Preparation of monoclinic $0.9(\text{BiFeO}_3)$ - $0.1(\text{BiCoO}_3)$ epitaxial films on orthorhombic YAlO_3 (100) substrates by r.f. magnetron sputtering

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Abstract

0.9BiFeO₃-0.1BiCoO₃ (BFCO) films ($t = 100$ nm) were prepared on orthorhombic YAlO₃ (YAO) (100) substrates by r.f. magnetron sputtering. Film flatness, crystallinity, crystal symmetry, and secondary phase formation, are strongly affected by the pressure of the sputtering gasses, Ar and O₂. Phi-scan measurements showed that the films were epitaxially grown on the substrates, with a crystal relation of $[101]_p(101)_p$ BFCO// $[101]_p(101)_p$ YAO. X-ray reciprocal space mapping revealed that the crystal symmetry of the BFCO films was a pseudo-cubic-like monoclinic structure, with M_C phase, rather than the Cm symmetry of the bulk BFCO. Cross-sectional transmission electron microscopy analysis revealed that the film had, as a result of a lattice misfit of 7%, strong compressive strain less than 10 nm from the interface, which relaxed monotonically with increasing distance from the interface. Magnetic measurements suggest that strained monoclinic BFCO showed smaller magnetization compared to rhombohedral BFCO.

Keywords:

A1. Monoclinic; B1. Perovskites; B1. BiFeO₃; B1. BiCoO₃; B1. YAlO₃ substrates; B2. Multiferroics

1. INTRODUCTION

BiFeO_3 (BFO), which possesses antiferromagnetism and ferroelectricity above room temperature (RT), is attractive to many researchers. Bulk BFO has a rhombohedrally distorted structure, with the space group (SG) of $R3c$, [1] and shows a large spontaneous polarization of $100 \mu\text{C}/\text{cm}^2$. [2] Materials based on BFO solid solutions have been investigated widely. In particular, tetragonal BiCoO_3 is of interest as the BiFeO_3 - BiCoO_3 solid solution $\text{Bi}(\text{Fe},\text{Co})\text{O}_3$ (BFCO), changes its crystal symmetry, together with ferroelectric and dielectric properties, as a function of composition ratio. [3] It has been reported that the crystal symmetry of BFCO changed from rhombohedral (SG: $R3c$) to tetragonal (SG: $P4mn$) at a composition ratio of approximately 80 at.% of BiFeO_3 . [4] At this composition, there exists the monoclinic phase (SG: Cm) between rhombohedral ($R3c$) and tetragonal ($P4mn$) phases. There are some reports of monoclinic bulk BFCO, [4 - 6] and no reports of monoclinic BFCO in film form. The crystal structure of BFO is easily changed into rhombohedral, tetragonal, and monoclinic forms by a combination of epitaxial strain, site-substitution, and fabrication conditions. Although monoclinic structures with $c/a \sim 1$ (rhombohedral-like) and with $c/a > 1$ (tetragonal-like) have been reported in the case of BFO [7], the rhombohedral-like monoclinic structure of BFCO is rarely reported, as Co-substitution has a tendency to increase c/a and form a tetragonal structure. Furthermore, as not only the ferroelectric and dielectric properties, but also the magnetic properties, are strongly affected by changes in crystal symmetry, the relationship between physical properties and crystal symmetry needs to be clearly

understood [5, 6, 8] in order to increase the feasibility of RT multiferroic devices. There are reports on monoclinic BFO on SrTiO₃ (100) substrates [9]; however, the production of single phase monoclinic BFO requires careful adjustment of the sputtering conditions. [10] In this study, BFCO films were grown on YAlO₃ (YAO) (100) substrates in order to obtain single phase monoclinic BFCO epitaxial films. The sample crystal structure was investigated in detailed and the magnetic properties were measured at 300 K.

2. EXPERIMENTS

A Bi-poor Bi_{0.9}Fe_{0.9}Co_{0.1}O_x sintered target was used for r.f. magnetron sputtering. BFCO films were grown on orthorhombic YAO (100) substrates. The Ar + O₂ sputtering gas (Ar : O₂ = 3 : 1) was introduced during sputtering, and the total gas pressure was varied between 0.08 and 0.14 Pa. In order to understand the strategy for fabricating monoclinic BFCO films on orthorhombic YAO substrates, the crystal relation is described in the Fig. 1. The monoclinic perovskite structure of YAO is contained in the orthorhombic YAO unit cell. [11] The relation for crystal orientations between the orthorhombic structure and the perovskite structure is [100]_o(001)_o YAO//[101]_p(101)_p YAO. In this paper, o and p stand for orthorhombic and monoclinic perovskite structure, respectively. As BFCO also has the perovskite structure, BFCO should grow as cube-on-cube with respect to the monoclinic structure of YAO. The formation of secondary phases and crystallinity were sensitive to the sputtering conditions, such as input r.f. power ($P_{\text{r.f.}}$) and substrate temperature (T_s). $P_{\text{r.f.}}$ =15 W was set

