Vacuum 107 (2014) 108–111

Contents lists available at ScienceDirect

Vacuum

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

Rapid communication

Influence of sputtering atmosphere on the structural and magnetic properties of $(Bi_{1-x}Nd_x)FeO_3$ thin films

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ARTICLE INFO

Article history:
Received 8 March 2014
Accepted 11 April 2014

Keywords:
$BiFeO_3$
Thin film
Magnetron sputtering
Preferred growth
Magnetic property

ABSTRACT

$(Bi_{1-x}Nd_x)FeO_3$ (BNF, $x = 0.075$ and 0.125) thin films were grown on Si(100) substrates by radio frequency magnetron sputtering with various deposition atmospheres. It was found that the sputtering atmosphere has affected the phase structure, surface morphology and magnetic properties of BNF thin films. X-ray diffraction revealed that the BNF thin films exhibit highly (012)-orientation crystallization when the sputtering atmosphere is nitrogen (N_2), while, the inter-phase Bi_2O_3 was observed when the sputtering atmosphere is the mixture of argon and oxygen (Ar/O_2). Compared with the thin film deposited in Ar/O_2, the films sputtered in N_2 showed a smoother surface and significantly enhanced ferromagnetism. It was also found that the crystallization and ferromagnetic properties of the BNF thin films were enhanced when x is increased from 0.075 to 0.125. The observed macroscopic magnetization was concluded to be the result of suppressed space-modulated spin structure of BNF thin films.

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Multiferroic materials, with the coexistence of spontaneous magnetization and spontaneous polarization, have been of great interest due to their potential applications in spintronic devices, functional sensors and actuators [1]. Unfortunately, since the unique electron configurations required, single phase multiferroics materials are rare in nature [2]. $BiFeO_3$ with a rhombohedrally distorted perovskite structure is one of the best candidates characterized by the high ferroelectric Curie temperature ($T_C \sim 1100$ K) and antiferromagnetic Néel temperature ($T_N \sim 643$ K) [3]. Its spontaneous polarization originates from the stereochemical activity of the Bi lone electron pair, which will hybridize with both the empty 6 p^0 orbits of Bi^{3+} ion and the 2 p^6 electrons of O^{2-} ion to form Bi–O covalent bonds, introducing off centering in the structure and hence ferroelectric order [4,5]. The G-type canted antiferromagnetic order in $BiFeO_3$ is mainly attributed to the Jahn–Teller structural distortion controlled by the partially filled 3 d orbits of the Fe^{3+}, and follows a cycloidal spiral along the (110)-direction with a period of ~620 Å [6,7]. As a result, the possible remnant magnetization permitted by the G-type canted antiferromagnetic order is canceled by the incommensurately space-modulated spin structure, significantly restricting the release of weak ferromagnetism and potential magnetoelectric effect [8].

Efforts to release macroscopic magnetization in pure $BiFeO_3$ have focused largely on rare earth substitution in the Bi sublattice. It has been reported that rare earth (e.g., La, Nd, Gd, Sm or Dy) carions substitution for Bi^{3+} can effectively modulate the crystal structure parameters of $BiFeO_3$, destroy the space-modulated spin structure, and realize the macroscopic ferromagnetism [9–13]. Among these, enhanced ferromagnetism and ferroelectricity in the $(Bi_{1-x}Nd_x)FeO_3$ (BNF) have been reported by previous literatures [14–16], and the simultaneous piezoelectricity was also realized [17]. Besides, the improvement of large ferroelectric coercivity [18] and the leakage current density in the BNF [19], which have been largely impeding the multiferroic applications of $BiFeO_3$, promote us to do more research on the BNF thin films. In the previous literature, much effort has been made to discuss the magnetic properties of BNF thin films deposited by chemical solution deposition [14,19] and pulsed laser deposition method [16,18], but the effect of deposition condition on the structure and magnetic properties of magnetron sputtering-derived BNF thin film has not been reported. It is know that the working atmosphere have influence on the structure and magnetic properties of Fe-doping or Mn-doping ZnO diluted magnetic semiconductor thin films

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http://dx.doi.org/10.1016/j.vacuum.2014.04.013
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[20,21], respectively. Thus, in this work, we prepared single-phase $(Bi_{1-x}Nd_x)FeO_3$ thin films by a radio frequency magnetron sputtering with various deposition atmospheres, and report the effect of deposition atmospheres on the structure and magnetic properties of $(Bi_{1-x}Nd_x)FeO_3$ thin films.

The $(Bi_{1-x}Nd_x)FeO_3$ ($x = 0.075$ and 0.125, respectively abbreviated as BNF7.5 BNF12.5) thin films were grown on Si(100) substrate using radio frequency (RF) magnetron sputtering with ceramic targets of BNF7.5 and BNF12.5. These ceramics prepared details were described the elsewhere [22]. During the sputtering process, the substrate temperature was kept at 550 °C, and the depositing atmosphere is Ar/O_2 (pressure ratio is 9:1) and N_2, respectively. The samples were then annealed at 650 °C by a rapid thermal annealing furnace under oxygen atmosphere for 5 min. Details of the deposition conditions are given in Table 1. The Samples 1 and 2 are the BNF7.5 thin films deposited in Ar/O_2 and N_2 atmospheres, respectively. And the Sample 3 is the BNF12.5 thin film deposited in N_2 atmospheres.

The thickness of the as-grown thin films on Si(100) substrates was measured by a surface profiler (KLA-Tencor P-10), which was about 200 nm. The crystalline structure of the BNF thin films was characterized at room temperature by X-ray diffraction (XRD, Rigaku D-MAX 2200) with CuKa radiation. The surface morphology of the sample was investigated by atomic force microscopy (BenYuan, CSPM5500). And the magnetic properties of the films were measured using a vibrating sample magnetometer (VSM, Quantum Design, PPMS-9) at room temperature.

