Acta Materialia 128 (2017) 451–464

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

# Room temperature ferromagnetism and ferroelectricity in strained multiferroic $BiFeO_3$ thin films on $La_{0.7}Sr_{0.3}MnO_3/SiO_2/Si$ substrates

M.C. Ramírez-Camacho [a, b], C.F. Sánchez-Valdés [b], J.J. Gervacio-Arciniega [b], R. Font [c], C. Ostos [d], D. Bueno-Baques [e], M. Curiel [f], J.L. Sánchez-Llamazares [g], J.M. Siqueiros [b], O. Raymond-Herrera [b, *]

[a] Posgrado en Física de Materiales, Centro de Investigación Científica y de Educación Superior de Ensenada, Carretera Tijuana-Ensenada 3918, Zona Playitas, 22860 Ensenada, Baja California, Mexico
[b] Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, AP 14, Ensenada 22860, Baja California, Mexico
[c] Facultad de Física, Universidad de La Habana, San Lázaro y L, 10400 La Habana, Cuba
[d] Instituto de Química, Universidad de Antioquia, UdeA, Calle 70 No. 52-21, Medellín, Colombia
[e] Center for Advanced Technologies and Optical Materials, Dept. of Physics and Energy Science, University of Colorado, Colorado Springs, CO 80918, USA
[f] Instituto de Ingeniería, Universidad Autónoma de Baja California, Mexicali 21280, Baja California, Mexico
[g] Instituto Potosino de Investigación Científica y Tecnológica A.C., Camino a la Presa San José 2055, Col. Lomas 4a, San Luis Potosí 78216, Mexico

ARTICLE INFO

*Article history:*
Received 29 September 2016
Received in revised form
7 February 2017
Accepted 9 February 2017
Available online 20 February 2017

*Keywords:*
Multiferroic
BFO/LSMO thin film
rf sputtering
Interlayer exchange coupling
Superexchange

ABSTRACT

A novel ferromagnetic state coexisting with ferroelectric ordering at room temperature in strained $BiFeO_3$ (BFO) thin films grown using a sputtering technique on $La_{0.7}Sr_{0.3}MnO_3/SiO_2/Si(100)$ (LSMO/SOS) substrates is reported. The properties of BFO films with different thicknesses ($t_{BFO}$ = 15, 50, 70, 120, and 140 nm) on 40 nm LSMO layers are explored. [012] *out-of-plane* highly textured BFO/LSMO stacks grew with rhombohedral structures. LSMO layers are nanostructured in nature, constituted by ferromagnetic single-domain nanoregions induced by the constrain of the $SiO_2$ surface, with $T_C$ ~200 K and high coercive field ($H_C$) of ~1100 Oe at 2.5 K. BFO films grew epitaxially nanostructured on LSMO, exhibiting ~4 nm spherical nanoregions. The BFO layers show typical antiferromagnetic behavior (in a greater volume fraction) when made thicker ($t_{BFO}$ > 70 nm). The thinner films ($t_{BFO}$ < 50 nm) display ferromagnetic behavior with $T_C$ > 400 K, $H_C$ ~ 1600 Oe for 15 nm and ~1830 Oe for 50 nm. We propose that such ferromagnetic behavior is originated by the establishment of a new magnetic configuration in the $Fe^{3+}$–O–$Fe^{3+}$ sublattice of the BFO structure, induced by strong hybridization at the interface as consequence of superexchange coupling interactions with the ferromagnetic $Mn^{3+}$–O–$Mn^{3+}/Mn^{4+}$ sublattice of LSMO. All BFO layers show excellent ferroelectric and piezoelectric properties (coercive field ~ 740 kV/cm, and $d_{33}$ = 23 p.m./V for 50 nm; ~200 kV/cm and 55 p.m./V for 140 nm), exhibiting 180° and 109° DWs structures depending on the thickness. Such multiferroic properties predict the potential realization of new magneto-electronic devices integrated with Si technology.



