 0.381 nm, respectively. The tetragonal distortion, (*c/a*)-1, is 22% which is 3.5 times larger than that of PbTiO₃ (6.3%). High-angle annular dark-field-scanning transmission electron microscopy images show clear *c/a*-domain structures with unusual boundary angles of 51°/39° due to the large *c/a* ratio of tetragonal phase. High temperature X-ray diffraction measurements reveal that the Curie temperature of this film is above 800 °C. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4816420>]

Inorganic ferroelectric materials have been widely used for various devices including non-volatile ferroelectric random access memories (FeRAMs), gyro sensors, and ultrasonic actuators.^{1–3} Tetragonal ferroelectric materials with *P*4mm symmetry, such as BaTiO₃, PbTiO₃, and (Bi_{1/3}K_{1/2})O₃, are important not only for fundamental understanding of ferroelectricity due to their simple crystal structure but also for practical applications. In fact, the commercial FeRAMs use tetragonal PbTiO₃-PbZrO₃ solid solution as the data storage media,¹ and piezoelectric actuators also use PbTiO₃-PbZrO₃ and PbTiO₃-Pb(Mg_{1/3}Nb_{2/3})O₃ solid-solutions that include tetragonal PbTiO₃ as an end member.⁴ In such materials, the tetragonal distortion, defined as (*c/a*)-1 (*c* and *a* correspond to lattice parameters parallel and perpendicular to the polar axis, respectively), is responsible for the large spontaneous polarization (*P*_s) because *P*_s² is known to be proportional to (*c/a*)-1.⁵ Since piezoelectric response is also proportional to *P*_s,⁶ large tetragonal distortion is the key to achieve superior ferroelectric and piezoelectric properties. At room temperature, PbTiO₃ has the largest tetragonal distortion of 6.3% among the currently known ferroelectric materials that can switch

polarization⁷ and is widely used as a key component in various commercial products. Note that complicated domain structure consisted of *c/a*-domains in PbTiO₃ develops superior extrinsic piezoelectricity originated from domain switching.⁸ Recently, intensive research has been devoted to find alternative lead-free ferroelectric materials in response to the environmental concerns over lead.

Since 2004, lead-free ferroelectric materials with *P*4mm symmetry and very large tetragonal distortion above 20%, such as BiCoO₃,⁹ Bi(Zn_{1/2}Ti_{1/2})O₃,¹⁰ and those of solid-solution,¹¹ have been reported mainly by high pressure synthesis technique. However, ferroelectric domain formation of *c/a*-domains, switchable polarization, and piezoelectric response have hardly been reported. This reason would be considered that the large electric field is needed to switch polarization direction in large distorted ferroelectric materials and the relatively low resistance of the samples including transition metal ions prevents to apply enough electric field to switch. We have been focusing on the Bi(Zn_{1/2}Ti_{1/2})O₃-based systems because the *B*-site of perovskite structure consists of ions with *d*⁰ and *d*¹⁰ electron configurations.^{12,13} This is expected well insulating property in the materials that can withstand the high electric field required for polarization switching. In the present study, we report on the growth of epitaxial (2/3)Bi(Zn_{1/2}Ti_{1/2})O₃-(1/3)BiFeO₃ thin films with a very large tetragonal distortion above 20% grown on SrTiO₃ substrates. The BiFeO₃ have prospects of stabilization to Bi(Zn_{1/2}Ti_{1/2})O₃ which can only be obtained by high

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pressure synthesis.¹⁴ Also, in case of films with large distortion, tetragonal-like BiFeO₃ thin films are widely investigated. However, strain-induced tetragonal-like BiFeO₃ shows actually monoclinic symmetry which has small tilting angle from tetragonal 90°, not as same as tetragonal symmetry.¹⁵ Note that strain-induced tetragonal-like BiFeO₃ thin films can be obtained within the thickness below 100 nm and on high strain-induced substrates from film/substrate mismatch such as LaAlO₃ are also reported.^{16,17} However such reports are absolutely different to our study, truly tetragonal distorted system. In addition, almost all of such tetragonal-like BiFeO₃ reports consist of only 180° domain or the mixture phase of tetragonal-like and rhombohedral-like domains.¹⁸ Contrary to these, our real tetragonal symmetry have the complex domain structure consisted of *c*-(180°) and *a*-(90°) domains, as similar to the tetragonal PbTiO₃ (Refs. 19 and 20) and BaTiO₃ (Ref. 21) but had unusual domain boundary due to its large tetragonal distortion. Unusual domain boundary angle of 51°/39° in 90° domain is a unique character of the films with large tetragonal distortion. In addition, we have also demonstrated polarization switching using piezoresponse force microscopy (PFM) for such highly distorted ferroelectric materials. In addition, we have observed that the Curie temperature of this material is above 800 °C, which is very suitable for high temperature applications. This study opens the door for the synthesis and application of lead-free perovskite ferroelectric materials with very large distortion.