Fig. 1 shows the XRD patterns of the BNF thin films on Si(100) substrates. When the sputtering atmosphere is Ar/O_2, a poor crystallization and inter-phase Bi_2O_3 was observed in sample 1. Reversely, when the sputtering atmosphere is N_2, the BNF thin films (sample 2 and 3) appear to be well crystallized at 650 °C, and no secondary phases were detected, showing a pure rhombohedral (R3c) distorted perovskite structure [17,23]. There are three peaks, i.e. (012), (104) and (024), are observed in the sample 2 patterns and the intensity of (012) peak is much stronger than that of (104) one. The relative peak intensity of $I(012)/[I(012) + I(104) + I(024)]$ is calculated to be 0.92, suggesting highly (012)-orientation growth for the BNF film on Si(100) substrate. The sample 3 (with more Nd ions) exhibits a more highly (012)-orientation growth with no (104) peak and good crystallization as well. The slight shift of the peak position (in sample 2 and 3) corresponds to the change of the lattice parameter, which was caused by the different concentrations of Nd substitution. The phase variation is consistent with the previous study, where single-phase $BiFeO_3$ films can only be obtained in a rather narrow range of oxygen pressure and higher pressure will result in the Bi_2O_3 precipitates [24].

The surface morphology of the BNF thin film was displayed in the Fig. 2. As we see, all samples exhibit a uniform microstructure with no cracks. When deposited in the Ar/O_2 atmosphere, the BNF7.5 thin film (sample 1) formed a relatively rough surface composed of cylindrical filaments, and the root mean square roughness (RMS) is 25.2 nm. However, N_2 depositing has significantly reduced the surface roughness, and resulted in the relatively smooth and dense surface. The RMS of the BNF7.5 thin film deposited in N_2 (sample 2) is 1.4 nm, which is much smaller than that of sample 1. Combined with the XRD results, the large RMS of the sample 1 is consistent with the poor crystallization, and the cylindrical filaments may be caused by the Bi_2O_3 grains or the amorphous BNF. Besides, the RMS of the thin film was further reduced with increasing Nd-doping, that is, a smoother and denser surface with the RMS of 1.2 nm was obtained in the BNF12.5 thin film (sample 3).

Table 1
Deposition conditions of BNF thin films by RF-magnetron sputtering method.

Deposition parameters	Sample nos.		
	1	2	3
Ceramic targets	$(Bi_{0.925}Nd_{0.075})FeO_3$		$(Bi_{0.875}Nd_{0.125})FeO_3$
Deposition temperature (°C)	550	550	550
Films thickness (nm)	200	200	200
Base vacuum (Pa)	2.67×10^{-4}	2.67×10^{-4}	2.67×10^{-4}
Sputtering power (W)	40	40	40
Deposition time (min)	300	300	300
Working pressure (Pa)	2.7	3.0	3.0
Sputtering atmosphere	Ar/O_2 (9/1)	N_2	N_2
Annealing temperature (°C)	650	650	650

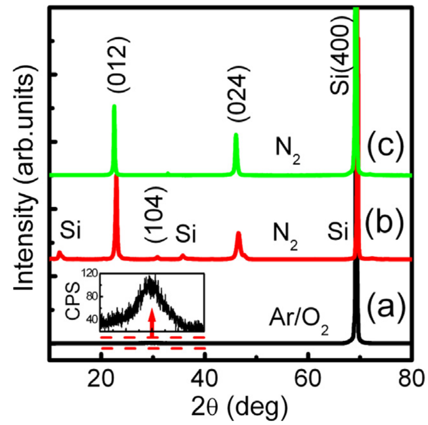

Fig. 1. X-ray diffraction patterns of the BNF thin films: (a) and (b) for BNF7.5 thin films deposited in Ar/O_2 and N_2 atmosphere, respectively; (c) for BNF12.5 thin film deposited in N_2 atmosphere.

Fig. 3 shows the magnetic hysteresis (M–H) loops of the BNF thin films measured at room temperature by applying an in-plane magnetic field, and the central region of the hysteresis loop obtained for BNF12.5 thin film was magnified and shown in the inset. It is found that the weak ferromagnetism has been obtained through Nd substitution in all the thin films, with a small but nonzero remnant magnetization. The BNF thin films deposited in N_2 atmosphere showed a better ferromagnetic property than the film deposited in the Ar/O_2. And the magnetization of the $(Bi_{1-x}Nd_x)FeO_3$ thin films exhibits a large rise when x is increased from 0.075 to 0.125. The largest magnetic moment was obtained in the BNF12.5 thin film with the saturated magnetization, remnant magnetization, and coercivity of 10.44 emu/cm^3, 0.70 emu/cm^3 and 84.40 Oe, respectively.

Combined with the XRD and AFM results, the magnetic difference between the sample 1 and sample 2 may be caused by the various phase structure, and the difference between the well crystallized sample 2 and sample 3 needs our further discussion. There are mainly two possible causes that may account for the spontaneous magnetization of the BNF thin films: one is the possible existence of Fe^{2+} [18,25,26], and the other is the canting of the antiferromagnetically ordered spin induced by the lattice distortion [10,16]. It was reported that when introducing the Fe^{2+} with an out shell electron configuration of 3 d^6 into Fe^{3+} with an out shell electron configuration of 3 d^5, the magnetic structure may be modified from antiferromagnetic to antiferrimagnetic at the Fe^{2+} site [16]. However, due to the enhanced structural stability induced by Nd substitution, the content of Fe^{2+} is supposed to decrease with the increase of x [14], and the magnetization of the thin film will also reduce with the increasing x, which is

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