Crystalline structure analysis of {100}-oriented epitaxial BiFeO$_3$-BiCoO$_3$ films grown by MOCVD
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Introduction

Piezoelectric materials have been widely investigated as actuators of micro-electro-mechanical systems (MEMS) applications. From the material point of view, they are mainly concentrated to lead-based materials, such as Pb(Zr, Ti)O$_3$, due to their large piezo response. However, the development of environmentally friendly lead-free materials has been highly sought. In 2004, Saito et al. reported novel lead-free materials with a large piezoelectric coefficient compatible to lead-containing materials, and the development of related materials has been widely investigated after this report. However, these materials include elements unsuitable for the Si-based device process, such as Li, Na, and K. This gives insight into the difficulty of the application of these materials to the Si-based device process, which has been widely used in MEMS fabrication. Therefore, the development of a novel type of lead-free materials is essential.

The key point of piezoelectric materials with a large piezo response is the discovery of the phase symmetry transition against composition, the so-called morphotropic phase boundary (MPB). In fact, Pb(Zr, Ti)O$_3$ shows the extremely large piezo response at MPB composition, where the crystal symmetry changes from tetragonal symmetry to rhombohedral symmetry.

For the development of a novel lead-free piezo material, we mainly focused on bismuth based-perovskite materials in this study, but research on their MPB composition has been hardly reported. This is due to the lack of materials having the tetragonal phase, even though there are many rhombohedral ones, such as BiFeO$_3$. Belik et al. reported in 2006 that BiCoO$_3$ has a tetragonal symmetry even if it is stable only at a high pressure. The high-pressure phase has a possibility to be stabilized by the epitaxial strain in film forms, as demonstrated in the case of the epitaxial SrIrO$_3$ film. In this study, we grew epitaxial films in BiCoO$_3$-BiFeO$_3$ solid solution by metal organic chemical vapor deposition (MOCVD) and investigated their crystal symmetry change with film composition.

Experimental

BiFeO$_3$-BiCoO$_3$ solid solution films were grown on (100) SrTiO$_3$ substrates at 700 °C by MOCVD using Bi[(CH$_3$)$_2$NCH$_2$]$_2$, Fe(C$_6$H$_5$CH$_2$)$_2$, Co(CH$_3$C$_6$H$_4$)$_2$, and oxygen gas as the source materials. A vertical glass-type reactor maintained at a pressure of 530 Pa was used for the film preparation. The films were deposited by MOCVD using pulse introduction of the mixture gases with Bi, Fe, and Co sources (pulse-MOCVD).

The crystal structure of the deposited films was characterized by high-resolution X-ray diffraction (HRXRD) analysis using a four-axis diffractometer (Philips X'pert MRD). HRXRD reciprocal space mapping (RSM) around SrTiO$_3$ 004 and 204 was also employed for a detailed analysis.

Results and Discussion

Analysis of the crystal structure was carried out by HRXRD-RSM measurements. Figure 1 shows the cross-sectional RSM around 004 and 204 of SrTiO$_3$. Typical 004 and 204 spots of rhombohedral BiFeO$_3$ phase were observed in Figs. 1(a) and 1(b), respectively, together with the spots from SrRuO$_3$ (marked as open circle) and SrTiO$_3$; a 004 spot at the surface normal direction and two 204 spots having the same in-plane lattice spacing.

On the other hand, for BiCoO$_3$-BiFeO$_3$ films with $x = 0.16$, the 004 spots were separated along the in-plane direction having the same out-of-lattice spacing, as shown in Figs. 1(c), 1(d) and 1(e), 1(f), respectively. Moreover, the additional spots identified as tetragonal symmetry shown in Figs. 1(e) and 1(f) and marked as open squares were observed in the film with $x = 0.22$.

Fig. 1. Cross-sectional HRXRD-RSMs measured at around [(a), (c), (e)]004 and [(b), (d), (f)] 204 xBiCoO$_3$-(1-x)BiFeO$_3$ films grown on (100),SrRuO$_3/(100)/$SrTiO$_3$ substrates: (a, b) $x = 0$, (c, d) $x = 0.16$, and (e, f) $x = 0.22$.