Epitaxial (2/3)Bi(Zn_{1/2}Ti_{1/2})O₃-(1/3)BiFeO₃ films with relatively thick 300 nm thickness were grown on (100)_cSrRuO₃/(100)SrTiO₃ substrates at 770 °C by pulsed metalorganic chemical vapor deposition (MOCVD) using Bi[(CH₃)₂(2-(CH₃)₂NCH₂C₆H₄)] (Tosoh Co. Ltd), Zn(C₁₂H₂₅O₂), Ti(O-*i*-C₃H₇)₄, Fe(C₂H₅C₅H₄)₂, and oxygen gas as the source materials. SrRuO₃ films were grown by RF magnetron sputtering method.²² Composition ratio of stoichiometric (2/3)Bi(Zn_{1/2}Ti_{1/2})O₃-(1/3)BiFeO₃ film were controlled by carrier gas flow rates of each source materials, respectively. Film thickness and composition were confirmed by surface profilometry and X-ray fluorescence calibrated using standard samples. Crystal structure of the deposited films was characterized by X-ray diffraction (XRD) analysis using a four-axis diffractometer with CuK_α radiation, X'Pert PRO MRD, PANalytical. High temperature XRD-RSMs (reciprocal space mappings) were carried out using D8 DISCOVER/SSS, Bruker AXS. Atomic microstructures of the films were observed by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). Pt/[(2/3)Bi(Zn_{1/2}Ti_{1/2})O₃-(1/3)BiFeO₃]/SrRuO₃ capacitor structure was used for the electrical measurements after making circular Pt top electrodes of 100 μm in diameter, which were deposited by e-beam evaporation. Piezoresponse mappings and longitudinal piezoelectric coefficient (*d*₃₃) was measured using piezoresponse force microscopy (PFM) calibrated by BaTiO₃ single crystal.

XRD study was carried out to analyze the crystal structure and symmetry of stoichiometric (2/3)Bi(Zn_{1/2}Ti_{1/2})O₃-(1/3)BiFeO₃ film. Figure 1(a) shows typical high resolution XRD θ -2 θ pattern of the films. Only (00*l*)-family peaks were observed along substrate surface normal. This measurement is not enough for phase and domain identifications in epitaxial films because diffractions related to tilted domains from

FIG. 1. (a) HR-XRD $2\theta - \theta$ pattern, (b) XRD $2\theta - \Psi$ mapping, (c) XRD $2\theta - \theta$ pattern integrated along Ψ direction, and (d) XRD pole figure plot measured at 30.31° and XRD $\Psi - \omega$ mappings of (e) 002 and (f) 200 diffractions in (2/3)Bi(Zn_{1/2}Ti_{1/2})O₃-(1/3)BiFeO₃ film grown on (100)_cSrRuO₃/(100)SrTiO₃ substrate. Red-circles, blue-circles, triangles, and squares in (b) correspond to peaks originated from *c*-domain, *a*-domain, SrRuO₃, and SrTiO₃, respectively.

substrate surface normal could not be detected. Figure 1(b) shows the $2\theta - \Psi$ area mapping of the film measured under ϕ -axis-rotation condition. This advanced X-ray mapping leads us to know all diffractions from the films, suggesting that crystal structure and domain structure could be investigated easily. The details of the measurement methods have been described in Ref. 23. This mapping reveals *d*-spacing information along both the substrate surface normal and off-normal directions. The diffraction spots from the films are marked in red and blue circles corresponded to film growth direction along 001 and 100, and the diffraction spots from SrRuO₃ and SrTiO₃ are also indicated by triangle and square symbols in Fig. 1(b), respectively. It must be noted that the broad peak along Ψ direction around $2\theta = 40^\circ$ in Fig. 1(b) was attributed to the 111 diffraction from Pt top electrodes. Figure 1(c) shows θ -2 θ pattern integrated along Ψ direction together with the reported XRD powder pattern of Bi(Zn_{1/2}Ti_{1/2})O₃.¹⁰ This integrated pattern includes all symmetric and asymmetric diffractions from the films and substrates. It is observed that all diffraction peaks from the films can

