Multiferroic nanoscale Bi_2FeCrO_6 material for spintronic related applications
Supporting Information

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1. STO substrate preparation The STO substrates were immersed in 6:1 buffered hydrofluoride (NH4F:HF ~BHF) solution for 30 s then rinsed with deionized water, and finally dried in blowing dry nitrogen. Second, the surface was recrystallized by thermal annealing for 15 min in O_2 atmosphere at temperatures between 950 and 1200 ℃ (depending on the width of terraces).

2. Material growth by pulsed laser deposition (PLD) Epitaxial $SrRuO_3$ (SRO) thin films were grown on TiO_2-terminated (100) $SrTiO_3$ substrates by PLD using a KrF Excimer laser (λ = 248 nm) with an energy density 1.5 J. cm^{-2} at a repetition rate of 2 Hz. The distance target-substrate was 6 cm. The layer by layer growth SRO was obtained on 100-250 nm wide STO terraces at 600 ℃ under an oxygen partial pressure of 100 mTorr. BFCO layers were deposited in an oxygen atmosphere of 8 mTorr on to heated substrates (600-680 ℃).

A high-density BFCO ceramic target was ablated at laser energy fixed between 1-2 J. cm^{-2} and laser repetition rate between 2-8Hz. These optimum deposition conditions have been chosen after studying the influence of different parameters, in particular, substrate temperature, oxygen pressure onto the BFCO growth mode and film.

3. Surface morphology of thin films by atomic force microscopy (AFM)

The surfaces of substrates and deposited films were studied by an atomic force

microscope Veeco Enviroscope AFM equipped with Co/Cr coated cantilevers (NSC

36) from MicroMasch, with an average resonance frequency of about 350 kHz. The

surface state of the substrate has an important influence on the early stages of film

growth. In order to properly study the growth mechanism, a well-defined reference

surface morphology is required. Therefore, $SrTiO_3$:Nb and STO (100) substrates were

subjected to a specific chemical and thermal treatment in order to obtain vicinal

surfaces with atomically flat single TiO_2-terminated terraces (cf Fig. 1a). Before and

after materials deposition, the surface morphology of the samples was systematically
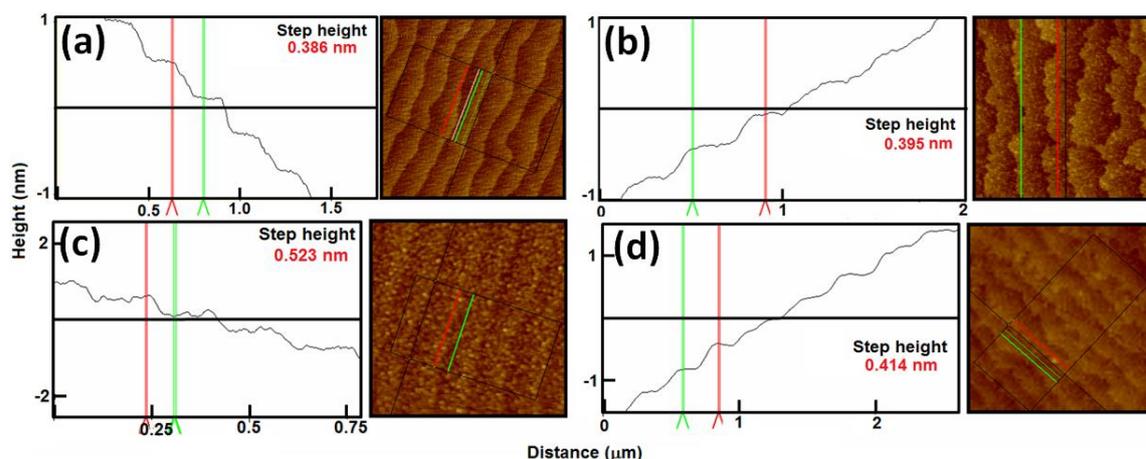
investigated by AFM.

Figure 1. Surface profiles and corresponding AFM images for **(a)** treated STO (100)

substrate, **(b)** SRO buffer layer, **(c)** 3D grown 2.5 nm-thick BFCO film and **(d)**

heterostructure BFCO/SRO.

The surface morphology of the vicinal substrates treated chemically and thermally

following the optimal procedure consists of well-defined terraces of 150 nm to 250

nm width with sharp terrace edges (cf. Fig. 1a). The height of the steps is ~0.4 nm

which corresponds to one unit perovskite cell of STO, indicating a unique TiO_2 surface termination. 2D growth of SRO is evidenced in the Fig. 2b where flat terraces with one unit cell step in observed. Using this latter as buffer layer for BFCO deposition promote the 2D growth of the BFCO (cf. Fig. 2d). The 3D growth of BFCO results in grainy layer with rough terraces (cf. Fig 2c).