## 1. Introduction

Single-phase or composite multiferroic (MF) materials, characterized by the coexistence of two or more ferroic orders (ferroelectric (FE), ferromagnetic (FM), ferroelastic, among others), have generated significant interest due to the possible additional functionality provided by the coupling between the different ferroic orders. In particular, special attention have been devoted to study of materials showing a magnetoelectric (ME) coupling (FE-FM) which has the potential to enable the control of electric polarization by a magnetic field and the control of magnetization by an electric field [1–8]. Among ME materials, a significant effort has been dedicated to artificially engineered materials that combine FE and FM constituents in materials with two- or more-phases in horizontal and/or vertical architectures [1,4,7,9,10]. In these compounds, the interplay between magnetic and electric ordering, and transport properties, reveals new physics that could be used to design novel functional devices based on FE/MF tunnel junctions, resistance switching, photovoltaic effect, tunable giant magnetoresistance spin valves, etc [1–10]. Such materials combinations enable the

* Corresponding author.
*E-mail address:* raymond@cnyn.unam.mx (O. Raymond-Herrera).

http://dx.doi.org/10.1016/j.actamat.2017.02.030
1359-6454/

development of a new family of electronic devices such as ultrahigh-density magnetic memories, ultralow-power tunable radio-frequency/microwave ME devices, low magnetic field sensors, to name a few [4,7].

Today, the ability to create atomically perfect, lattice-matched heterostructures of complex perovskite oxides using thin film growth techniques as molecular beam epitaxy (MBE), pulsed laser deposition (PLD), and atomic layer deposition (ALD), has generated new physical phenomena at interfaces where exotic properties and unexpected states are originated from the lattice, charge, orbital, and spin coupling [1,2,6,11,12]. In the last years, many detailed studies on MF epitaxial interfaces have been reported where strong coupling effects such as exchange bias, electronic orbital reconstruction, orbital switching, exchange-spring magnet, and interdiffusion processes phenomena occur [1–3,6,11–18].

Among the single-phase MF compounds, many complex oxides families have been extensively investigated, especially those with perovskites or perovskite-like structure such as the rare-earth manganates and the well-known Bi-based materials [1,2]. However, most of those reported multiferroics so far are antiferromagnetic (AFM) with Curie or Néel temperatures far below room temperature (RT). In this field, the AFM-FE $BiFeO_3$ (BFO) compound with Curie temperature of ~1090 K and Néel temperature of ~640 K is, perhaps, the most investigated MF material from the experimental and theoretical points of view, appealing for RT applications [1–21]. Nevertheless, taking in to account its AFM behavior many efforts have been focused on the control of the FE domain structure, the domain switching mechanisms and the ME coupling through the extrinsic exchange coupling between its MF ordering and other FM, FE, or MF compounds in epitaxial heterostructures or nanocomposites where the above mentioned interface phenomena arise [1–22]. In particular, one of the FM materials used to investigate and understand the interfacial coupling is the well-known half-metallic ferromagnet $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) which exhibits fascinating physical properties such as a high Curie temperature ~ 370 K, colossal magnetoresistance at RT, magnetic anisotropy, and a measured spin polarization of nearly 100% [22,23] with high potential for applications in spintronics and novel functional electronic devices [4,7,19,20]. Under this premise, the BFO/LSMO bilayers grown on different substrates have been widely investigated in the academic world. On the other hand, due to incompatibility of the monocrystalline oxide substrates (SrTiO3 (STO), $LaAlO_3$, $DyScO_3$, and $NdGaO_3$) used to date with the actual Si-based technology, some works have been directed to explore silicon integrated multiferroic heterostructures as in recent studies in epitaxial BFO/LSMO stacks grown on traditional Si substrates, buffered with STO/MgO/TiN stacks [17,19,20].

Motivated by the physical phenomena arising at the multiferroic heterostructures interfaces and to explore different deposition techniques compatibles with Si technology, the aim of this work is the study of the multiferroic properties of BFO/LSMO thin films grown on SiO2/Si(100) substrates using rf-sputtering, with different nanoscale thicknesses of the BFO layer. A detailed study of the structural, magnetic and ferroelectric properties is presented. A novel nanostructured ferromagnetic phase coexisting with the ferroelectric order at RT for the BFO films with thickness smaller than 50 nm was found. A model based on strong superexchange coupling interactions arising at the interface between the strained $Fe^{3+}$–O–$Fe^{3+}$ sublattice of BFO with the ferromagnetic $Mn^{3+}$–O–$Mn^{3+}$/$Mn^{4+}$ sublattice of LSMO is discussed.

