Thin Solid Films 519 (2011) 8334–8337

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Preparation and magnetic properties of $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ thin films with magnetic order above room temperature

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ARTICLE INFO

Available online 13 April 2011

Keywords:
Multiferroics
Ferroelectric antiferromagnet
Aurivillius family
Bi oxides
Chemical solution deposition
Epitaxy
Mössbauer spectoroscopy

ABSTRACT

Thin films of $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ (BFTO) with $m \leqq 9$ have been successfully grown on (100) $SrTiO_3$ by chemical solution deposition. These films had the *c* axis normal to the film plane. The conversion electron Mössbauer spectoroscopy (CEMS) showed that the spectra of BFTO thin films exhibit an asymmetric quadrupole doublet for $m = 8$ at 300 K, indicative of being paramagnetic, while, for $m = 9$, clearly show six hyperfine lines indicating presence of magnetic order at 300 K. From the intensity ratio of asymmetric peaks, the polarization axis of BFTO films with $m \geq 8$ was deduced to be likely along <101> of the perovskite-like unit. On the other hand, it was found from the spectral fitting that the BFTO thin film with $m = 9$ has the Néel temperature around 310 K and the spin axis making an angle of about 60° to the *c*-axis. These indicate that the BFTO ($m = 9$) thin film is a promising candidate for room-temperature multiferroics.

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1. Introduction

Multiferroic materials exhibiting simultaneously ferromagnetism and ferroelectricity have attracted much interest because of their potential for a large magnetoelectric effect due to order-coupling. One of the Aurivillius family of bismuth oxides, $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ (BFTO) is a promising candidate. This oxide is characterized by a layered crystal structure in which a $(Bi_2O_2)^{2+}$ layer and *m* layers with a perovskite-like unit are periodically stacked [1,2]. The unit cell has orthorhombic distortion (the ratio of lattice constant $b/a \sim 1.002$). The well-known ferroelectric $Bi_4Ti_3O_{12}$ with Curie temperature (T_C) as high as 675 °C [3] is an end member of this compound. The typical ferroelectric antiferromagnet $BiFeO_3$ (BFO) with $T_C \sim 1103$ K and Néel temperature ($T_N \sim 643$ k [4,5]) can be regarded as a limiting case of layered perovskite-like structures with $m = \infty$ though the structure is not layered. As intermediates between them, $BiFe_{1-x}Ti_xO_{3+\delta}$ ($x \leq 0.2$) with chemical compositions close to BFO was also investigated [6–8]. However, the prepared oxides were not with layered structure characteristic of the Aurivillius family but with a simple perovskite structure as same as that of BFO.

Thus, the Aurivillius family oxide BFTO is unique as a multiferroic and of considerable interest: The perovskite-like packets allows ion replacement and thereby has flexibility in adjusting the order parameters as compared to BFO. In addition, the layered structure of BFTO is also interesting from the viewpoint of magnetoelectric effect of a natural magnetic superlattice. Sultanov et al. showed that exchange interaction between Fe atoms in BFTO occurs only within the confines of a single perovskite-like packet sandwiched between diamagnetic $(Bi_2O_2)^{2+}$ layers [9,10]. Magnetic anisotropy of Fe in such a packet with a small volume should be susceptible to energetic change of spin-orbit interaction via dielectric ion displacement as well as to thermal energy. Therefore, if BFTO has the magnetic order above room temperature, it is expected to show a magnetoelectric response of great interest.

It has been reported that the BFTO compounds exhibit ferroelectric Curie temperatures as high as nearly 650 K and antiferromagnetic order below room temperature for $m \leq 8$ [2,9,10]. The increase of *m* is expected to elevate the Néel temperature because Fe ions randomly occupying the octahedral sites of the perovskite-like layers increase and the magnetic long-range order is enhanced. However, BFTO synthesized so far was up to $m = 8$ and, in addition, likely included other phases for $m \geq 5$ because of volatility of Bi and/or structural instability increased with increasing *m* [1]. Thus, preparation of pure BFTO with larger *m* is requisite for achieving magnetic order above room temperature. To overcome this issue, we tried to epitaxially grow the thin films of BFTO with larger *m* using the chemical solution deposition (CSD). The epitaxy facilitates the film growth of BFTO phase on a substrate surface with a similar ionic arrangement because the lattice matching lowers interface energy between BFTO and the substrate. This leads to inhibiting the production of other phases. In addition, the CSD cause no compositional deviation.

In this paper, we describe the thin film growth of BFTO with $m \geq 8$ and discuss the structural and magnetic properties of them.

2. Experimental

The nitrates of Bi and Fe and a water-soluble Ti complex compound ($(NH_4)_4[Ti_2(C_6H_4O_7)_2(O_2)_2] \cdot 4H_2O$) were used as sources for

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doi:10.1016/j.tsf.2011.04.025

the precursor solution. These were dissolved into the mixture of 2-methoxyethanol and nitric acid at the metal ion concentration of 0.68 mol/l. The thin films were prepared on (100) $SrTiO_3$ (STO) single crystal substrates by repeating the following process 5 times; spin-coating of the precursor solutions, drying at 200 °C, decomposition at 400 °C and rapid thermal annealing for 10 min at 900 °C. The structural and magnetic properties of the obtained thin films were evaluated by X-ray diffraction (XRD), reflection high energy electron diffraction (RHEED), vibrating sample magnetometer (VSM) and the conversion electron Mössbauer spectoroscopy (CEMS). The CEMS spectra were measured in the temperature range of 80 K to 300 K. To obtain clear CEMS spectra, a sample of BFTO ($m=9$) was prepared with Fe all replaced by the isotope ^{57}Fe. Another merit of using the CSD for fabrication is the easy preparation of these samples.

