Composition dependence of crystal structure and electrical properties for epitaxial films of $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--BiFeO}_3$ solid solution system

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Epitaxial $x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}(1-x)\text{BiFeO}_3$ films were grown on $(100)\text{SrRuO}_3/(100)\text{SrTiO}_3$ substrates by metal organic chemical vapor deposition (MOCVD). The effects of x value on the crystal structure and the electrical properties were investigated. Constituent phase changed from rhombohedral symmetry to two types of tetragonal ones with different unit cell volume and tetragonality. Rhombohedral phase and the tetragonal phase with smaller tetragonality were not ascertained to transform to cubic phase up to 800°C from high temperature XRD results. Relative dielectric constant measured at room temperature showed the maximum value at $x = 0.21$ near the phase boundary between tetragonal and rhombohedral symmetries. Leakage current became small when the measurement temperature decreased at 80 K and the ferroelectricity monotonously decreased with increasing x values and was not ascertained above 0.26.

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Key-words : $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--BiFeO}_3$, Solid solution, Lead-free material, MOCVD, Crystal structure, Electric property, Epitaxial film, Composition dependency

[Received April 19, 2010; Accepted June 17, 2010]

1. Introduction

Piezoelectric materials are very attractive for micro-electro-mechanical systems (MEMS) and energy harvesting applications.¹⁾ Piezoelectric materials having large piezoelectric response include tetragonal perovskite PbTiO_3 as an end member, such as $\text{PbTiO}_3\text{--PbZrO}_3$ [PZT], $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ [PMN-PT] and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ [PZN-PT]. Excellent piezoelectric properties were observed near the composition where the constituent phases transform from tetragonal to non tetragonal phase.^{2)–5)} One of the major concerns for the large-variety of applications of conventional piezoelectric materials is that their main constituent element, Pb, is toxic for the environment. Thus, to develop the “green piezoelectric materials”, it is essential to replace the PbTiO_3 -based piezoelectric by the lead-free ones. Tetragonal perovskite BaTiO_3 has been investigated as alternative to PbTiO_3 ,⁶⁾ unfortunately its low Curie temperature limits its practical application potential. Tetragonal $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ -based materials are promising candidates,⁷⁾ but their uses in Si-based MEMS devices are hindered by the alkaline metal diffusion into Si.

We focused on the lead-free Bi-based perovskites with tetragonal symmetry. Recently, it has been found that the $\text{BiCoO}_3\text{--BiFeO}_3$ system, which was synthesized by high pressure methods and MOCVD, showed the existence of the phase boundary between tetragonal and rhombohedral phases.^{8)–10)}

Furthermore, an additional low-symmetry monoclinic phase at the phase boundary was found,¹⁰⁾ which is pointed out to be one of the key issues for the enhancement of the piezoelectric properties.^{11),12)} However, this system showed relative large leakage current. Therefore, we focus on the new tetragonal material of $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ having d^0 and d^{10} electronic coordinations, instead of tetragonal BiCoO_3 .

In the previous paper, we tried to grow the epitaxial films of the solid solution system of tetragonal $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ and rhombohedral BiFeO_3 .¹³⁾ $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ is also reported to have a tetragonal symmetry from the crystal structure analysis.¹⁴⁾ Systematic change of the peak position with the film composition was discovered from XRD analysis. In the present study, we tried the crystal structure analysis more in detail to determine the crystal symmetry of the films as well as the phase stability against the temperature. In addition, the electrical properties of these films were also systematically investigated.

2. Experimental procedure

Epitaxial films of $x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}(1-x)\text{BiFeO}_3$ ($x = 0\text{--}0.68$) with a thickness of about 300 nm were grown at 770°C on $(100)\text{SrRuO}_3/(100)\text{SrTiO}_3$ substrates by pulsed-metalorganic chemical vapor deposition (MOCVD). $\text{Bi}[(\text{CH}_3)_2(2\text{--}(\text{CH}_3)_2\text{NCH}_2\text{C}_6\text{H}_4)]$, $\text{Zn}(\text{C}_{12}\text{H}_{25}\text{O}_2)_2$, $\text{Ti}(\text{O-}i\text{-C}_3\text{H}_7)_4$, and $\text{Fe}(\text{C}_2\text{H}_5\text{C}_5\text{H}_4)_2$ were used as Bi, Zn, Ti and Fe source materials, respectively, while oxygen gas was used as an oxidant. The mixture of the source gases was flowed down to the substrate in the vertical cold-wall type reactor. Film composition was changed by controlling the input gas flow rate of each source gases. Epitaxial

