Journal of Alloys and Compounds 675 (2016) 257–265

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Multiferroic and magnetoelectric properties of $BiFeO_3/Bi_4Ti_3O_{12}$ bilayer composite films

Jieyu Chen, Zhehong Tang, Yulong Bai, Shifeng Zhao*

School of Physical Science and Technology, Inner Mongolia Key Lab of Nanoscience and Nanotechnology, Inner Mongolia University, Hohhot, 010021, PR China

ARTICLE INFO

Article history:
Received 9 February 2016
Received in revised form
12 March 2016
Accepted 16 March 2016
Available online 18 March 2016

Keywords:
Magnetoelectric effect
Composite films
Multiferroic properties
Coupling interaction
Chemical solution deposition

ABSTRACT

Multiferroic $BiFeO_3/Bi_4Ti_3O_{12}$ bilayer films were prepared using chemical solution deposition. Well-defined interfaces between $BiFeO_3$ and $Bi_4Ti_3O_{12}$ layers and clear domain structures were observed. The ferroelectric, leakage, dielectric, piezoelectric, magnetic as well as magnetoelectric properties were investigated for the composite films. It is shown that the composite films not only exhibit ferromagnetic and ferroelectric properties, but also possess strong magnetoelectric effect at room temperature. Thus outstanding magnetoelectric properties are attributed to the excellent coupling effect between $BiFeO_3$ and $Bi_4Ti_3O_{12}$ layers, which leads to a strong coupling interaction between ferromagnetic and ferroelectric orders. The present work provides a feasible way of preparing magnetoelectric composite films and facilitating their applications in micro-electro-mechanical system and information storage devices.

1. Introduction

Multiferroic materials have drawn an increasing attention due to the strong magnetoelectric coupling effect between (anti)ferroelectric and (anti)ferromangnetic orders. However, because of mutual exclusiveness of ferroelectric and ferromagnetic orders, there are only few single-phase multiferroic materials that exist in nature [1,2]. The scarcity of single phase multiferroics has motivated the design and development of composite materials combining ferroelectric and magnetic materials with transition temperature above room temperature and thus an artificial coupling can be engineered between the order parameters [3], without any constraint of coexistence of these orders in single phase. Thus multiferroic composites and heterostructures combining ferroelectric and ferromagnetic materials exhibit room-temperature magnetoelectric effect greatly exceeding those of single-phase magnetoelectric materials known to date. In fact, to meet the requirements of the rapidly developing micro- and nano-electro-mechanical systems (MEMS&NEMS) devices the ability to create high quality multiferroic magnetoelectric films stands as the more significant landmark toward technological application in micro-devices. Multiferroic composite films possess the unique advantages such as the modulation of their thickness, composition, connectivity, and orientation at nanoscale. However, for magnetoelectric composite films, giant magnetoelectric effect is limited to some shortcomings such as the interface diffusion coming from chemical reactions between the constituents, the loss of the mechanical stress mediating between the ferroelectric and ferromagnetic phases, and low resistivity of the ferromagnetic phase or eddy currents induced in the conducting phase by the applied ac voltage [4]. These difficulties limit the further application for magnetoelectric composite films. The magnetoelectric coupling in these composite films relies on strain which induce crystal deformations in either the ferroelectric phase or the magnetic phase through magnetostriction or the converse piezoelectric effect. In order to achieve large magnetoelectric effect, it is urgent to select strong ferroelectric and ferromagnetic materials with excellent coupling between them. Up to date, much work has been carried out to prepare the composite films by combining perovskite ferroelectric oxides [e.g., $PbZr_{0.52}Ti_{0.48}O_3$ (PZT)] with ferromagnetic materials e.g., ($CoFe_2O_4$, ReFe) [5–7], which present obvious magnetoelectric coupling effect. However, these kinds of lead based magnetoelectric composite films are neither favorable to require of environmental protection nor easy to obtain strong magnetoelectric coupling due to the crystal mismatch between ferroelectric and ferromagnetic phases. So it is attractive to find lead-free based

* Corresponding author.
E-mail address: zhsf@imu.edu.cn (S. Zhao).

http://dx.doi.org/10.1016/j.jallcom.2016.03.119
0925-8388/

magnetoelectric composite films with similar structure, which can obtain outstanding magnetoelectric properties. $BiFeO_3$ (BFO) is multiferroic materials with both ferromagnetic and ferroelectric orders occurring above room temperature: high ferroelectric Curie temperature and Neel temperature, which has attracted interesting because of their potential magnetoelectric coupling behaviors [8,9]. However, its first-order and second-order ME coefficients were reported 10–20 mV/cm·Oe [10], which does not satisfy the actual demand on magnetoelectric performance. Thus, BFO based magnetoelectric composite films with similar structure (perovskite structure) are promised to obtain strong magnetoelectric effect. As a kind of environmental friendly lead-free ferroelectric film, $Bi_4Ti_3O_{12}$ (BTO) films can be hopefully applied in magnetoelectric composite as ferroelectric phases due to their excellent piezoelectric, ferroelectric and leakage properties [11,12]. More importantly, BFO and BTO have similar structures with perovskite structure, which can form enhanced magnetoelectric coupling due to the excellent crystal lattice matching. Therefore, BFO/BTO bilayer composite films are expected to obtain strong magnetoelectric effect.

Based on those above, this work prepared BFO/BTO bilayer composite films by chemical solution deposition, and systematically investigated the microstructure, domain structure, ferroelectric, piezoelectric, dielectric, leakage, magnetic, magnetoelectric properties of BFO/BTO composite films. The origins of the strong magnetoelectric effect are discussed in detail.

