Current Applied Physics xxx (2017) 1–9

Contents lists available at ScienceDirect

Current Applied Physics

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

Multiferroic effect of multilayer low-distorted doped bismuth ferrite thin films as a function of sputtering power and crystallographic texture

G. Rojas-George [a, b], A. Concha-Balderrama [a], H. Esparza-Ponce [a], J.J. Gervacio-Arciniega [b, c], M.P. Cruz [b], V. Orozco-Carmona [a], A. Reyes-Rojas [a, *]

[a] Centro de Investigación en Materiales Avanzados S.C. (CIMAV), Department of Physics, Miguel de Cervantes 120, Complejo Industrial Chihuahua, Cd. de Chihuahua, Chihuahua, Mexico
[b] Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Km. 107, Carretera Tijuana-Ensenada, C.P. 22800, Ensenada, B.C., Mexico
[c] Cátedras CONACYT- Facultad de Ciencias Físico-Matemáticas, Benemérita Universidad Autónoma de Puebla, Av. San Claudio, Col. San Manuel Ciudad Universitaria, Puebla, Pue., 72570, Mexico

ARTICLE INFO

Article history:
Received 29 November 2016
Received in revised form
3 February 2017
Accepted 12 March 2017
Available online xxx

Keywords:
Multilayers
Chemical synthesis
Elastic properties

ABSTRACT

Low-distortion rhombohedral multilayer barium-nickel co-doped $BiFeO_3$ ($Bi_{0.75}Ba_{0.25}Fe_{0.975}Ni_{0.025}O_3$) multiferroic thin films were grown on $Pt/TiO_2/SiO_2/Si$ substrates by reactive RF magnetron sputtering, as a function of sputtering power. X-ray diffraction showed that $Bi_{0.75}Ba_{0.25}Fe_{0.975}Ni_{0.025}O_3$ multilayer films have a pseudocubic-type structure. Piezoresponse force microscopy demonstrated polarization switching in all films at room temperature. Scanning electron microscopy showed different morphologies depending on the sputtering power used during the deposition process and that the thickness of the film decreases from about 142 nm to 72 nm as the sputtering power decreases. Magnetization results showed that as the thickness of the film decreases, the magnetization of the film increases. Thus, there is a direct relation between the sputtering power, thickness and the magnetization of the film. A direct relation between in-plane residual stress and thin film thickness has been obtained. This causes the main axe of the BO_6 octahedra to be tilted from 90 to 45° (from thin-film surface) by a texture crystal volume of 29 and 18% in the (012) and (110) crystallographic planes respectively.

1. Introduction

Bismuth ferrite ($BiFeO_3$), a monophasic multiferroic possessing a rhombohedral distorted perovskite structure with *R3c* as space group, is the only multiferroic exhibiting both ferroelectricity and G-type antiferromagnetism at room temperature (with a Curie temperature T_c of 830 °C and Néel temperature of 370 °C) [1,2], which has an antiferromagnetic spin module between 62 and 64 nm along $[10\bar{1}]$ [3]. $BiFeO_3$ has been the target of several studies to elucidate its possible applications in several fields such as spintronic (but not limited to) [4], storage media [5], magneto-electric coupling [6], photovoltaics [7], actuators [8], electro-optics [9]. The ferroelectric and magnetic properties have been the main study of several hundred works found on the literature focusing primarily on improving these properties. On recent years, studies have focused mainly on the thin film area, where several approaches to synthesized $BiFeO_3$ have been taken. Such techniques include sol-gel [10], Atomic Layer Deposition [11], Chemical Solution Deposition [12], Sputtering [13], PLD [14], among others. Not only has the technique played an important role in the final characteristics and properties of $BiFeO_3$ films. Parameters such as substrates (buffer layers) [15], doping elements [16], thickness [17], and structure [18] should also be considered. The basic idea is, to improve the atomistic interaction, as our case; a modified sol-gel is developed and the nanoparticles obtained are used to produce dense thin films of co-doped $BiFeO_3$.