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Fig. 1. XRD θ – 2θ patterns of $x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ – $(1-x)\text{BiFeO}_3$ films with various x values. 2θ angle region; (a): 10–50°, (b): 37–48°. Inset in (a) is X-ray pole figure fixed 2θ angle corresponding to 110 assuming cubic symmetry for the films with $x = 0.68$.

Fig. 2. XRD reciprocal space mappings around [(a), (c), (e) and (g)] SrTiO_3 003 and [(b), (d), (f) and (h)] SrTiO_3 103 for $x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ – $(1-x)\text{BiFeO}_3$ films with [(a), (b)] $x = 0$, [(c), (d)] $x = 0.21$, [(e), (f)] $x = 0.44$, [(g), (h)] $x = 0.65$. Open circles originated to SrTiO_3 , while closed ones to SrRuO_3 .

SrRuO_3 bottom electrode layers were grown by rf magnetron sputtering method.¹⁵⁾

Film composition was determined by X-ray fluorescence (XRF, PANalytical PW2404, Bruker D8 Discovery) calibrated using standard samples. Only x value was ascertained to be systematically changed from $x = 0$ to 0.38, while other elements were ascertained to have almost stoichiometric.

High-resolution X-ray diffraction (HR-XRD, PANalytical X'pert MRD) including XRD reciprocal space mapping (XRD-RSM) was employed to characterize the crystal structure and to determine the lattice parameters. Electrical properties were measured at room temperature and 80 K using Pt/[$x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ – $(1-x)\text{BiFeO}_3$]/ SrRuO_3 capacitor structures. Pt top electrodes (100 μm in diameter) were prepared by the electric beam evaporation. Polarization state and piezoelectric properties were measured by using piezoresponce force microscopy (PFM, SII Nano Technology Inc., SPI 1380) connected to a ferroelectric tester (Toyo Corporation, FCE).

3. Results and discussions

3.1 Crystal structure

Figure 1(a) shows XRD θ – 2θ patterns of $x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ – $(1-x)\text{BiFeO}_3$ films grown on $(100)_c\text{SrRuO}_3$ /(100) SrTiO_3 substrates. {100}-oriented pure perovskite phase without any impurity phase was ascertained to be observed up to $x = 0.68$. In-plane orientation of all films was ascertained by X-ray pole figure measurement as shown in the inset figure in case of $x = 0.68$, in which 2θ angle was fixed corresponding to 110 assuming cubic symmetry. This shows the epitaxial growth of these films.

Figure 1(b) shows the enlarged 2θ range from 37 to 48°. There were three series of peaks labeled as *peak A*, *peak B*, and *peak C* as shown in Fig. 1(b). Only *peak A* was observed at $x = 0$ [*Peak A* was overlapped with SrRuO_3 one, which was ascertained by X-ray diffraction reciprocal space mapping (XRD-RSM) (see Figs. 2(a) and (b))], both *peak A* and *peak B* at $x = 0.15$ – 0.21 , and the coexistence of *peak B* and *peak C* at $x = 0.26$ – 0.44 .

Finally only *peak C* was observed at $x = 0.65$ – 0.68 . These results are the basically the same for those on (100)SrTiO₃ substrates.¹³⁾ The film beyond $x = 0.68$ is under investigation.

