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Effect of processing parameters on the structural, electrical and magnetic properties of BFO thin film synthesized via RF magnetron sputtering

Xiaoling Deng [a, b, d, *, 1], Jiamu Huang [a], Yuanyang Sun [b], Kaihua Liu [c], Rongli Gao [b, d], Wei Cai [b, d], Chunlin Fu [b, d]

[a] College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China
[b] School of Metallurgy and Materials Engineering, Chongqing University of Science and Technology, Chongqing 401331, China
[c] Material Science and Engineering, Yonsei University, Seoul 120749, South Korea
[d] Chongqing Key Laboratory of Nano/Micro Composite Materials and Devices, Chongqing 401331, China

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ABSTRACT

Pure-phase perovskite $BiFeO_3$ thin films were successfully deposited on the Pt substrates via radio frequency magnetron sputtering. The effect of O_2/Ar ratio on the microstructure of BFO thin film was firstly investigated. The result shows that when O_2/Ar ratio is 1:10, the BFO thin film exhibits a single perovskite phase with a dense structure. The effect of annealing temperature on the microstructure, ferroelectric, dielectric and magnetic properties of obtained thin film was subsequently investigated. The XRD result indicates that impurity phases appear whenever the annealing temperature is increased or decreased. Compared with other annealing temperatures, the BFO thin film annealed at 600 °C exhibits higher remnant polarization $2P_r$ of 23.26 $\mu C/cm^2$, relatively larger coercive electric filed $2E_c$ of 563 kV/cm, higher dielectric constant of 150, lower dielectric loss of 0.03, lower leakage current density of 3.6×10^{-4} A/cm^2, and saturation magnetization of 0.0036 emu/cm^3. Our results provide useful information with preparing single and pure BFO thin films prepared by radio frequency magnetron sputtering to some extent.

1. Introduction

Multiferroic bismuth ferrite ($BiFeO_3$, short for BFO) materials, which possess higher remnant polarization (~100 $\mu C/cm^2$), lower band gap than other ferroelectrics, high Curie temperature ($T_C = 850$ °C) and Neel temperature ($T_N = 370$ °C) [1,2], have attracted increasing interests in the past several years due to their fundamental physical properties and the potential applications in non-volatile memories, such as ferroelectric random-access memories (FeRAM) and magnetoresistive random-access memories (MRAM) [3,4]. However, the well-known problem of high leakage current of BFO thin film, caused by defects, surface roughness and nonstoichiometry, is still the main obstacle which severely limits its practical application [2,5,6].

Recent years, several techniques have been developed to synthesize high quality BFO thin films, such as hydrothermal synthesis [7], pulsed laser deposition (PLD) [8], sol-gel methods [9], electrophoretic deposition [10,11] and radio-frequency (RF) sputtering [12–14]. Among those fabrication methods, RF sputtering has many advantages, such as high reproducibility with an accurate stoichiometry and easy controlling process, and therefore it is considered as the most suitable way to prepare thin film with a smooth surface and dense structure as well as being applied to fabricate the integrated circuit device [15,16]. It is well known that the properties of films strongly depends on its microstructure, which is greatly affected by parameters controlled in the sputtering process, such as optimal pressure of the background gas, a suitable temperature for deposition and an appropriate rate of deposition [15]. In the past few years, many research groups have studied the effect of deposition rate and deposition temperature on the electrical properties of BFO thin films [17–19]. However, there are limited reports on the systematical investigation of the effect of O_2/Ar ratio and annealing temperature on the microstructures, electrical and magnetic

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[*] Corresponding author. College of Materials Science and Engineering, Chongqing University, Chongqing 400030, China.

E-mail address: dgxmd@163.com (X. Deng).

[1] Permanent address: College of Materials Science and Engineering, Chongqing University, Shapingba, Chongqing 400030, China.

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properties.

In this work, pure-phase perovskite BFO thin films were synthesized by RF magnetron sputtering. Effects of O_2/Ar ratio and annealing temperature on the anisotropic BFO thin films in phase formation, microstructures, electrical and magnetic properties were systematically investigated.

2. Experimental

BFO thin films were deposited on Pt/TiO_2/SiO_2/Si substrate via RF magnetron sputtering system with a computer-controlled shutter. BFO ceramic target was prepared by solid state reaction using Fe_2O_3 and Bi_2O_3. 10% excess of Bi_2O_3 was added to compensate the loss of Bi in the calcination process. The oxide mixture of BFO composition was firstly heated at 450 °C for 2 h to remove the organics and then calcined at 850 °C for 5 h in air. Then calcined powder was ball milled 24 h to get a homogeneous composite. Then a ceramic target with diameter and thickness of 1 inch and 8 mm, respectively, was prepared for RF sputtering using 5% PVA as a binder. The target was then heated at 450 °C for 1 h and sintered at 900 °C for 3 h. For the thin film deposition by RF sputtering, the base pressure inside the chamber was controlled at 9×10^{-4} Pa and substrate temperature was kept at room temperature. Thin films were then deposited under a RF power and working pressure of 110 W and 3.0 Pa, respectively, with a highly purified gas mixture of oxygen and argon in various O_2/Ar ratios. The total gas flow of mixture of oxygen and argon was set at 20 sccm. Finally, thin films were annealed at 600 °C for 15 min with a heating rate of 4 °C/min in oxygen atmosphere by a tube furnace.