Many authors have considered the well-known, but expensive $SrTiO_3$ substrate as a good candidate to growth epitaxial films; however by using the less expensive $Pt/TiO_2/SiO_2/Si$ substrate good ferroelectric properties have been achieved [19]. In order to

* Corresponding author.
E-mail address: armando.reyes@cimav.edu.mx (A. Reyes-Rojas).

http://dx.doi.org/10.1016/j.cap.2017.03.011
1567-1739/

improve the ferroelectric or magnetic properties the A-site and/or B-site cations in the crystal structure have been substituted. For example, to increase the magnetic properties the A cation has been substituted by alkali-earth elements, since these suppress the spin magnetic cycloid of $BiFeO_3$ [20]. Similarly doping with transition elements such as Co^{2+}, Ni^{2+}, Mn^{2+} in the B-site increases the magnetic properties as well [21,22]. Similarly, by modifying the thickness of the film the spin cycloid could be suppressed and the magnetic properties can be improved. Several authors have attempted to increase the electrical properties of $BiFeO_3$ thin films, by increasing the film thickness [23], doping [24], using several substrates or buffer layer, such as $LaNiO_3/SrTiO_3$ substrates [25] and even the orientation of the film contribute to the ferroelectric properties [26].

There are studies where the nature of the structural behavior determined the ferroelectric character of $BiFeO_3$ thin films. These structural changes can be induced by several factors such as substrate or ion doping mainly. Ion doping effects are primarily on the degree of distortion induced by the size of the substituting ion. This distortion, if controlled, can be oriented along the [111] and propagate a distortion leading to an increased in polarization. In this aspect, there have been studies where a co-existence of phases, mainly tetragonal and rhombohedral have been found and both have resulted in saturated ferroelectric loops [27–29]. This phase co-existence or morphotropic phase boundary (MPB) [30] needs to be further studied in order to fully understand the effect of the structural behavior on the ferroelectric properties.

Previous works have demonstrated different preferred orientation as a function of the substrate; which can occur in the [100] crystallographic direction, as it was confirmed by phi scans of the (101) reflections ratify the perfect in-plane orientation without rotation domains [31]. Evidently it depends on the a-b/c ratio between the substrate and the $BiFeO_3$, therefore the in-plane texture of the films can induce a change in its texture component when the thickness varies between 4 and 12 nm, bringing a texture in the (104) crystallographic plane [32]. However, the volume of the texture has not been determined; therefore, in order to determine the texture volume in multilayer barium-nickel co-doped $BiFeO_3$ ($Bi_{0.75}Ba_{0.25}Fe_{0.975}Ni_{0.025}O_3$) multiferroic thin films, an in-situ Rietveld analysis and March Dollase equation are employed to determine the texture degree and relate it with their ferroelectric and ferromagnetic character.

The rhombohedral structure of $BiFeO_3$ with $a/b = 5.5876$ Å and $c = 13.867$ Å unit cell parameters can slightly be longer or shorter than the lattice constant of the substrate; therefore, an in plane compressive or tensile strain in the $BiFeO_3$ films will generate, and this strain will gradually relax as the thickness of the $BiFeO_3$ thin films increases [33]. Also, it has been known the coexistence of Fe^{2+} and Fe^{3+} ions inside the BO_6 octahedra, which can increase the spin canting angle when the thin film of $BiFeO_3$ decreases inducing a strain [34]. Theses strains will be reflected as tensile or compressive residual stress components in the $BiFeO_3$ thin films depending on their atomic arrangement in the film [35]. Base on to these findings, we had determined the orientation dependence of $BiFeO_3$ thin films with the residual stress and relation with the thickness, texture and their ferroelectric and ferromagnetic properties.