4. Chemical analysis of heteroepitaxial BFCO/SRO structure

The BFCO film stoichiometry was analyzed by RBS with a 2 MeV He++ beam in both random and aligned modes with detector placed at 170° backscattering angle. RBS analysis of the BFCO/SRO/STO(100) heterostructure (cf. Fig. 2a) indicates that the cationic ratio Bi/(Fe + Cr) was close to unity (within experimental resolution of 3%).
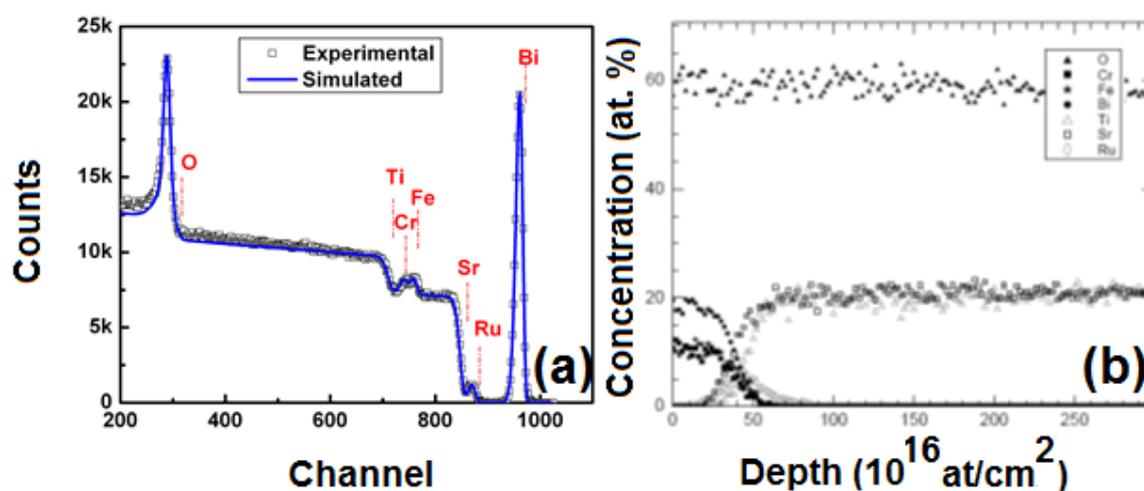

Figure 2 (a) He^{++} ion RBS spectrum of a 18 nm thick BFCO film deposited on 15 nm SRO buffered layer STO substrate. The graph shows a simulation of the sum of element contributions, fitting the experimental data. (b) The corresponding ERDA measurement giving the chemical stoichiometry of the sample with the depth.

The Fe/Cr ratio and the oxygen content are difficult to determine due to the close position of the Fe and Cr peaks and the small oxygen scattering cross section, respectively. However, an accurate Elastic Recoil Detection analysis (ERDA) has confirmed the correct stoichiometry of the obtained epitaxial heterostructures (cf. Fig. 2b).

6. Transmission electron microscopy analysis

The microstructure of the BFCO/SRO/STO heterostructure and interfaces were investigated by cross section high-resolution transmission electron microscopy (HRTEM). High-resolution analytical electron microscopy was carried out with a JEOL 2010F scanning transmission electron microscope equipped with a field emission source, an electron energy loss spectrometer (Gatan GIF, Pleasanton, CA), a high angle annular field (HAADF) detector (E.A. Fischione Instruments Inc., Export, PA).
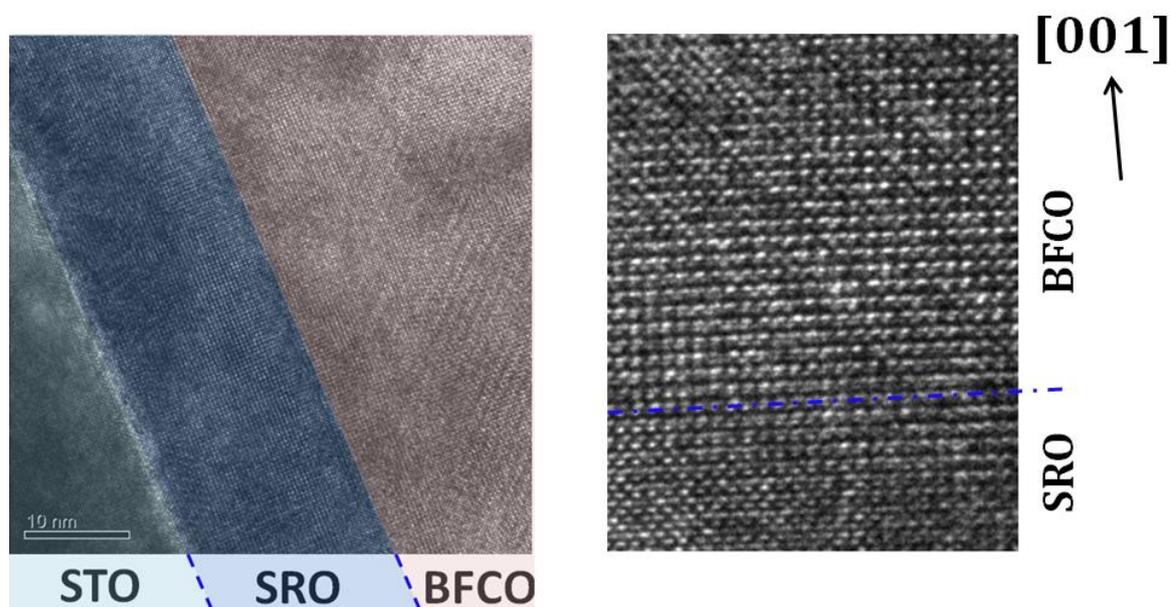