be identified to tetragonal $P4mm$ symmetry as same as $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$, and a single perovskite phase is achieved to fabricate. In addition, the diffraction spots circled in red in Fig. 1(b) correspond to c -domains with (001) axis along the surface normal direction, while those circled in blue correspond to a -domains with (100) axis that tilts away from the surface normal direction by about 11° . Volume fraction of c -domains is calculated to be around 93% based on the diffraction area intensity of the integrated pattern in Fig. 1(c). The inset of Fig. 1(d) shows the pole figure measured at $2\theta = 30.31^\circ$ of 101 diffraction which shows strongest intensity in perovskite structure. Four symmetric spots attributed to $\{101\}$ and $\{110\}$ diffractions in $\Psi = 30^\circ$ and 51° at intervals of 90° each along ϕ direction were observed, suggesting the following epitaxial relationship: $(001)/(100) [(2/3)\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-(1/3)\text{BiFeO}_3]/(100)_c\text{SrRuO}_3/(100)\text{SrTiO}_3$. Note that tilted angle of $(001)/(100)$ domains from substrates are ignored. Figures 1(e) and 1(f) present the XRD plan-view Ψ - ω mappings around 002 and 200 diffraction peaks, respectively. ω -axis is perpendicular to Ψ -axis and parallel to the surface normal. One and four spots were observed in Figs. 1(e) and 1(f), respectively. The shape of these patterns are in agreement with the typical 90° domain structure reported for $(001)/(100)$ -oriented epitaxial PbTiO_3 films;²⁴ however, tilted angles from substrate surface normal are unusual of $\sim 11^\circ$ along (100) or (010) directions in Fig. 1(f). It must be noted that such tetragonal c -/ a -domain structure in Figs. 1(e) and 1(f) have not been reported in case of tetragonal-like BiFeO_3 . Here, it is important that the tilting angle of 200 diffractions from the surface normal, δ angle, is approximately 11° , much larger than that of PbTiO_3 (3.6° in the fully relaxed films),²⁵ consistent with the very large tetragonal distortion in the present film.

In order to calculate the tetragonality accurately, we conducted XRD-RSMs for the same films as shown in Fig. 1. The peaks were attributed to the 003 and 103 diffractions of the c -domains in Fig. 2. The constituent internal angle between the out-of-plane (c -axis) and in-plane (a -axis) is 90.0° , suggesting that this result is an evidence of tetragonal symmetry in the present films. It must be emphasize that the in-plane lattice of the film is not clamped from the substrate that showed that this tetragonal symmetry is not originated from the clamping from

the substrate such as “tetragonal-like BiFeO_3 .” In addition, “tetragonal-like BiFeO_3 ” has additional peaks on 103 XRD-RSM due to monoclinic asymmetric distortion,²⁶ but present study just showed one peak on 103 diffraction peak due to the simple tetragonal symmetry. The out-of-plane (c -axis) and in-plane (a -axis) lattice parameters calculated from diffractions are 0.465 nm and 0.381 nm, respectively, resulting in a giant tetragonal distortion of $(c/a)-1 = 22\%$. This value is 3.5 times larger than the 6.3% of PbTiO_3 . In addition, this $[(c/a)-1]$ is larger than the reported one for pure $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$, $[(c/a)-1] = 21\%$.¹⁰ Similar enlargement of the $[(c/a)-1]$ by the substitution with BiFeO_3 has been reported in PbTiO_3 - BiFeO_3 , even if the substituted BiFeO_3 has rhombohedral symmetry.²⁷ In addition, the large δ angle in Fig. 1(e) could be explained by following equation: $\delta = 2 \tan^{-1}(c/a) - 90^\circ = 11.3^\circ$.²⁸ For tetragonal ferroelectric PbTiO_3 case, δ angle of about 3.6° was reported.²⁵ Therefore, this result indicates that unusual domain structure with large tilting angle between domains boundaries are constituted by ferroelectric materials with large tetragonal distortion.