Fig. 2. [(a)-(c)] Plan-view XRD-RSMs measured at around 002 xBiCoO$_3$-(1-x)BiFeO$_3$ films grown on (100),SrRuO$_3/(100)/$SrTiO$_3$ substrates and [(d)-(f)] their schematic drawing of the unit cell: (a, d) $x = 0$, (b, e) $x = 0.16$, and (c, f) $x = 0.22$.
For the more detailed analysis, plan-view XRD-RSMs, omega-psi scan, shown in Figs. 2(a)-2(c), were carried out at the fixed d(200) of the films. Only one center spot and four spots tilted along [110] (about 0.6° in the omega and psi directions) were observed for x = 0 [Fig. 2(a)], and x = 0.16 [Fig. 2(b)] and 0.22 [Fig. 2(c)] respectively. The results shown in Figs. 1 and 2 reveal that the films with x = 0 and 0.16 have both rhombohedral-based symmetry; the unit cells with x = 0 and 0.16 were distorted rhombohedral with a fixed film/substrate interface [see Fig. 2(d)] and rhombohedral one with the film/substrate interface whose tilting angle was approximately 0.6° [see Fig. 2(e)]. The possible reason for this symmetry change is that the Curie temperature (T_c) of the films were changed from above to below the growth temperature (700°C) with increasing x as predicted from the results of Azuma et al. When x = 0, the film having rhombohedral symmetry was directly deposited and its symmetry down to room temperature was maintained without any transformation. In this case, the crystal symmetry was distorted by the thermal stress as well as the misfit stress. On the other hand, when x was high and the film was deposited above T_c, the film transforms from cubic to rhombohedral symmetry during cooling, which released the strain in the film. This possibly induced the relaxed structure similar to that of the bulk. In this case, the present tilted angle of about 0.6° at x = 0.16 being almost in agreement with the reported one for the BiFeO_3 bulk was a reasonable result because the tilted angle of the rhombohedral symmetry in PZT and PZN-PT systems having MPB composition was kept almost stable relatively independent of the composition.

Note that the center spot in Figs. 2(b) and 2(c) included that from the SrTiO_3 substrate, owing to the close lattice spacing of SrTiO_3 and films. However, by taking account of the results shown in Fig. 1, it can be concluded that the center spot of x = 0.16 consists of only SrTiO_3, while that of x = 0.22 consists of SrTiO_3 and films. Moreover, the center spot in Fig. 2(c) will overlap with that from the tetragonal symmetry phase as discussed above for the film with x = 0.22. Therefore, the film with x = 0.22 is a mixture of the tetragonal and rhombohedral symmetries. These results show that the constituent phase changes from rhombohedral [see Figs. 2(d) and (e)] to a mixture of tetragonal and rhombohedral [see Fig. 2(f)] between x = 0.16 and 0.22, which is different from the results of previous reports; it is located below x = 0.16. There are two possible explanations for the difference between the present study and the previous one, i.e., types of substrate and the film thickness, because the previous one was for 200-nm-thick films on (100)SrTiO_3 substrates, while the present one was for 400-nm-thick films on (100)SrRuO_3/(100)SrTiO_3 substrates. To check the possibility of the types of the substrate, BiCoO_3-BiFeO_3 films with x = 0.16 were grown both (100)SrTiO_3 and (100)SrRuO_3/(100)SrTiO_3 substrates. No clear difference was detected for the films grown on (100)SrTiO_3 and (100)SrRuO_3/(100)SrTiO_3 substrates. In addition, for the film with x = 0.16 and about 200 nm in thickness grown on (100) SrTiO_3 substrate, the authors already confirmed that the crystal symmetry was a mixture of tetragonal and rhombohedral symmetries. By taking account of the results, this indicates that the crystal symmetry was changed by the film thickness. A similar phenomenon of the crystal structure change with the film thickness has already been observed for the epitaxial PZT films grown on (100),SrRuO_3/(100) SrTiO_3 substrates.

Conclusions

The 100°-oriented xBiCoO_3-(1-x)BiFeO_3 films (x = 0-0.22) of 400 nm thickness were grown on (100)SrRuO_3/(100)SrTiO_3 substrates by MOCVD. The crystal symmetry of the films grown on (100)SrRuO_3/(100)SrTiO_3 substrates changed from rhombohedral to a mixture of tetragonal and rhombohedral with increasing BiCoO_3 content, x values, and the composition where the crystal symmetry change was different from that of 200-nm-thick films grown on (100)SrTiO_3 substrates. This is considered to be due to the thickness dependence of the constituent phase rather than the difference in the type of substrate because the constituent phase was confirmed to be basically the same for the films on both substrates with the same thickness. Therefore, the film thickness dependence of the constituent phase was one factor for the change in the MPB composition.

Future work

The electrical property will be examined at room temperature and 80 K using a Pt/xBiCoO_3-(1-x)BiFeO_3/SrRuO_3 capacitor after making platinum top electrodes of 100 μm diameter, which were deposited by electric beam evaporation. Piezoelectric property will be measured by piezo force microscopy (PFM) and in-situ lattice observation technique under electric field using synchrotron X-ray (SPRIng-8, BL13XU).

Publications

Oral Presentations


Papers
