Journal of Alloys and Compounds 690 (2017) 412–416

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Ferroelectric and magnetic properties in 85 nm-thick $Bi_6Fe_2Ti_3O_{18}$ thin films by a modified sol-gel processing

Dongpo Song [a, b], Jie Yang [a, **], Linghua Jin [a, b], Xianwu Tang [a], Jianming Dai [a], Wenhai Song [a], Xuebin Zhu [a, c, *], Yuping Sun [a, b, d, e]

[a] Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[b] University of Science and Technology of China, Hefei 230026, People's Republic of China
[c] Hefei Science Center, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[d] High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[e] Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, People's Republic of China

ARTICLE INFO

Article history:
Received 4 May 2016
Received in revised form
7 August 2016
Accepted 17 August 2016
Available online 19 August 2016

Keywords:
$Bi_6Fe_2Ti_3O_{18}$ thin films
Sol-gel
Ferroelectric
Magnetic

ABSTRACT

$Bi_6Fe_2Ti_3O_{18}$ thin film on $Pt/Ti/SiO_2/Si$ substrate with a thickness of 85 nm is successfully prepared by a monoethanolamine-modified sol-gel processing. The prepared thin film is polycrystalline and shows dense morphology. The room temperature remnant polarization is higher than 10 μC cm^{-2} at 5 V driving voltage both from polarization-voltage hysteresis loop and positive-up negative-down measurements. The polarization after 10^7 switching cycles and a retention time of 10^4 s shows no obvious degradation, suggesting good fatigue-resistant characteristics. Weak ferromagnetism is observed at 5 K with a saturated magnetic moment of 11.7 emu/cm^3. The results will provide an effective route to optimize $Bi_6Fe_2Ti_3O_{18}$ thin films with thickness below 100 nm by low-voltage driving.

1. Introduction

Among various ferroelectric materials, bismuth layered Aurivillius compounds with the general formula $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ (typically, the 12-coordinated A-site is occupied by mono-, di- or trivalent cations such as Na^+, K^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Pb^{2+}, Bi^{3+} or Ln^{3+}, and the coordinated B-site is occupied by d^0 tetra-, penta- or hexavalent cations such as Ti^{4+}, Nb^{5+}, Ta^{5+}, W^{6+}, where n refers to the numbers of the perovskite-like $(A_{n-1}B_nO_{3n+1})^{2-}$ layers between the fluorite-like $(Bi_2O_2)^{2+}$ layers.) have been widely investigated because of the fatigue-free behaviors, the good retention characteristics and the low leakage [1,2]. Combined with the above advantages and the environment-friendly (Pb-free) behaviour, Aurivillius compounds with $n = 2$ such as $SrBi_2Ta_2O_9$ and $n = 3$ such as $Bi_{3.25}La_{0.75}Ti_3O_{12}$ are considered to be candidate materials for nonvolatile random access memory applications [3].

Recently, the Aurivillius-based materials with higher perovskite-like layers ($n \geq 4$) have been reported as one very important type of single-phase multiferroics by doping magnetic species at the B site such as $Bi_5Fe_{0.5}Co_{0.5}Ti_3O_{15}$, $Bi_6FeCoTi_3O_{18}$ and $Bi_7Fe_{1.5}Co_{1.5}Ti_3O_{21}$ [4–7]. Moreover, long-range magnetic ordering has been reported in $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$ (BFTO) [8–10]. Ferroelectric polarization as one of the important parameters for multiferroics should be optimized to realize the magnetoelectric coupling in multiferroics. On the other hand, the optimization of ferroelectric properties in bismuth layered Aurivillius compounds will provide an alternative selection of Pb-free ferroelectrics.

In our previous report, BFTO thin films with thickness about 450 nm have been successfully prepared by sol-gel processing and the ferroelectric polarization can reach more than 20 μC/cm^2 by processing optimization [11]. Considering the potential applications (all Si-based devices work at ≤ 5 V), it is desirable to prepare BFTO thin films with high remnant polarization by low-voltage driving, naming BFTO thin films with low thickness [12]. In this paper, BFTO thin films with thickness of 85 nm have been prepared by monoethanolamine (MEA) modified sol-gel and the properties are investigated, which has been reported that MEA can promote

* Corresponding author. Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China.
** Corresponding author.
E-mail addresses: jyang@issp.ac.cn (J. Yang), xbzhu@issp.ac.cn (X. Zhu).

http://dx.doi.org/10.1016/j.jallcom.2016.08.153
0925-8388/

the properties of the ferroelectric thin films due to the improved microstructures [13–15]. The results show that ferroelectric properties can be sustained in the sub-100 nm BFTO thin films, providing a facile route to optimize Aurivillius thin films with low thickness.

2. Experimental procedure

BFTO thin films with 85 nm thickness were prepared on Pt/Ti/SiO_2/Si (100) substrates by monoethanolamine modified sol-gel. The precursor solution was prepared by dissolving appropriate amounts of bismuth acetate with 10 mol% excess to compensate for bismuth loss during processing, iron acetate and tetrabutyl titanate into propionic acid. After completely dissolving, monoethanolamine was added into the above solution, which is beneficial to improve the microstructures resulting in the enhanced properties. The volume ratio between propionic acid and monoethanolamine was of 6: 1. The used solution concentration was 0.1 M in BFTO. The obtained solution was stable for more than six months. Spin coating was used to deposit BFTO thin films with a speed of 6000 rpm and a time of 20 s. The deposited BFTO films were then baked in a 400 °C preheated tube furnace for 10 min in air. The spin coating and baking processing were repeated for two times to obtain films with 85 nm in thickness. Finally, the baked films were annealed at 700 °C in air for half of an hour by rapid thermal annealing processing.

