Piezoresponse force microscopy and magnetic force microscopy characterization of γ-Fe$_2$O$_3$–BiFeO$_3$ nanocomposite/Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ multiferroic bilayers

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ABSTRACT

The multiferroic behavior of epitaxial γ-Fe$_2$O$_3$–BiFeO$_3$ (composite)/Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ bi-layered heterostructures grown on SrRuO$_3$/SrTiO$_3$ (111) substrates has been studied using piezoresponse force microscopy, magnetic force microscopy and magnetometry. The ferroelectric domain structure is ascribed to the BiFeO$_3$ phase while the magnetism originates in the γ-Fe$_2$O$_3$ phase of the composite layer. Our studies demonstrate the presence and switching of magnetic and ferroelectric domains within the same area of the sample. This confirms the presence of multiferroic behavior at the nanoscale in our γ-Fe$_2$O$_3$–BiFeO$_3$ nanocomposite thin films.

1. Introduction

Multiferroic materials simultaneously exhibit ferroelectricity and ferro-(ferri) magnetism. They have attracted the attention of scientists both for their potential applications [1–3] and their fundamental interest in understanding and predicting their functional properties. Bismuth ferrite (BiFeO$_3$; BFO) is one of the most investigated multiferroic materials and it also happens to be one of the rare materials being both ferroelectric and magnetic at room temperature. Indeed it is a ferroelectric and (G-type) antiferromagnetic. The ferroelectric transition temperature of bulk BFO is about 1103 K and magnetic transition temperature is about 643 K [4]. Thus, it possesses both electrical and magnetic ordering temperatures well above the room temperature. Hence, it is a good candidate for studying magnetoelectric coupling at room temperature and is also a material of particular interest for potential applications in various spintronic devices, such as data storage media [3] and multiple-state memory elements [5].

However, BFO thin films exhibit a sizable leakage current and it has been suggested that the presence of high saturation magnetization in BFO thin films is not intrinsic in nature, but it may originate from the presence of a secondary phase γ-Fe$_2$O$_3$ (maghemite, FO) in the BFO matrix [6]. By choosing a Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ (BLT) epitaxial insulating buffer layer, we have enhanced the various ferroelectric properties, such as resistance to ferroelectric fatigue and reduction of the ferroelectric coercivity of BFO-based nanocomposite thin film heterostructures [7]. Furthermore, we have also increased the value of the saturation magnetization of our films by controlling the concentration of magnetic γ-Fe$_2$O$_3$ in the BFO matrix. This has been achieved by selecting the appropriate deposition conditions and the thickness of the BFO layers. The inclusion of epitaxial γ-Fe$_2$O$_3$ develops while the BFO film relaxes due to the epitaxial strain induced by the underlying BLT layer as the film grows thicker. Thus, it allows the design of nanocomposite heterostructures composed of γ-Fe$_2$O$_3$ and BFO.

The multifunctional properties of these nanocomposite heterostructures may differ from their corresponding bulk properties at the nanoscale due to their local structural design. Hence a detailed characterization as well as the correlation of the structural and physical properties at the nanoscale are essential in order to

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understand and predict the overall global properties of such heterostructures. In the present work, we report our preliminary investigations towards the characterization of magnetic and ferroelectric domain structures at the ultralocal scale of epitaxial γ-Fe$_2$O$_3$–BiFeO$_3$/Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ bi-layered thin film heterostructures. Furthermore, we establish a correlation between their structural and their macroscopic multiferroic properties.

2. Experiment

The composite bi-layered thin film heterostructures were grown by pulsed laser deposition (PLD) on (111)-oriented (40 nm) SrRuO$_3$ (SRO)-coated (111) SrTiO$_3$ (STO) substrates under optimized growth condition. The detailed deposition parameters as well as the structural and ferroelectric properties at the macroscopic scale have been reported earlier [7]. The thicknesses of both γ-Fe$_2$O$_3$–BiFeO$_3$ and Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ layers were about 200 nm. The temperature and magnetic field dependence of the magnetization were measured using a superconducting quantum interference device (SQUID) magnetometer from Quantum Design. Hysteresis (M–H) loops are measured with the field applied along both the in-plane (IP) and out-of plane (OP) directions. Local ferroelectric and magnetic domain characterizations were performed using scanning probe techniques, viz., piezoresponse force microscopy (PFM) with both out-of-plane and in-plane domain detection for ferroelectric properties, and magnetic force microscopy (MFM) to detect the magnetic domain structure [8,9]. In the following, we present the PFM signal as the mixed amplitude and phase response, i.e. Amplitude $\times$ cos(phase). We used a Co/Cr-coated tip for both PFM and MFM techniques. It should be mentioned here that MFM of non-conducting samples is also sensitive to electrostatic interactions, therefore special care should be taken when interpreting the MFM data [8].