## 2. Experimental details

Multiferroic BFO/LSMO bilayers were deposited on $SiO_2$/Si(100) (SOS) commercial substrate using the rf-magnetron sputtering technique. Stoichiometric LSMO and BFO ceramic targets were fabricated by typical solid state reaction. LSMO thin films with 40 nm thickness were directly grown on SOS. The LSMO/SOS stack is labeled L40 across the paper. All films thicknesses were obtained using transmission electron microscopy (TEM). The deposition parameters for LSMO films were: $2.0 \times 10^{-5}$ Torr base pressure, 5 cm target–substrate distance, 500 °C substrate temperature, 250 W rf-power, partial pressures of Ar (15 mTorr) and O (5 mTorr) totaling 20 mTorr, and 15 min deposition time. For the BFO film deposition process, the parameters used were: 400 °C substrate temperature, 150 W rf-power, partial pressures of Ar (20 mTorr) and O (5 mTorr) totaling 25 mTorr, and deposition times of 5, 10, 15, 20, and 30 min leading to BFO film thickness ($t_{BFO}$) values of 15, 50, 70, 120, and 140 nm, respectively. The labeling convention for the BFO/LSMO/SOS stacks studied in this work is, according to the BFO films thickness, B15, B50, B70, B120 and B140, respectively.

The structural and chemical compositions characterization was realized by X-ray diffraction (XRD) using a PanAnalytical X-Pert PRO MRD diffractometer with monochromatic Cu $K\alpha_1$ radiation (1.540598 Å) and by scanning transmission electron microscopy (STEM) with energy dispersive spectroscopy (STEM + EDS) using a JEOL JEM-2100F and a JEOL JEM2200FS microscopes with 200 kV accelerating voltage. Cross-sectional specimens were prepared using a JEOL JIB-4500 scanning electron microscope equipped with focused ion beam technique (SEM + FIB). All the specimens were first coated with Au at room temperature using argon-ion sputtering technique to protect the film's surface from Ga beam damage. Structural simulation was carried out using the *Diamond* software (version 3.2k) [24].

The magnetic characterization was performed using a Physical Properties Measurement System equipped with a vibrating sample magnetometer option from Quantum Design (9 T Dynacool® platform). All samples were prepared rectangular in shape with similar dimensions (in lengths and area). The magnetic field was *in-plane* applied, along the larger dimension, to minimize the demagnetization field effect. The temperature-dependence magnetization curves $M(T)$ in zero-field-cooling (ZFC) and field-cooling (FC) modes were measured at low magnetic field $H = 200$ Oe, between 2.5 K and 400 K, with a heating and cooling ramp of 1 K/min. The $M(T)$ curves under high magnetic field (50 kOe) were only performed in FC from 400 K to 2.5 K using the same cooling rate. The hysteresis loops were recorded at a maximum magnetic field of ±40 kOe at selected temperatures from 2.5 K to 400 K, using a magnetic field sweep rate of 100 Oe/s. All magnetization values reported here were normalized to the total volume of the LSMO single layer or of the BFO/LSMO bilayers, using the thickness and area values pertinent to the individual case. Moreover, the diamagnetic contribution of the SiO2/Si substrate was subtracted for all samples.

Surface topography, *out-of-plane* FE domain structure, domain switching, and FE hysteresis behavior were studied by piezoresponse force microscopy (PFM) using an XE-70 (Park Systems) equipped with an SR865 lock-in amplifier (Stanford Research Systems), using Multi75-G probes with chrome-platinum conductive coating (Budget Sensors). An AC voltage signal of 1 $V_{pp}$, at a frequency value near the contact resonance of 342.5 kHz was used. The LSMO film was used as bottom electrode. All PFM characterizations were carried out at 9% humidity and 21 °C.

## 3. Results and discussion

### 3.1. Structural characterization

The collected XRD data of the BFO/LSMO/SOS and LSMO/SOS stacks are shown in Fig. 1a, where intensities are illustrated in