To investigate the crystal structures in more detail, XRD-RSM were carried out. Figure 2 shows the XRD-RSM results for the films with x value of 0, 0.21, 0.44 and 0.65 around SrTiO₃ 003 [(a), (c), (e) and (g)] and 103 [(b), (d), (f) and (h)]. Open and closed circles in the figures respective corresponded to those from SrTiO₃ and SrRuO₃. At $x = 0$, there was one spot of the films in Fig. 2(a), corresponding to the *peak A*, whereas two spots in Fig. 2(b), suggesting that this films had a rhombohedral symmetry at $x = 0$. The film with $x = 0.21$ had two 003 spots as shown in Fig. 2(c). One of them near SrTiO₃ in Figs. 2(c) and (d) correspond to *peak A* identified as rhombohedral symmetry as already observed in Figs. 2(a) and (b), while the other spot corresponding to *peak B* in Fig. 1(b) was observed that had the elongated lattice along the surface normal direction of the substrate. Its axial angle was almost 90°, so that it can be identified as the tetragonal phase (*T1*). In case of the film with $x = 0.44$, there were two spots corresponding to *peak B* and *peak C* in Figs. 2(e) and (f), respectively. Out-of-plane lattice parameter of *peak C* was larger than that of *peak B*. *Peak C* can be also identified as tetragonal phase (*T2*) because axial angle was 90° and the lattice parameter of *c*-axis was elongated and was different from that of *a*-axis as shown in Figs. 2(e) and (f). The only one peak was found at $x = 0.65$ [*peak C* in Figs. 2(g) and (h)], suggesting that the film with $x = 0.65$ is in the single phase state with tetragonal symmetry (*T2*).

Dependence of the lattice parameters and the unit cell volume on the x value is shown in Fig. 3 together with the constituent phase of the films. Reported data for BiFeO₃ and Bi(Zn_{1/2}Ti_{1/2})O₃ are also plotted for comparison.^{14),16)} Continuous changes of the lattice parameters and the unit cell volumes in each phase can

Fig. 3. (a) Lattice parameters and (b) unit cell volume as a function of x value in $x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-(1-x)\text{BiFeO}_3$ films together with the reported data for BiFeO₃ (Ref. 14)) (open diamonds) and Bi(Zn_{1/2}Ti_{1/2})O₃ (Ref. 13)) (open squares). Constituent phase identified by XRD was also shown in the figure. (Closed diamonds): Rhombohedral phase (*R*), (Closed triangles): Tetragonal phase (*T1*), (Closed squares): Tetragonal phase (*T2*).

be seen. Based on the obtained results, the boundary between the rhombohedral and tetragonal phases, between *R* and *T1* phases, was identified around $x = 0.21$ – 0.26 . It must be noted that the in-plane lattice parameter of *T1* phase was almost the same with that of SrRuO₃¹⁵⁾ as shown in Fig. 3(a), suggesting the possibility that the *T1* phase was in-plane clamped by the underling layers of the films. This shows the possibility that *T1* phase is existed near the underling layers, while other phase is near the surface of the film. Details analysis using transmission electron spectroscopy including compositional analysis is now under investigation.

Figure 4 shows the high temperature XRD-RSM results around SrTiO₃ 103 from room temperature to 800°C for the films with $x = 0.21$. It must be noted that this films consisted of (*R* + *T1* + *T2*) in Figs. 1–3, but the *T2* peak intensity was very weak due to the small volume fraction and was hardly detected in Fig. 4. Change of the XRD-RSMs was very small up to 700°C and the spots from the films were disappeared at 800°C, suggesting the decomposition of the film. In fact, there were no spots from the film in XRD-RSMs measured at 30°C for the films after heated up to 800°C. Figure 5 summarizes the lattice parameters change with the temperature obtained from the results shown in Fig. 4 as well as the lattice parameter ratio of *c*-axis to *a*-axis, *c/a* ratio of *T1* phase. The change of the lattice parameters and the *c/a* ratio with the temperature was very small up to 750°C. This suggests the high phase change temperature and the phase boundary between *R* and *T1* was very stable up to 750°C against the x value.

3.2 Electrical properties

Relative dielectric constant and dielectric loss against the film composition measured at 150 kHz and room temperature are shown in Fig. 6. Both maximum values were observed near the phase boundary between the *R* and *T1* phase as shown in Fig. 3.