We have also conducted cross sectional high resolution HAADF-STEM for visualization of the crystal structure directly. Figure 3 shows an HAADF image covering the 90° domains, and inset shows schematic illustration of c -/ a -domain boundary model in this film system obtained by XRD measurement in Fig. 1. The “ 90° domain boundary” has a $51^\circ/39^\circ$ angle due to the large tetragonality, which is in good agreement with $50.7^\circ/40.3^\circ$ value based on the crystal structure information obtained by XRD measurement as shown in Figs. 1 and 2. High resolution HAADF-STEM image of the film is presented in Fig. 4(a). The brighter dots are bismuth ions in perovskite A -site, while the slightly light ones located at the center between brighter ones are Fe, Zn, or Ti ions in perovskite B -site. To analyze the existed position of perovskite cations, the intensity profiles of perovskite A -site and B -site cations along $[001]$ and $[100]$ directions are shown in Fig. 4. Concerning $[001]$, B -site cations in Fig. 4(c) obviously existed off-center way to $[00\bar{1}]$ compared with A -site cations in Fig. 4(b). On the other hand, cations of perovskite A -site and B -site respective remained center position along $[100]$ as shown in Figs. 4(d) and 4(e). In addition, expanded

FIG. 2. XRD reciprocal space mappings around (a) 003 and (b) 103 in $(2/3)\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-(1/3)\text{BiFeO}_3$ film grown on $(100)_c\text{SrRuO}_3/(100)\text{SrTiO}_3$ substrate.

FIG. 3. Cross sectional HAADF-STEM images of macroscopic c -/ a -domain boundary in $(2/3)\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-(1/3)\text{BiFeO}_3$ film grown on $(100)_c\text{SrRuO}_3/(100)\text{SrTiO}_3$ substrate. Inset schematic illustration is a domain boundary model of c -/ a -domain.

FIG. 4. (a) Z-contrast images focused on *c*-domain in the films, intensity profiles of perovskite cations along (b), (c) [001] and (d), (e) [100] directions. (b), (d) Green and (c), (e) blue lines, respectively, correspond to perovskite A- and B-site cations. (f) Z-contrast image and (g) schematic illustration of averaged *c*-domain unit cell.

z-contrast image to perovskite unit cell shown in Fig. 4(f) shows that the B-site ions are also displaced along [001] significantly away from the center as schematic drawing in Fig. 4(g) in good agreement with the results shown in Figs. 4(b) and 4(c). It must be noted that B-site peak are broad, suggesting that B-site cations of Zn^{2+} , Ti^{4+} , and Fe^{3+} exist in the perovskite B-site position with different off-centering. There are in good agreement with structure analysis of the $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ prepared by high pressure synthesis. In addition, as XRD results showed no super lattice peaks, B-site cations are not ordered. These results clearly indicate that this material is characterized as displacive-type ferroelectric, and unusual angle of the 90° domain is originated from large tetragonal distortion.

To investigate the Curie temperature of this film, we performed temperature dependence structural analysis using high-temperature XRD-RSMs. Figures 5(a) and 5(b) show the *c*- and *a*-axes lattice parameters as well as $[(c/a)-1]$ up to 800°C . The reported data of $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (Ref. 10) and PbTiO_3 powders⁷ are also shown in Figs. 5(a) and 5(b) using red and blue symbols for comparison. The *c*-axis lattice parameter decreases with increasing temperature, while the *a*-axis lattice parameter decreases. However, no phase transition is observed even up to 800°C , at which point the film starts to decompose. The tetragonality only decreases slightly with increasing temperature. However, it remains much larger than that of PbTiO_3 as shown in Fig. 5(b). Therefore, the Curie temperature of this material could be above 800°C at least. It is clear that the $[(c/a)-1]$ behavior of our film is almost similar with $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ one but not PbTiO_3 one.