as the minimum $P_{\text{r.f.}}$, as the plasma appears above 10 W, and secondary phases such as BiO_x form with increasing $P_{\text{r.f.}}$. The total gas pressure also influences the formation of secondary phases, because of an increase in bombardments resulting in metallic Bi forming with low gas pressure during sputtering. [12] In our previous study, [13] Bi compounds were formed by relatively low sputtering gas pressure using a stoichiometric target; therefore, in this study, a Bi-poor target was used. The films crystalized above approximately 700 K, and crystallinity increased with increasing T_s until approximately 1000 K. The formation of secondary phases, such as BiO_x , was observed above 973 K, which was in accordance with previous study. [14] $P_{\text{r.f.}}$ and T_s were fixed at 15 W and 873 K, respectively. The main focus of this study is the pressure of the sputtering gas, $\text{Ar}+\text{O}_2$ ($P_{\text{Ar}+\text{O}_2}$), which was changed from 0.08 Pa to 0.14 Pa. The thickness of all films was 100 nm. Film structure was evaluated by X-Ray Diffraction (XRD) with a $\theta/2\theta$ scan, rocking curve scan, and ϕ -scan with Cu K_α radiation. In our previous study, it was suggested that the BFO film surface becomes rough when secondary phases, such as BiO_x , form; therefore, surface roughness was checked by an atomic force microscope (AFM). [13] In order to analyze the crystal symmetry of the BFCO films, X-ray reciprocal space mapping (XRSM) was undertaken. The cross-sectional structure of BFCO films was observed by a transmission electron microscopy (TEM). The magnetic property of BFCO films was evaluated with superconducting quantum interference device (SQUID) magnetometer at 300 K. The magnetic field was applied to the in-plane direction of the film.

3. RESULT and DISCUSSION

Fig. 2(a) shows the $\theta/2\theta$ XRD scans, and 2(b) shows the integrated intensity of Bi_2O_3 (402). Bi_2O_3 (402) peaks were selected because they did not overlap with other diffraction peaks. Bi_2O_3 was observed as a secondary phase in samples with $P_{\text{Ar}+\text{O}_2} = 0.08 - 0.10$, and 0.14 Pa. For the sample with $P_{\text{Ar}+\text{O}_2} = 0.11 - 0.13$ Pa, secondary phases were not observed [Fig. 2(a)]. The relationship between $P_{\text{Ar}+\text{O}_2}$ and formation of secondary phases of Bi_2O_3 is thought to depend on (i) lack of oxygen, and (ii) heat of formation energy. Lack of oxygen may break the perovskite structure, which consists of oxygen-octahedral, leading to excess metal as impurity. The heat of formation energy toward oxides is different in Bi, Fe and Co - Bi_2O_3 ; -574 kJ/mol, Fe_3O_4 ; -1118 kJ/mol, Fe_2O_3 ; -823 kJ/mol, and Co_3O_4 ; -891.0 kJ/mol. It can be seen that Bi can easily form oxides compared to Fe or Co; these Bi_2O_3 grains became large enough to be detected by XRD. Formation of Bi_2O_3 at low $P_{\text{Ar}+\text{O}_2}$ might be considered to be preferential, considering the small heat of formation energy of Bi compared with Fe and Co. It should be noted that we cannot exclude the existence of small grains related to secondary phases of Fe or Co compounds in the film. The rocking curves measurement, shown in Fig. 2(c), of BFCO (101)_p showed sharp curves for the sample without the secondary phases. The full width at half maximum (FWHM) of the rocking curves increase with the secondary phase formation, [Fig. 2(d)] and the value for $P_{\text{Ar}+\text{O}_2} = 0.12$ Pa is 1.3° .

Figure 3 shows the ϕ -scan and pole-figure-scan for the sample with $P_{\text{Ar}+\text{O}_2} = 0.12$ Pa. It was confirmed that the BFCO film grew epitaxially on the YAO (100)_o substrate with the crystallographic

relation of $[101]_p(101)_p$ BFCO// $[101]_p(101)_p$ YAO. The other samples also grew epitaxially on the YAO $(100)_o$ substrates, regardless of formation of the secondary phases. XRD investigation indicates that single-phase BFCO epitaxial films, with a high degree of crystallinity, were obtained at $P_{Ar+O_2} = 0.11 - 0.13$ Pa.

