Supplementary Information

Strong perpendicular exchange bias in epitaxial La$_{0.7}$Sr$_{0.3}$MnO$_3$:BiFeO$_3$ nanocomposite films through vertical interfacial coupling†

Wenrui Zhang, a Aiping Chen, b,c Jie Jian, b Yuanyuan Zhu, a Li Chen, a Ping Lu, d Quanxi Jia, c Judith L. MacManus-Driscoll, e Xinghang Zhang, f Haiyan Wang * a,b

a Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77843, USA
b Department of Electrical and Computer Engineering, Texas A&M University, College Station, Texas 77843, USA
c Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
d Sandia National Laboratories, Albuquerque, New Mexico 87185, USA
e Department of Materials Science & Metallurgy, University of Cambridge, Cambridge, CB2 3QZ, UK
f Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843, USA
†Electronic Supplementary Information (ESI) available: Supporting HRTEM images and physical property measurement results are available.

*Corresponding author: Email: wangh@ece.tamu.edu
Section 1. Experimental section

Sample preparation

The LSMO:BFO composite targets with different composition ratios were prepared by a conventional ceramic sintering method. In brief, a stoichiometric mixture of high purity La$_2$O$_3$, SrCO$_3$ and MnO$_2$ powders were ground, pressed and then sintered at 1200 °C in air for 24h to synthesize La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) powders. The BFO powders were prepared from the stoichiometric mixture of high purity Bi$_2$O$_3$ and Fe$_2$O$_3$ with 5 mol% excess of Bi$_2$O$_3$ for compensation of Bi loss and sintered at 700 °C in air for 3h. The calcined LSMO and BFO powders were then reground and mixed in different ratios and pressed into disks and subsequently sintered at 1300 °C in air for 12h to make the composite targets. The thin film deposition was conducted by a standard pulsed laser deposition method. The LSMO:BFO VAN films were grown on (001) single-crystal SrTiO$_3$ substrates at 700 °C in 100 mTorr of oxygen by pulsed laser deposition (PLD) with a KrF laser (Lamda Physik, $\lambda$ = 248 nm). The growth rate for the VAN films is ~0.5 Å/s. The target to substrate distance is 5 cm. The repetition rate is 10 Hz and the laser energy density is 2.2 J/cm$^2$. After deposition, samples were cooled down in an oxygen pressure of 500 Torr at a cooling rate of 5 °C/min. The LSMO:BFO films with different compositions were obtained by changing the target composition.

Microstructure characterization and property measurements

The high-resolution X-ray diffraction (XRD) was carried out with a PANalytical Empyrean diffractometer using Cu-K$_{\alpha}$ radiation. The conventional low-magnification and high-resolution transmission electron microscopy (TEM) and energy-dispersive X-ray
spectroscopy were performed using a FEI Tecnai G² F20 microscope operated at 200 kV. Selected-area diffraction patterns (SAED) were also collected. For the high-resolution scanning TEM (STEM) analysis, an aberration-corrected FEI Titan microscope equipped with a high brightness Schottky-field emission electron source operated at 300 kV was employed. The magnetic measurements were conducted by the vibrating sample magnetometer (VSM) mode in a Physical Properties Measurement System (PPMS, Quantum Design). For the filed cooling (FC) and zero filed cooling (ZFC) measurements, the samples were cooled down from 300 K to target temperatures. The signals from substrates have been subtracted for all measured samples. Local piezoresponse force microscopy (PFM) measurements were conducted using a Pt/Ir-coated tip at optimized resonance frequency with an alternating current voltage of 0.5 V.
Fig. S1 Out-of-plane lattice parameter versus the vertical lattice strain in $L_{1-x}B_x$ films.
Fig. S2 (a)-(d) Cross-sectional (S)TEM images of $L_{1-x}B_x$ ($x=0.2, 0.25, 0.5, 0.67$) films. Scale bars are 100 nm. (e) Plan view STEM image of $L_{0.75}B_{0.25}$ VAN films showing a clear pillar-in-matrix morphology. The inset shows the EDS line results across a pillar-matrix region.
**Fig. S3** Magnetization hysteresis curves of 120-nm-thick (a) $L_{0.5}B_{0.5}$ and (b) $L_{0.8}B_{0.2}$ VAN films measured at 10 K after field cooling from 300 K in +1 T (blue) and 0 T (black) field.
Fig. S4 (a) Magnetization hysteresis curves of pure LSMO (out-of-plane) measured at 5 K after ZFC (pink line) and FC (blue line with squares) procedure with an out-of-plane magnetic field. (b) IP magnetization hysteresis loop of pure LSMO measured at 5 K.
Fig. S5 Magnetization hysteresis curves of (a) $\text{L}_{0.75}\text{B}_{0.25}$ and (b) $\text{L}_{0.33}\text{B}_{0.67}$ VAN films measured at 5 K after field cooling from 300 K with +1 T field parallel to film surface.
Fig. S6 (a)-(c) ZFC and FC M-T curves of pure LSMO, L0.75B0.25 and L0.33B0.67 films.
**Fig. S7 (a)-(c)** The simultaneously acquired PFM topography, phase and amplitude images on an area of 1.7×1.7 μm² of the $L_{0.33}B_{0.67}$ film after writing the central area (0.8×0.8 μm²) with a 5 V tip bias.