In order to confirm the ferroelectricity of the film, we measured the polarization-electric field (*P-E*) hysteresis loop of the films. Unfortunately, non-saturated *P-E* hysteresis loop was observed even under a huge electric field of 2.0 MV/cm . If we further increase the electric field, the film system is broken down. This result suggests that coercive field might be more than 2.0 MV/cm , and it could be expected from unusual very large tetragonality of $\sim 22\%$, too. We then turned to measure piezoresponse mappings to ascertain polarization switching in this film and measured the longitudinal d_{33} coefficient

FIG. 5. (a) In-plane *a*-axis and out-of-plane *c*-axis lattice parameters and (b) $[(c/a)-1]$ as a function of temperature in $(2/3)\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-(1/3)\text{BiFeO}_3$ film grown on $(100)\text{SrRuO}_3/(100)\text{SrTiO}_3$ substrate. Powder data in $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (Ref. 10) and PbTiO_3 (Ref. 7) were also added as red squares and blue triangles, respectively.

using PFM technique which can apply large electric field at local area on the film bare surface. The piezoresponse phase mapping and d_{33} intensity hysteresis loop are shown in Fig. 6. Before piezoresponse mappings measurement, an area of $3\text{ }\mu\text{m} \times 4\text{ }\mu\text{m}$ was written by applying $+30\text{ V}$ through the conducting Pt-coated cantilever during the scan. Polarization switching is demonstrated in piezoresponse image, where the original purple color (polarization pointing up) changes to yellow (polarization pointing down) within the written area as shown in Fig. 6(a). Thus, we have confirmed that the tetragonal $(2/3)\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-(1/3)\text{BiFeO}_3$ epitaxial film with large tetragonal distortion has ferroelectricity. Polarization in some small regions was not switched, maybe due to domain pinning by local defects. From this piezoresponse image, *a*-domain region was not observed due to small volume fraction below 7% and narrow strip width about 5 nm from TEM results in Fig. 3. We have also measured the piezoelectric d_{33} hysteresis loops at room temperature under by superimposing a $2\text{ V}_{\text{p-p}}$ AC bias on top of the DC bias applied. The sample vibration amplitude was recorded and used to calculate the d_{33} coefficient. A typical d_{33} loop from the film is shown in Fig. 6(b). The average d_{33} value at zero DC-bias is approximately 70 pm/V which was calculated from positive and negative d_{33} that including the clamping effect from the substrates.²⁹ This value is larger than that of PbTiO_3 film about 50 pm/V .^{29,30} The data shown in Fig. 6 also confirm polarization switching under external electric field; thus, this result is one of the evidence of ferroelectric nature in the present materials. However, this is not perfect evidence of ferroelectricity, because it may result from the strain-induced metastable states of the structures. Fortunately, TEM results in Fig. 3 showed

FIG. 6. (a) Piezoresponse phase mapping image after writing +30 V and −30 V and (b) longitudinal piezoelectric d_{33} loops as a function of DC voltage together with the for $(2/3)\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ – $(1/3)\text{BiFeO}_3$ film grown on $(100)\text{SrRuO}_3/(100)\text{SrTiO}_3$ substrate.

ferroelectric c -/ a -domain structure which have been observed in conventional tetragonal ferroelectrics of PbTiO_3 and BaTiO_3 . We believe that this is the report of polarization reversal for ferroelectric materials with such a large tetragonality and high Curie temperature beyond 800 °C.

In summary, we prepared tetragonal $(2/3)\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ – $(1/3)\text{BiFeO}_3$ epitaxial films, different from tetragonal-like BiFeO_3 strained thin films, on $(100)\text{SrRuO}_3/(100)\text{SrTiO}_3$ substrates by MOCVD. Deposited films had similar c -/ a -domain structure as observed in conventional tetragonal PbTiO_3 thin films, but its tetragonality, $[(c/a)-1]$, was 22%, which was 3.5 times larger than 6.3% of PbTiO_3 . c -/ a -domain structure with unusual domain boundary angle of $51^\circ/39^\circ$ originated to the large c/a ratio in tetragonal ferroelectric materials was observed for both of XRD and TEM measurements. In addition, HADDF image showed non-centro symmetric polar c -domains. Temperature dependent XRD analysis also revealed that the Curie temperature was above 800 °C at least, higher than any ferroelectric materials with perovskite structure as known today. Polarization switching was confirmed through PFM mapping and d_{33} measurement. Our work presents direct experimental evidences of lead-free giant tetragonal ferroelectrics with c -/ a -domain structure which could be an alternative of the commonly used lead-based materials.

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