Figure 4 shows the dependence of average roughness (R_a) and peak to valley distance ($P-V$) on P_{Ar+O_2} . R_a varied over the range 0.5 - 8.0 nm, and it can be seen that the surface morphology is strongly dependent on P_{Ar+O_2} . In the case of $P_{Ar+O_2} = 0.08 - 0.10$ Pa and 0.14 Pa, a rough surface was obtained and the columnar growth was confirmed from the AFM images. The smallest R_a and $P-V$ were obtained in the case of $P_{Ar+O_2} = 0.12$ Pa. It can be seen that the flatness of the films is adversely influenced by the presence of secondary phases, which was consistent with our previous results. [13]

Crystal symmetry cannot be identified by XRD with conventional $\theta/2\theta$ scans; therefore, XRSM measurements were carried out. According to Saito's report, the crystal symmetry is determined by number of peak splits in $(H0L)$ and (HHL) diffraction. [15] Fig. 5 shows the XRSM images for $(003)_p$, $(301)_p$, $(202)_p$, and $(221)_p$ for the sample prepared under $P_{Ar+O_2} = 0.12$ Pa. In order to show the peak splitting, a line intensity profile was made from the XRSM images. $(H0L)$ diffraction, such as $(301)_p$ and $(202)_p$, split into three spots, while (HHL) diffraction, such as $(221)_p$, split into two spots. The BFCO films were identified as monoclinic crystal symmetry. The samples with Bi_2O_3 also showed the monoclinic structure, which implied the YAO $(100)_o$ substrate has a tendency to grow monoclinic BFCO, when compared with the $SrTiO_3$ (100) substrate. [10] In the

case of monoclinic BFO epitaxial films, there exist three different types of phases, namely, M_A , M_B , and M_C , for [100] growth of perovskite [16, 17]. M_A and M_B belong to the Cm SG, and the M_C belongs to Pm SG. According to H. M. Christen's report, when (HHL) and (HOL) split into three and two respectively, the crystal symmetry was identified as M_A phase. Alternately, when (HHL) and (HOL) split into two and three respectively, the crystal symmetry was identified as M_C phase. [9] Therefore, the XRSM results revealed that the BFCO films had monoclinic structure, and classified as an M_C phase. The lattice constants, based on a monoclinic structure, were calculated from the XRSM image as approximately: $a = b = 0.399$ nm, $c = 0.397$ nm, and $\alpha = \gamma = 90^\circ$, $\beta = 89.4^\circ$. The lattice constants are almost same value, meaning that the crystal symmetry is relatively close to the pseudo-cubic-perovskite structure. The monoclinic structure pseudo-cubic-perovskite with M_C phase of the BFCO films is different from the bulk BFCO Cm symmetry.

Based on the epitaxial relation shown in Fig. 1, the lattice misfit between BFCO and the YAO substrate is 7%. In order to clarify epitaxial strain from the YAO substrates, the cross-sectional structure was observed by TEM. Fig. 6(a) and 6(b) show the cross-sectional TEM images for the BFCO-YAO interface and whole area of BFCO film, respectively. Fig. 6(c) - 6(g) show the nano-beam diffraction (NBD) patterns. The high resolution TEM image at the interface indicates the BFCO film grew epitaxially on the YAO substrates without any intermixing layer [Fig. 6(a)]. The splits of the NBD spots from the BFCO film, caused by the compressive strain from the YAO substrate, were observed at the interface between the film and the YAO (100)_o substrate [Fig. 6(f)].

The split of the NBD spots was observed until 10 nm away from the interface, [Fig. 6(e)] and these spots were merged above 40 nm [Fig. 6(d)]. XRD cannot detect the very thin region near the interface; therefore, the split in NBD peaks at $t \leq 10$ nm might be not observed in the XRSM. The XRSM information was obtained mainly from the thicker area not strongly influenced by lattice strain from substrate. In fact, the lattice parameters estimated from the XRSM agreed with those from NBD patterns collected ≥ 40 nm away from the interface. At 60 nm from the interface, the shift of the diffraction spots to lower angle was observed [Fig. 6(c)]. Classification of the monoclinic structure at the interface to M_A , M_B , or M_C needs further detailed analysis by observing NBD spots from different angles. The above results imply that the compressive strain at the interface relaxes with increasing distance from the interface, and therefore, the properties of this film ($t = 100$ nm) should be observed as summation of the one of a relaxed region and a distorted region.