3. Results and discussion

The localization and distribution of the phases within the γ-Fe$_2$O$_3$–BiFeO$_3$/Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ bi-layered heterostructures have been already reported in Ref. [7] and can be seen on the image of the heterostructure cross-section (Fig. 1a) obtained by annular dark-field scanning transmission electron microscopy (ADF-STEM). The system is composed of a γ-Fe$_2$O$_3$–BiFeO$_3$ composite layer on an insulating BLT layer. One should note that all phases grown onto a SRO-coated STO (111) substrate are epitaxial, including the γ-Fe$_2$O$_3$ inclusions with the following epitaxial relationships: γ-Fe$_2$O$_3$(111)‖BFO(111)$_{pseudocubic}$‖BLT

(104)‖SRO(111)‖STO(111) [7]. The γ-Fe$_2$O$_3$ inclusions are embedded transversally in the film at the BiFeO$_3$ grain boundaries. The morphology of the γ-Fe$_2$O$_3$–BiFeO$_3$ composite layer (Fig. 1b) has been characterized by scanning electron microscopy (SEM) in the secondary electron emission imaging mode. Since scattering of heavy elements provide the highest intensities detected, the bright contrast region is attributed to BiFeO$_3$ phase (Bi being the heaviest element of the compound) and the dark contrast region to γ-Fe$_2$O$_3$ phase. Using the surface area of bright contrast and dark contrast regions, we have roughly estimated the fraction of the different phases in our composite layers. We find that the films are composed of 74% of BiFeO$_3$ and 26% of γ-Fe$_2$O$_3$.

Excellent macroscopic ferroelectric properties in terms of polarization hysteresis have been obtained [7] and were confirmed at the nanoscale by PFM measurements (Fig. 2) which showed regions exhibiting a strong PFM contrast, surrounded by regions without a response. Switching properties were tested as follows: the surface was first poled at a probe bias of -10 V over an area of $15 \times 15\,\mu m^2$. Within this area, an opposite poling bias of $+10$ V was subsequently applied over an area of $5 \times 5\,\mu m^2$. Fig. 2b showing a $20 \times 20\,\mu m^2$ PFM image recorded afterwards clearly shows the negative and positive domains of 15×15 and $5 \times 5\,\mu m^2$, respectively, as well as its surrounding unpoled surface. The PFM image indicates that the perpendicular component of polarization can be switched between two stable states: bright and dark contrast inside and outside of the square region. Higher PFM magnification images showed that the regions without piezoresponse exhibit a strong contrast in the MFM image as seen in Fig. 3a and b. We therefore assert that these grains are the free surface of γ-Fe$_2$O$_3$ inclusions within the BiFeO$_3$ matrix, as deduced from Fig. 1a. The IP and OP converse piezoelectric coefficients versus applied electric field hysteresis loops of one BiFeO$_3$ grain (encircled in Fig. 2b) are plotted in Fig. 2c. While a correlation between the two loops can be noticed, the IP signal being maximum when the OP signal passes through zero, their apparent coercive field is different. This difference may be understood as follows: First, the piezoelectric tensor for the rhombohedral symmetry is complex, resulting in an effective piezoelectric coefficient that is not proportional to the component of polarization along the detection direction, as explained in Ref. [10]. In this scenario, the IP (OP) response may not change its sign upon polarization switching, while the OP (IP) response does. Second, the 180° switching process may take place via two non-180° (i.e., 71° and/or 109°, [11]) switching steps, which also implies switching of only one component of the electrical polarization.

Magnetic force microscopy of the same region of our heterostructure was carried out using the same AFM tip as the one used
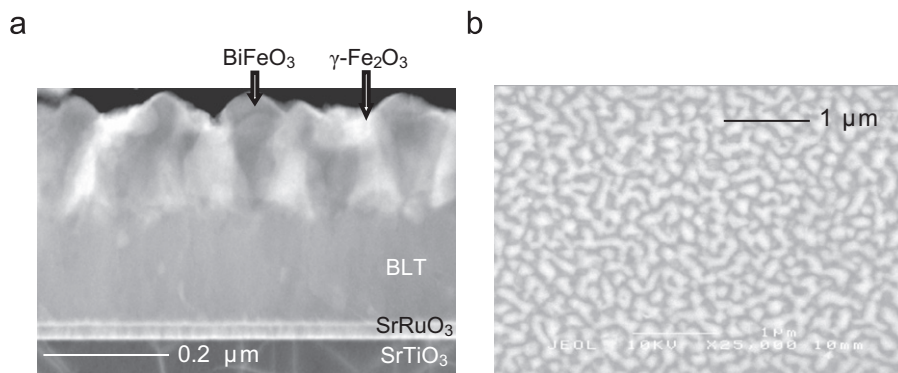

Fig. 1. (a) Annular dark-field scanning transmission electron microscopy (ADF-STEM) image of the cross-section of a γ-Fe$_2$O$_3$–BiFeO$_3$/Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ composite bi-layer grown on a (111) SrTiO$_3$ substrate with a SrRuO3 bottom electrode and (b) scanning electron microscopy image of the surface of the same layer ($5 \times 3.5\,\mu m^2$) in the secondary electron imaging mode.