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Preparation of monoclinic 0.9($BiFeO_3$)–0.1($BiCoO_3$) epitaxial films on orthorhombic $YAlO_3$ (100) substrates by r.f. magnetron sputtering

T. Ichinose*, H. Naganuma, K. Mukaiyama, M. Oogane, Y. Ando

Department of Applied Physics, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

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ABSTRACT

$0.9BiFeO_3$–$0.1BiCoO_3$ (BFCO) films (t=100 nm) were prepared on orthorhombic $YAlO_3$ (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 O_2. Phi-scan measurements showed that the films were epitaxially grown on the substrates, with the crystal relation $[101]_p(101)_p$ BFCO$\parallel[101]_p(101)_p$ 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 show that strained monoclinic BFCO has smaller magnetization compared to rhombohedral BFCO.

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 *R*3*c* [1], and shows a large spontaneous polarization of 100 $\mu C/cm^2$ [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 Bi(Fe,Co)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: *R*3*c*) to tetragonal (SG: *P*4*mn*) at a composition ratio of approximately 80 at% of $BiFeO_3$ [4]. At this composition, there exists the monoclinic phase (SG: *Cm*) between rhombohedral (*R*3*c*) and tetragonal (*P*4*mn*) 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 $c/a\sim1$ (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 $SrTiO_3$ (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 $YAlO_3$ (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+O_2 sputtering gas (Ar:O_2=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 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

* Corresponding author. Tel.: +81 227957949; fax: +81 227957947.
E-mail address: ichinose@mlab.apph.tohoku.ac.jp (T. Ichinose).

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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 ($P_{r.f.}$) and substrate temperature (T_s). $P_{r.f.}=15$ W was set as the minimum $P_{r.f.}$, as the plasma appears above 10 W, and secondary phases such as BiO_x formed with increasing $P_{r.f.}$. The total gas pressure also influences the formation of secondary phases, because of an increase in bombardments resulting in metallic Bi formation 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 is in accordance with previous study [14]. $P_{r.f.}$ and T_s were fixed at 15 W and 873 K, respectively. The main focus of this study was the pressure of the sputtering gas, $Ar+O_2$ (P_{Ar+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 Kα 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

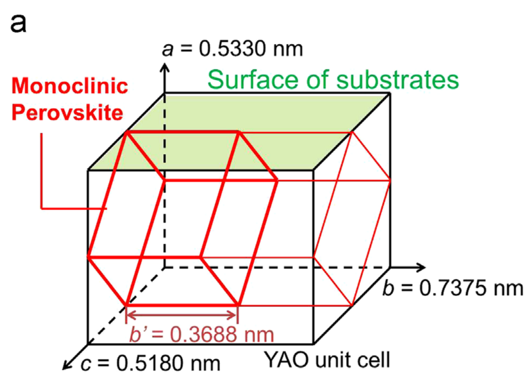

Fig. 1. (a) Schematic image for crystal structure of $YAlO_3$ and (b) crystal relation between $BiFeO_3$–$BiCoO_3$ and $YAlO_3$ that is seen from *b*-axis.

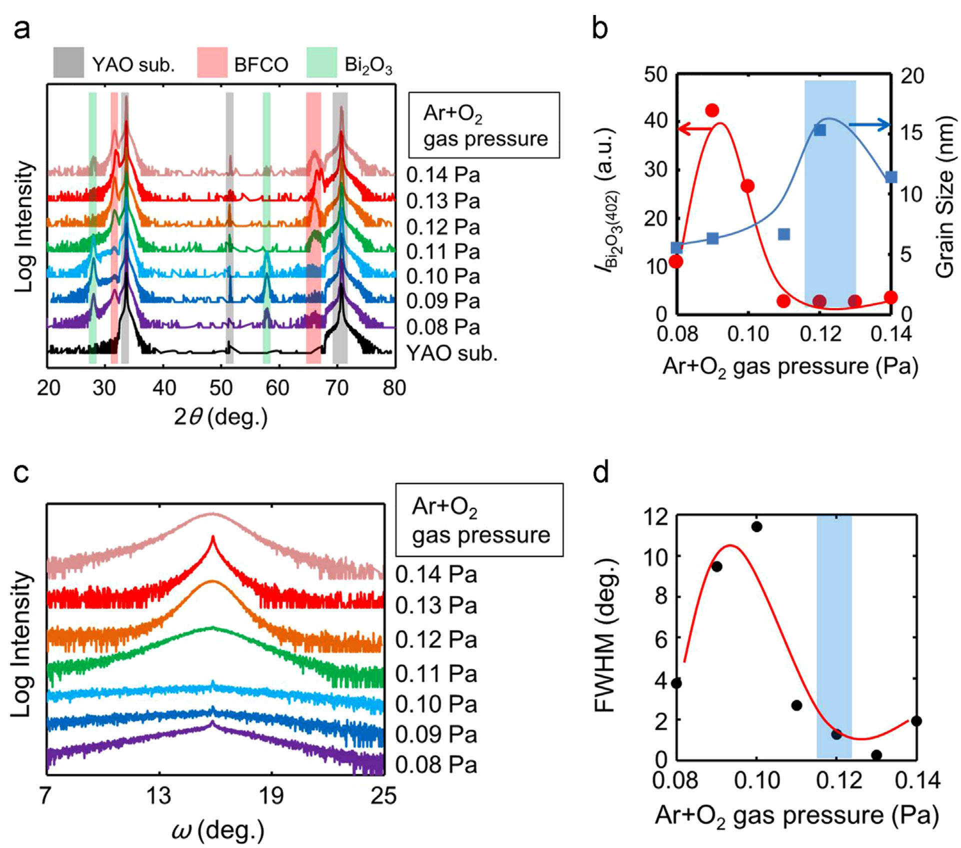

Fig. 2. (a) $\theta/2\theta$ scan for YAO$(100)_o$ sub./BFCO, (b) $Ar+O_2$ gas pressure dependence of integrated intensity of Bi_2O_3 (402) and grain sizes which were estimated by Scherrer's formula, (c) rocking curves for BFCO (101) and (d) $Ar+O_2$ gas pressure dependence of FWHM of the rocking curves.