Polarization (*P*)–electric field (*E*) hysteresis loops were measured at room temperature, but the ferroelectricity was not clearly ascertained due to the large contribution of the leakage current. To overcome this problem, room temperature polarization switching was ascertained for the films with $x = 0.21$ using PFM method. Local polarization reversal under the applied voltage was observed in PFM image as shown in Fig. 7, suggesting the ferroelectricity of the films consisted of (*R* + *T1* + *T2*) having maximum dielectric response in Fig. 6.

Figure 8 shows the leakage current density (*J*) as a function of the electric field (*E*) measured at room temperature and 80 K for the same films shown in Fig. 7. Leakage current density dramatically decreased with decreasing measurement temperature, which indicates the possibility of the *P*–*E* hysteresis loop measurement at 80 K by decrease the contribution of the leakage.

Figure 9 shows the *P*–*E* hysteresis loops at 80 K for the films with various x values. Clear hysteresis loops originated to the ferroelectricity were observed for $x = 0$ – 0.21 , however these were not above $x = 0.26$. Figure 10 shows the saturation properties in remnant polarization (*P_r*) and the coercive field (*E_c*). *P_r* and *E_c* values respective monotonously decreased and increased with increasing x as described in Fig. 10. Taking account of the fact that the phase transition temperature corresponding to the Curie temperature (*T_c*) was above 750°C from the results shown in Figs. 4 and 5 as well as the fact that the ferroelectricity was observed at room temperature (see Fig. 7) for the films with $x = 0.21$, increase of the *E_c* with x value is due to the increase of *T_c* because *T_c* of Bi(Zn_{1/2}Ti_{1/2})O₃ is estimated to be 1500°C¹⁴⁾ compared to 820°C of BiFeO₃. The increase of *T_c* accompanies the increase of *E_c*, which results in the difficulty of the ferroelectric switching in *P*–*E* hysteresis loops due to the

Fig. 4. High temperature XRD-RSM results around SrTiO_3 103 from room temperature to 850°C for the films with $x = 0.21$. Continuous and dot circles respective correspond to R and Tl phases.

Fig. 5. Lattice parameters change with the temperature obtained from the results shown in Fig. 4 as well as the lattice parameter ratio of c-axis to a-axis, c/a ratio, of Tl phase. Lattice parameters of SrTiO_3 are also shown in the figure.

requirement of the high applied electric field to get the hysteresis loops originated to the ferroelectricity.

Fig. 6. Relative dielectric constant, ϵ_r , and the dielectric loss, $\tan\delta$, measured at 150 kHz and room temperature as a function of x value for $x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-(1-x)\text{BiFeO}_3$ films.

4. Summary

Crystal structure and the electrical properties were investigated for $\{100\}$ -oriented epitaxial $x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-(1-x)\text{BiFeO}_3$ films grown on $(100)\text{SrRuO}_3/(100)\text{SrTiO}_3$ substrates by MOCVD. Constituent phase changed from rhombohedral symmetry to two types of tetragonal ones with different unit cell volume and tetragonality. Noticeable change of the constituent phase against the temperature was not detected up to 750°C for the films with $x = 0.21$. Room temperature dielectric constant showed the maximum value at the x value of the phase boundary between tetragonal and rhombohedral symmetries. Ferroelectricity at 80 K monotonously decreased with increasing x values and was not ascertained above $x = 0.26$.

Fig. 7. Polarization reversal image by piezoresponse force microscopy for 0.21Bi(Zn_{1/2}Ti_{1/2})O₃-0.79BiFeO₃ film.

Fig. 8. Leakage current density (J) as a function of the electric field (E) measured at room temperature and 80 K for the same film shown in Fig. 7.

Fig. 9. P - E hysteresis loops measured at 80 K for x Bi(Zn_{1/2}Ti_{1/2})O₃-(1- x)BiFeO₃ films with x = (a) 0, (b) 0.15, (c) 0.20, (d) 0.21, (e) 0.26 and (f) 0.44.

Fig. 10. Saturation properties of (a) remanent polarization (P_r) and (b) coercive field (E_c) obtained from the data shown in Fig. 9.

Acknowledgement This research was partially supported by Grants-in-Aid for Scientific Research and the Elements Science and Technology Project from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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