Figure 3. High resolution TEM images showing typical atomic arrangements in heteroepitaxial BFCO/SRO/STO (001) structure.

The interfaces between SRO/ STO and BFCO/SRO substrate are typically well-defined and sharp (cf. Fig. 3-Left). An epitaxial growth of the BFCO layer on SRO with the usual epitaxial relations is observed (cf. Fig. 3-Right). The crystalline quality of the interface, which is a key parameter for tunnel-type transport, is good.

7. Magnetic properties vs. temperature measurements

Magnetic properties of the films and heterostructures were studied using a superconducting quantum interference device (SQUID) magnetometer in 10 to 400 K temperature range.
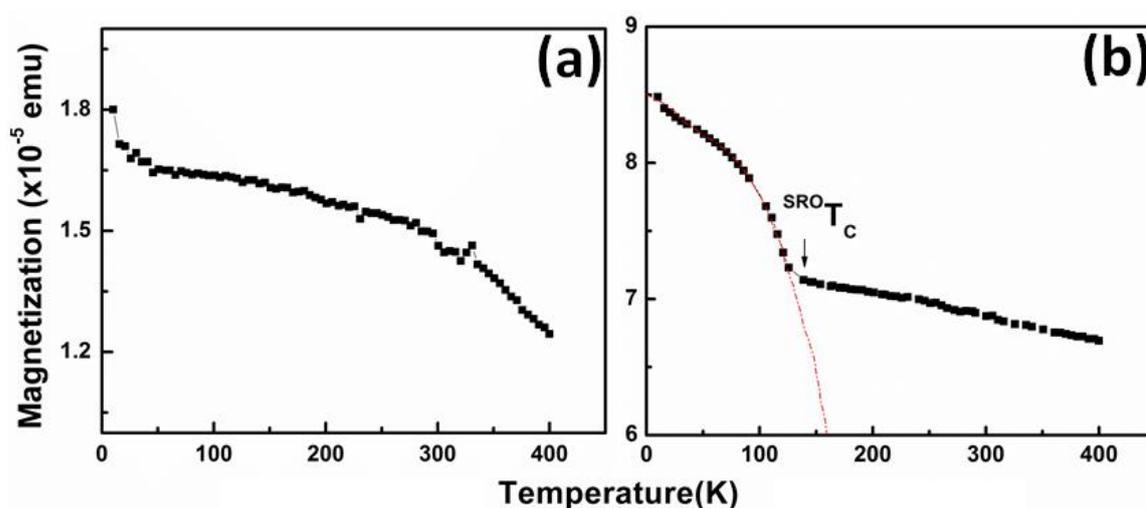

Figure 4. Magnetic properties vs. temperature measurement obtained for **(a)** BFCO/STO and **(b)** BFCO/SRO/STO structures.

A magnetic field of 500 Oe was applied parallel to the surface during the cooling. No any drop is visible in $M(T)$ curve obtained for single BFCO layer deposited directly on STO substrate (cf. Fig. 4a). This indicates that the magnetic transition temperature of BFCO film is above 400K. For the BFCO/SRO/STO heterostructure a clear drop of the magnetization in observed around 160K which corresponds to ferromagnetic Curie temperature of SRO (cf. Fig. 4b).