The crystal structure of BFO thin film was analyzed using the X-ray diffraction (XRD, D8 Advance, Bruker, Germany) with Cu K_α radiation ($\lambda = 0.154056$ nm). The microstructure of the BFO films was performed using atomic force microscopy (AFM, S-3700N, Hitachi, Japan). In order to measure the electrical properties of BFO films, the Au top electrodes with the diameter of 200 μm were deposited on the BFO films using a DC magnetron sputtering (JGP280, SKY, China). The thickness of the BFO films is about 500 nm determined by step profiler (Dekatk 150, Veeco, USA). The capacitance of the films was determined by impedance analyzer (LCR, HP 4980A, Agilent, USA) at room temperature. The dielectric constant was calculated from the capacitance using the following equation:

$$\varepsilon = Cd/\varepsilon_0 A \qquad (1)$$

where C is the capacitance (F), ε_0 is the free space dielectric constant value (8.85×10^{-12} F/m), A represents the capacitor area (m^2) and d is the thickness (m) of the sample. The room temperature hysteresis loop was measured by ferroelectric test system (TF2000E, aix ACCT, Germany). The magnetic properties were studied by using vibrating sample magnetometer (VSM, VSM-300, YP Magnetic Technology Development CO. LTD, China).

3. Results and discussions

3.1. Effect of O_2/Ar ratio on the phase structure and surface morphology

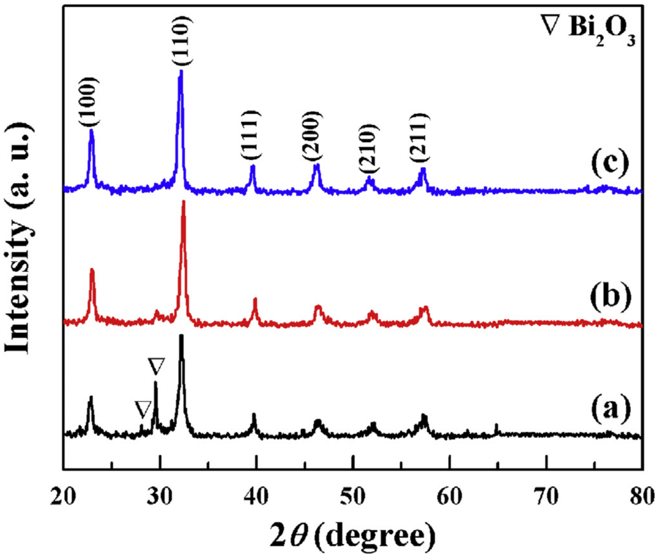

Fig. 1. XRD patterns of BFO thin films synthesized with various O_2/Ar ratios of (a) 1:4, (b) 1:8, (c) 1:10.

Fig. 1 shows the XRD patterns of BFO thin films synthesized with various O_2/Ar ratios and annealed at 600 °C. It is noted that the impurities decrease (indexed to Bi_2O_3 and $Bi_2Fe_4O_9$) with decrease of O_2/Ar ratio. Thin film prepared with O_2/Ar ratio of 1:10 shows single perovskite phase indexed to $R3m$ space group of rhombohedral structure (PDF No. 73-0548). In order to estimate the purity of BFO films, the XRD quantitative analysis was applied and the mass fraction of BFO phase was calculated by the equation as follows [11]:

$$W_{BFO} = \frac{I_{BFO}}{I_{BFO} + \sum_{i}^{n} \frac{I_{Xi} K_{BFO}}{K_{Xi}}} \qquad (2)$$

where W_{BFO} is the mass fraction of BFO phase, I_{BFO} and I_{Xi} is the intensity of reflection of (hkl) in BFO phase and the secondary phase (Bi_2O_3), respectively. K_{BFO} (8.89) and K_{Xi} is the *RIR* value of BFO phase and secondary phase (Bi_2O_3), respectively. The calculated W_{BFO} of thin film prepared with O_2/Ar ratio of 1:4, 1:8 and 1:10 are 81.3%, 92.6% and 99.8%, respectively. The presence of impurities with an increase in the O_2/Ar ratio may be attributed to the deficiency of Bi in the annealing process. The average grain size was estimated using the Scherrer formula [20]:

$$D = \frac{K\lambda}{\beta COS\theta} \qquad (3)$$

where D is the crystallite size (nm), K is the shape factor (0.89), λ is the wavelength of X-rays ($\lambda = 0.15406$ nm for Cu $K\alpha$ radiation), β is the width of the diffraction peak at half maximum for the diffraction angle 2θ. The calculated result suggests that the average grain size increases from 20 nm to 45 nm with decrease of O_2/Ar ratio, indicating that the O_2/Ar ratio has apparent influence on the grain size of BFO thin films, similar result was also found by Juan et al. [21].

Fig. 2 shows the atomic force microscope (AFM) topography images of BFO thin films synthesized with various O_2/Ar ratios. It is obvious that all samples exhibit smooth surfaces with regular shaped grains. No obvious crack is observed in all samples. With the decrease of O_2/Ar ratio, the grains become more uniform. The average grain size of the thin films prepared with different O_2/Ar ratio was calculated by linear intercept method and was found to increase from 45.5 nm to 52.8 nm with O_2/Ar ratio decrease from 1:4 to 1:10. In addition, as the roughness and surface morphology can influence the ferroelectric properties [22], the thin film with denser microstructure and lower roughness prepared with O_2/Ar ratio of 1:10 is expected to exhibit better electrical property.

Accordingly, the sample prepared with O_2/Ar ratio of 1:10 was