3. Results and discussion

3.1. Epitaxial growth of BFTO thin films

Fig. 1 shows the XRD θ–2θ scans of the films with m of 4 to 11. Only the peaks assigned to $(00\underline{2l})$ reflections of BFTO are clearly observed for all m. The position and linewidth of the $(00\underline{2l})$ ($l=m+1$, $2m+2$) reflections are nearly independent of m. This is because they are fundamental reflections originated from the periodicity in units of $m+1$ layer and the lattice constant of c-axis increases roughly in proportion to the layer number $m+1$ of crystal unit. On the other hand, the $(00\underline{2l})$ satellite peaks around the fundamental reflections shift to higher angle for $l<m+1$ or $2m+2$ and to lower angle for $l>m+1$ or $2m+2$, along with broadening. The increased broadness is presumably associated with structural disorder of each perovskite-like layer due to defects of oxygen and/or Bi ions.

Fig. 2 shows typical RHEED images of a BFTO ($m=5$) thin film taken along (a) <100> and (b) <110> azimuths of STO substrate. The wider spacing between the streak lines observed in (b) than (a) means that the film has in-plane epitaxial relationship of film <100> or <010>//STO <110>. This epitaxy is inferred from that the in-plane lattice matching between STO <110> and BFTO <100> or <010> is roughly within 0.5% (e.g. for $m=5$, the unit cell parameters: $a=0.5490$ nm, $b=0.5500$ nm, $c=5.0185$ nm) [2]. These suggest that the BFTO film with $m=5$ was epitaxially grown along the c-axis on (100) STO. While, we could not observe clear RHEED images of streak lines evidencing epitaxy for the BFTO film of $m=9$. This is likely due to the increased broadness of XRD peaks.

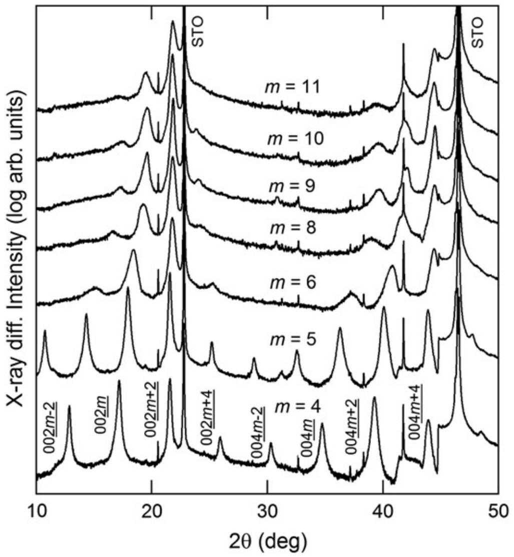

Fig. 1. XRD θ–2θ scans of the films with m of 4 to 11.

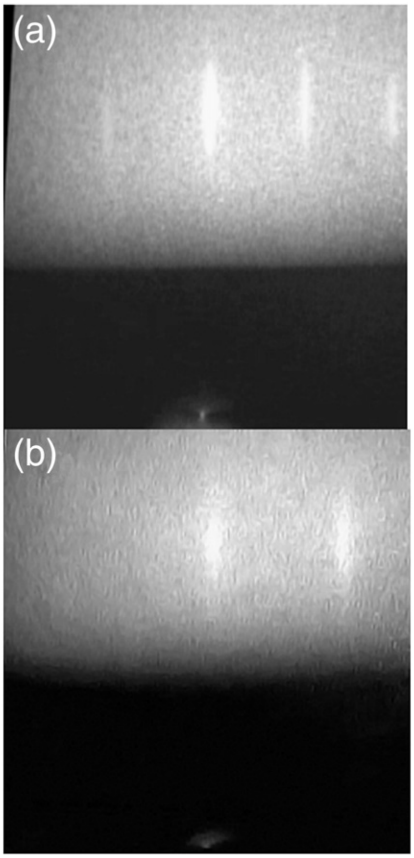

Fig. 2. RHEED images of a BFTO ($m=5$) thin film taken along (a) <100> and (b) <110> azimuths of STO substrate.

In order to examine whether the BFTO crystals with a large m were grown, the practical m values of thin films were estimated from the observed ratio d_{002m+2}/d_{002m} using the relationship of $c=2md_{00\underline{2m}}=2(m+1)\,d_{00\underline{2m+2}}$, where c denotes the lattice constant of c-axis, $d_{00\underline{2m}}$ and $d_{00\underline{2m+2}}$ the spacing of $(00\underline{2m})$ and $(00\underline{2m+2})$ planes, respectively. Fig. 3 shows the results. The m values of the thin films equal to the nominal values within experimental error up to $m=9$, while become much smaller than them for $m\geq 10$. This indicates a limit for the number of stacking layers of crystalline BFTO film grown under thermal equilibrium. The lattice constants of c-axis obtained assuming in-plane stress-free were 7.32 nm for $m=8$ and 8.14 nm for $m=9$.

3.2. Magnetic properties

Magnetization measurements for the BFTO film of $m=8$ and 9 showed that the films exhibit small magnetization proportional to applied magnetic field at room temperature, being paramagnetic or antiferromagnetic. However, presence of magnetic order in the films could not be confirmed from the temperature dependences of magnetic susceptibility within experimental errors because of smallness of the induced magnetization.

Fig. 4 shows the CEMS spectra measured for the BFTO ((a) $m=8$, (b) $m=9$) films. The BFTO ($m=8$) thin film exhibits a quadrupole doublet, indicative of being paramagnetic at 300 K. The doublet is asymmetric, having a quadrupole splitting (QS) of 0.55 mm/s. From the intensity ratio of two peaks, the angle between the principal axis of electric field gradient at the iron nuclei and the incident direction of

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