The crystal structure was determined with a Philips X'Pert PRO X-ray diffractometer (XRD, Philips, Holland) using Cu-K_α radiation at room temperature. High resolution transmission electron microscopy (HRTEM) was performed using a JEM-2010 transmission electron microscope (JEM-2010, JEOL Ltd., Japan) to obtain more detailed crystal structures. The surface morphology and thickness of the films were examined by a field emission scanning electron microscopy (FE-SEM, Sirion 200, FEI Company, USA). Top Au electrodes with an diameter of 0.2 mm were sputtered onto thin films surfaces by a sputter (SCB-12 type Miriam small ion sputter, China) through a shadow mask to measure the electrical properties. Leakage and ferroelectric properties were measured using a Sawyer-Tower circuit attached to a computer-controlled standardized ferroelectric test system (Precision Premier II, Radiant Technology, USA). The principle of PUND test specified by the Radiant Technologies Precision Premier II system is depicted previously [16].

3. Result and discussion

Fig. 1(a) shows the XRD pattern of the prepared BFTO thin film. It is seen that the film is polycrystalline and phase-pure without detectable impurity phases. The diffraction peaks can be well indexed by the Aurivillius structure with an orthorhombic lattice of the *B2cb* space group, which is in agreement with the previous results [17]. The calculated lattice constant is $a = 5.7864(2)$ Å, $b = 5.4465(7)$ Å and $c = 49.595(4)$ Å using the Bragg formula, which is similar to the previous reports [18]. To further determine the layered structure of the thin film, HRTEM observations are carried out and the results are shown in Fig. 1(b) together with a half of the unit cell of Aurivillius structure of n = 5 [19]. It is seen that a crystal structure with four perovskite layers sandwiched by two $(Bi_2O_2)^{2+}$ layers can be clearly observed, confirming the derived Aurivillius structure with n = 5. The *c*-axis is determined as ~4.98 nm, which is consistent with the result from XRD measurement.

The surface FE-SEM results for the BFTO thin film are shown in Fig. 1(c). It is observed that the grain shape is granular and the surface is very dense. As compared with our prevous report about 450 nm-thick BFTO thin films [11], the grain size of the present

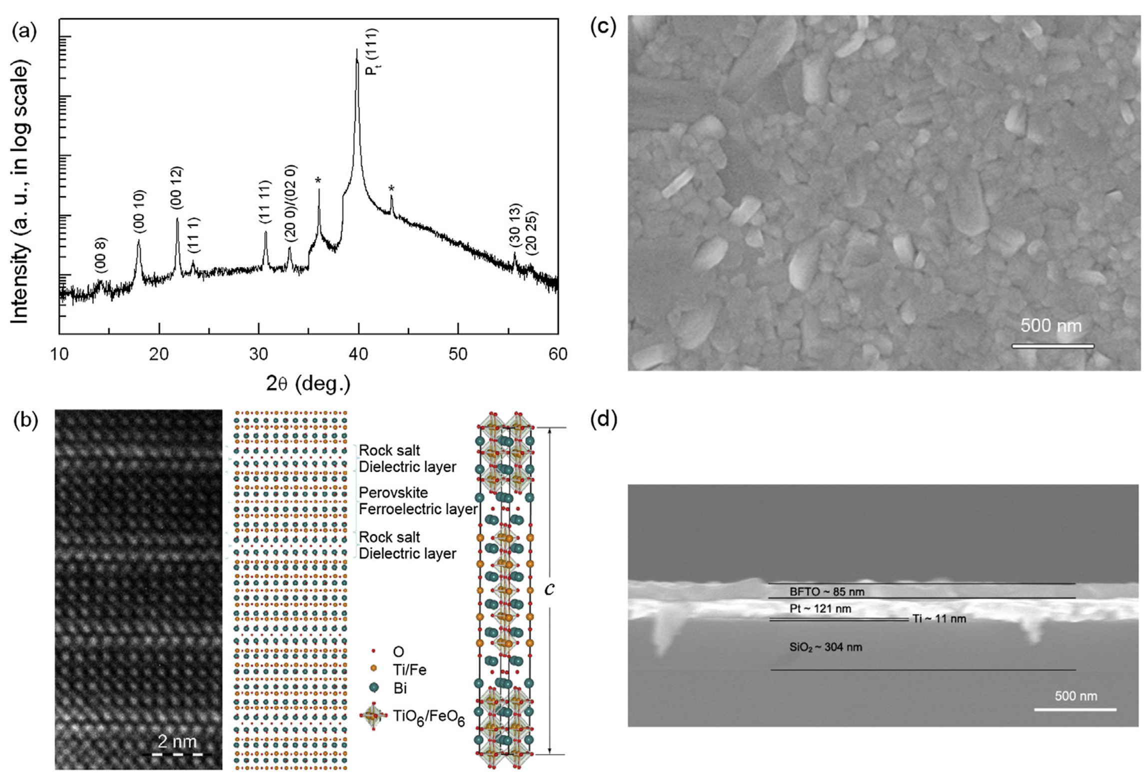

Fig. 1. (a) XRD pattern of the derived BFTO thin films at room temperature. The asterisks represent the diffraction peaks from the substrates. (b) HRTEM image of the obtained film and a half of the unit cell of Aurivillius structure with n = 5 in the right. (c) Surface FE-SEM results for the derived BFTO thin film and (d) Cross-section FE-SEM results to give the thickness.