Magnetization (M - H) curves were measured by a SQUID magnetometer at 300 K. Fig. 7(a) shows the M - H curves for the sample with $P_{\text{Ar+O}_2} = 0.09, 0.12$ and 0.13 Pa. Expanded M - H curves near 0 kOe are shown in Fig. 7(b). The samples made with $P_{\text{Ar+O}_2} = 0.08 - 0.10$ and 0.14 Pa had the secondary Bi_2O_3 phase, while the samples made with $P_{\text{Ar+O}_2} = 0.11 - 0.13$ Pa were single phase of BFCO. The magnetization was relatively large for the sample including the secondary phases, which might be caused by small Fe or Co oxide particles. The single phase monoclinic BFCO ($P_{\text{Ar+O}_2} = 0.12$ Pa) showed the smallest remnant magnetization of $0.002 \mu_B/\text{u.c.}$. According to a previous report, [6] monoclinic BFCO (BCO content of 20 at.%) with Cm symmetry showed small magnetization.

Therefore, it might be suggested that the monoclinic BFCO (BCO content of 10 at.%) did not possess large magnetization; even though, crystal symmetry similar to pseudo-cubic-perovskite and film has compressive strain. The disappearance of magnetization in the monoclinic structure might be the reason for the fluctuation of valence, decrease of spin-canting angle, and/or preservation of cycloidal spin structure; [18] however, further investigation is necessary to understand the magnetic structure in monoclinic BFCO.

SUMMARY

BFCO films were epitaxially grown on orthorhombic YAO (100) substrates with the epitaxial relation of $[101]_p(101)_p$ BFCO// $[101]_p(101)_p$ YAO. The suppression of secondary phases, such as BiO_x , required careful control of $\text{Ar}+\text{O}_2$ gas pressures owing to heat of formation against oxygen. The BFCO film had compressive strain less than 10 nm from the interface owing to lattice misfit of 7% between BFCO and the YAO substrate, and this strain relaxed monotonically with increasing the distance from the interface. The crystal symmetry of BFCO films was not identified as the bulk monoclinic Cm structure, but a pseudo-cubic-perovskite-like monoclinic structure, which is classified as an M_C phase. Magnetic measurement suggested that the magnetization enhancement at RT for monoclinic BFCO seems smaller compared with the rhombohedral BFCO, regardless of the existence of compressive strain or pseudo-cubic structure. For use in spintronic devices such as spin-filter materials, the rhombohedral is more promising crystal symmetry in the case of BFCO.

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Figure captions

Fig. 1 (a) Schematic image for crystal structure of YAlO_3 . (b) Crystal relation between BiFeO_3 - BiCoO_3 and YAlO_3 that is seen from b -axis.

Fig. 2 (a) $\theta/2\theta$ scan for $\text{YAO}(100)_o$ sub./BFCO. (b) $\text{Ar} + \text{O}_2$ gas pressure dependence of integrated intensity of $\text{Bi}_2\text{O}_3(402)$ and grain sizes which were estimated by Scherrer's formula. (c) Rocking curves for BFCO(101). (d) $\text{Ar} + \text{O}_2$ gas pressure dependence of FWHM of the rocking curves.

Fig. 3 (a) ϕ -scan profiles, and pole figures for the (b) (101) peak of a BFCO film prepared with $P_{\text{Ar}+\text{O}_2}=0.12$ Pa, and (c) (101) peak of the YAO substrate.

Fig. 4 Surface morphology of (a) the YAO substrate and BFCO films fabricated with $\text{Ar} + \text{O}_2$ gas pressure of (b) 0.08 Pa, (c) 0.10 Pa and (d) 0.12 Pa. (e) $\text{Ar} + \text{O}_2$ gas pressure dependence of Roughness and Peak to Valley distance.

Fig. 5 XRSM images for (a) 003, (b) 202, (c) 301, and (d) 221 peaks of the BFCO epitaxial film

which was fabricated with Ar + O₂ gas pressure of 0.12 Pa. (*H0L*) and (*HHL*) diffraction spots split into two and three, respectively, implying the crystal structure is monoclinic.

Fig. 6 TEM images and nano-beam diffraction (NBD) patterns for monoclinic BFCO grown on a YAO(100)_o substrate with Ar + O₂ gas pressure of 0.12 Pa. The subscript pc corresponds to a pseudo-cubic-perovskite structure. At the interface between the BFCO film and the YAO substrate, the BFCO diffraction spots split showing the compressive strain resulting from the lattice mismatch. The split was observed until 10 nm past the interface.

Fig. 7 (a) The *M-H* curves of BFCO films fabricated with Ar + O₂ gas pressure of 0.09 Pa, 0.12 Pa and 0.14 Pa. (b) The enlarged view of (a) around 0 kOe. (c) Ar + O₂ gas pressure dependence of magnetization *M* at 10 kOe and remnant magnetization *M_r*.

Figure1

Figure2

Figure3

Figure4

Figure5

Figure6

Figure 7