In this paper we report, structural, crystallographic texture, electric and magnetic properties in low-distorted rhombohedral multilayer co-doped $BiFeO_3$ multiferroic thin films deposited on $Pt/TiO_2/SiO_2/Si$ substrates using the RF sputtering technique as a function of sputtering power. The final grain morphology and thickness of the films play an important role in the texture, magnetic and electrical properties of the barium-nickel doped $BiFeO_3$ (BNBFO) films. Furthermore, the residual stress component has been measured and it has an influence in the thickness as well. The local ferroelectric behavior was investigated mainly by atomic force microscopy-piezoresponse force microscopy obtaining a polarization switching on all samples. Even though the samples appear to not have rhombohedral-distorted perovskite symmetry, they must possess a non-centrosymmetric crystal class, which has its origin in the large displacement of the Bi^{3+} cations along the [111] direction and the FeO6 octahedral distortion continuous along the same direction [36] in order for these samples to show the polarization switching.

2. Experimental procedure

Multiferroic-multilayer thin films of barium-nickel co-doped bismuth ferrite ($Bi_{0.75}Ba_{0.25}Fe_{0.975}Ni_{0.025}O_3$) were deposited over $Pt/TiO_2/SiO_2/Si$ substrates using a reactive RF magnetron sputtering system; introducing an O_2 (99.99) and Ar (99.99) gas mixture in the chamber. The co-doped bismuth ferrite (BNBFO) target used to growth the multilayer thin films was synthesized by a modified Pechini sol-gel method, as describe in a previous report, named *polyvinyl alcohol-ethylene glycol method* [37] and the complete details of the target preparation are describe on a previous work [38]. In order to growth the BNBFO multilayer thin films; $Pt/TiO_2/SiO_2/Si$ substrates were used. The as-grown films were deposited as a function of sputtering power in dynamic mode, with a rotational speed of 10 rpm on the substrate holder. During the deposition process the magnetron was tilted 25° with respect to the surface substrate, varying the working distance according to the sputtering power. In order to study the sputtering power on the multiferroic, structural and morphological properties of high-quality multiferroic multilayer thin films, several sputtering powers were used during the deposition process. The Ar and O_2 flow rate were constant at 14sccm and 6sccm respectively, keeping the chamber pressure constant at 3.3×10^{-2} Torr during the deposition. For this particular study, four different powers were used: 10, 20, 30 and 50 Watts. Two multilayer thin films were grown using 10 and 20 Watts using a working substrate-target distance of 5 cm. These films were grown using a multilayer system which consists in depositing one layer of BNBFO for 20 min using the conditions mentioned earlier and subsequently applied an annealing treatment for 15 min at 600 °C in an argon atmosphere, using a tubular furnace with a heating rate of 5 °C/min. This process was repeated seven times until the total deposition time was 140 min. Two other multilayer films were grown using 30 and 50 Watts, using a working substrate-target distance of 6.5 cm, using the same parameter mention before. In order to study the dielectric properties of the multilayer thin films, 200 μm diameter circular Ag electrodes were screen printed over the films.

Quantitative analysis of the texture distribution and the crystal structure of annealed BNBFO thin films were analyzed by grazing incidence x-ray diffraction (GIXRD, PANalytical XPert'PRO) using a CuKα ($\lambda = 1.5405$ Å) monochromatic radiation and Rietveld analysis. GIXRD patterns were obtained from 20 to 60° 2θ range using step-scanning mode, step size of 0.05°, step counting time of 50 s and the omega angle was fixed at 0.5°. It is well known that the Rietveld method is applied only to XRD patterns measured with Bragg-Brentano geometry. Therefore the intensity of the GIXRD patterns in asymmetrical condition was corrected by the James factor [39]; and finally, the corrected patterns were refined by the Fullprof software using a Pseudo-Voigt profile peak function to adjust the broadening effect. All XRD patterns were refined using an *R3c* space group with low distortion symmetry. March-Dollase equation was used to fit the texture of the *hkl* planes.

Please cite this article in press as: G. Rojas-George, et al., Multiferroic effect of multilayer low-distorted doped bismuth ferrite thin films as a function of sputtering power and crystallographic texture, Current Applied Physics (2017), http://dx.doi.org/10.1016/j.cap.2017.03.011