2. Experiment

BTO/BTFO films were deposited on Pt (100)/Ti/SiO_2/Si substrates using chemical solution deposition. The details on the preparation of BTO precursor solutions could be found elsewhere [14]. The raw materials of BFO films used for the precursor solutions were bismuth nitrate pentahydrate [$Bi(NO_3)_3 \cdot 5H_2O$] and iron nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$]. Bismuth nitrate pentahydrate and iron nitrate nonahydrate were added to the ethylene glycol solvent in proportions of 1.1:1, with an excess 10% Bi to compensate for its loss during annealing. Then, the solution was stirred until it was transparent at room temperature. Both solutions with the concentration of 0.2 mol/L were filtered to form the final solutions. Then BFO/BTO composite films were deposited by spin coating the above solutions onto Pt(100)/Ti/SiO_2/Si. BTO layers were deposited by spin coating BTO solutions onto Pt(100)/Ti/SiO_2/Si wafers at 4000 rpm for 30 s, which were dried at 350 °C in a thermostatic oven for 300 s. Then, the dried deposited films were annealed at 700 °C for 5 min under an oxygen atmosphere with a flow of 1.5 L/min. The above steps were repeated 10 times for BTO layers. On the final time, BTO layers were annealed at 700 °C for 30 min. On this basis, BFO layer were deposited by spin coating BFO solutions onto BTO/Pt(100)/Ti/SiO_2/Si wafers at 3500 rpm for 30 s, which were dried at 300 °C in a thermostatic oven for 300 s. Then, the dried deposited films were annealed at 700 °C for 5 min under an oxygen atmosphere with a flow of 1.5 L/min. The above steps were repeated 10 times for BFO layers. On the final time, BFO layers were annealed at 550 °C for 30 min. Thus BFO/BTO bilayer composite films was prepared in this way.

The crystalline phases of the films were characterized by X-ray diffraction (XRD, PANalytical-Empyrean) on a D/MAX-RA diffractometer using CuKa radiation. The surface morphologies of the films were investigated by a scanning electron microscope (SEM, Hitachi SU-3500) with an operating voltage of 15 kV. For the fabrication of BFO/BTO composite films capacitors, Au top electrodes with a diameter of 0.2 mm were deposited on the surface of the films using an ion-sputtering method. Their ferroelectric, leakage properties were studied by a multiferroic tester system (MultiFerroic100V, Radiant Technology, USA). The domain structure and piezoelectric coefficients d_{33} were investigated by an piezoresponse force microscopy (PFM, Asylum Research Cypher™). All PFM images are from out-of-plane. Dielectric constant and dielectric loss were studied by a precision impedance analyzer (Agilent E4990A). The magnetic properties for BFO/BTO composite films were measured by using a physical property measurement system (PPMS, Quantum Design). For the magnetoelectric coupling measurement of BFO/BTO composite films, a magnetic bias field H_{bias} together with a small alternating magnetic field $H_{ac} = 7.1$ Oe and frequency $f = 1$ kHz was applied parallel to the film plane. The induced magnetoelectric voltage V_{ME} was recorded by a lock-in amplifier (SRS Inc., SR830). All measurements above were performed at room temperature.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of BFO/BTO bilayer composite films deposited on Pt(100)/Ti/SiO_2/Si substrates. It can be seen that XRD patterns of BTO/BTFO composite films can be disassembled to two sets of well-defined peaks, one of which belongs to BTO phase and the other belongs to BFO phase from their individual XRD patterns available in the JCPDS data card No. 38-1257 and 20-0169, respectively. With all of preferable process parameters, the overall crystallinity of BFO/BTO composite films were apparently preferably established, as shown in the XRD traces, where the sharpness of the features indicates a high quality polycrystalline films. BFO/BTO composite films show diffraction peaks of BTO consistent with an perovskite orthorhombic structure of space group [B2cb], and diffraction peaks of BFO consistent with perovskite rhombohedral structure belonging to the space group R3c as the (104) and (110) diffraction peaks are almost completely separated [13,14]. It reveals the coexistence of both BTO and BFO phases, confirming the prepared films containing both ferromagnetic and ferroelectric phases. However, the weak (0016) diffraction peak of BTFO phase is observed for the composite films, which shows that the connecting interface between BTO and BFO film layer will form minor amounts of BTFO phase during the process of annealing. Fig. 1(b) shows the surface morphology of BFO/BTO composite films deposited on the Pt (100)/Ti/SiO_2/Si substrates, which demonstrates that the top BFO films with comparatively homogeneous and smooth surface. The compact microstructures containing variable grain size with significantly reduced intergranular porosity are observed in BFO/BTO composite films. Thus relatively dense microstructure is beneficial to its ferroelectric, dielectric and piezoelectric properties. Fig. 1(c) further shows the cross-sectional SEM image of BFO/BTO composite films. It can be seen that the thickness of BTO layers and BFO layers is about 600 nm and 750 nm, respectively. The interface between BTO and BFO film layers is clear and a very thin BTFO intermediate layer with thickness of 80 nm is observed, which indicates that BTO and BFO film layers are not seriously destroyed and there are only less chemical action or atomic diffusion between BTO and BFO film layers. Thus good interfaces are the essential condition to obtain excellent magnetoelectric coupling between ferromagnetic and ferroelectric phases for BFO/BTO composite films because the chemical interaction between the ferroelectric and ferromagnetic phases may lead to the degrades of their ferroelectric or magnetic properties [15].

Fig. 2(a)–(c) shows the simultaneously obtained typical surface topography, PFM amplitude and phase images with $1.2 \times 1.2\ \mu m^2$ scanning area of the as-grown BFO/BTO composite films, respectively. In PFM amplitude and phase images, different colors represent different response intensities and local polarization orientations respectively. As can be seen from Fig. 2(a), BFO/BTO composite films show the smooth, crack-free surface morphology