Tunnel magnetoresistance and robust room temperature exchange bias with multiferroic BiFeO₃ epitaxial thin films

H. Béa^{a)}*Unité Mixte de Physique CNRS-Thales and Université Paris-Sud XI, RD 128, 91767 Palaiseau, France*

M. Bibes

Institut d'Electronique Fondamentale, CNRS, Université Paris-Sud, 91405 Orsay, France

S. Cherifi

Laboratoire Louis Néel, CNRS, BP166, 38042 Grenoble, France

F. Nolting

Paul Scherrer Institut, 5232 Villigen-PSI, Switzerland

B. Warot-Fonrose

CEMES, CNRS, 12 Rue Jeanne Marvig, 31400 Toulouse, France

S. Fusil, G. Herranz, C. Deranlot, E. Jacquet, K. Bouzehouane, and A. Barthélémy

Unité Mixte de Physique CNRS-Thales and Université Paris-Sud XI, RD 128, 91767 Palaiseau, France

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The authors report on the functionalization of multiferroic BiFeO₃ epitaxial films for spintronics. A first example is provided by the use of ultrathin layers of BiFeO₃ as tunnel barriers in magnetic tunnel junctions with La_{2/3}Sr_{1/3}MnO₃ and Co electrodes. In such structures, a positive tunnel magnetoresistance up to 30% is obtained at low temperature. A second example is the exploitation of the antiferromagnetic spin structure of a BiFeO₃ film to induce a sizable (~ 60 Oe) exchange bias on a ferromagnetic film of CoFeB at room temperature. Remarkably, the exchange bias effect is robust upon magnetic field cycling, with no indications of training. © 2006 American Institute of Physics. [DOI: 10.1063/1.2402204]

Multiferroic materials^{1,2} that display several long-range orders among ferroelectricity, ferromagnetism (FM), and ferroelasticity can bring interesting additional functionalities to spintronics.³ For instance, the magnetoelectric coupling existing in these compounds could be used to rotate the magnetization of a ferromagnetic multiferroic element by applying an electric field, rather than a magnetic field. Unfortunately, very few multiferroics exhibit a finite magnetization. Most of them are antiferromagnetic (AF) or weak ferromagnets. Still, many spintronics applications can also be devised exploiting the new functionalities provided by antiferromagnetic multiferroics (AFMs). For example, Binek and Doudin⁴ have proposed to use a thin AFM layer as a tunnel barrier in a FM/AFM/FM magnetic tunnel junction (MTJ). In this type of device, the magnetoelectric coupling is used to tune the effective direction of the exchange bias (EB) by an electric field. In other words, the magnetic configuration of the MTJ can be changed from parallel (P) to antiparallel (AP) (hence the resistance level from low to high) by applying an electric field across it. This type of device would allow to write a magnetic bit electrically with a low power consumption, which is a major challenge for the future of magnetic random access memories (MRAMs) and other spin-based devices.

Following these suggestions, we report here on the use of room temperature (RT) multiferroic BiFeO₃ (BFO) epitaxial films as tunnel barriers in MTJs and as exchange-biasing layers. We show that these BFO films have an excellent structural quality when integrated into perovskite-based spintronics architectures and display an AF behavior combined with ferroelectric properties. A positive tunnel magnetoresis-

tance (TMR) of up to 30% is obtained at low temperature (T) in CoO/Co/BFO/La_{2/3}Sr_{1/3}MnO₃ (LSMO) MTJs. Finally, we show that such BFO layers can also be used to induce a robust EB of ~ 60 Oe at 300 K on Co₇₂Fe₈B₂₀ (CoFeB), a high Curie temperature (T_C) highly spin-polarized soft ferromagnet, widely used in last generation MTJs.⁵

We have grown BFO thin films and BFO/LSMO (15 nm) heterostructures on (001)-oriented SrTiO₃ (STO) by pulsed laser deposition.^{6,7} To define a MTJ, we then sputtered on a BFO (5 nm)/LSMO (15 nm) bilayer a top electrode of Au/CoO/Co and etched $30 \times 30 \mu\text{m}^2$ junctions.⁸ Figure 1 displays a high resolution transmission electron microscopy (TEM) micrograph of a BFO (8 nm)/LSMO (15 nm)//STO sample observed in cross section on a Tecnai F20 microscope equipped with a spherical aberration corrector. An epitaxial growth of the LSMO layer on the STO with the usual epitaxial relations is observed and no dislocations are detected in the BFO layer. This has been checked in different parts of the sample. The crystalline quality of the interface, which is a key parameter for tunnel-type transport,⁹ is excellent, even though it is impossible to rule out the presence of some oxygen vacancies. The electrical quality of the barrier has been checked previously by conducting-tip atomic force microscopy.⁷

We have measured the resistance R of several CoO/Co/BFO/LSMO junctions as a function of a magnetic field H applied along the [100] direction after field cooling ($H=6$ kOe) along the same direction. $R(H)$ curves measured at 3 K and a bias of 10 mV show a clear positive TMR for several junctions with 2 or 5 nm thick BFO barriers, see an example for a TMR of about 14% [calculated from $\text{TMR}=(R_{\text{AP}}-R_{\text{P}})/R_{\text{P}}$ with R_{ap} and R_{p} the antiparallel and

^{a)}Electronic mail: helene.bea@thalesgroup.com

FIG. 1. TEM cross section of a BFO (8 nm)/LSMO (15 nm)//STO (001) sample.

parallel resistances, respectively] in Fig. 2(a) for a 5 nm BFO. The resistance switchings at $H = -170$ and 165 Oe correspond to the reversal of the LSMO magnetization and the ones at 350 and -1110 Oe to the reversal of Co exchange biased by CoO. This positive TMR of 14% reflects a positive spin polarization of $P_{\text{Co}} = 7.3\%$ for Co at the interface with BFO [from the Jullière formula¹⁰ and using a spin polarization P of 90% for LSMO (Ref. 8)]. The maximum TMR we have obtained in such junctions amounts to $+31.3\% \pm 2.4\%$, yielding a maximum $P_{\text{Co}} = 15.0\% \pm 1.0\%$. Previous TMR studies on Co/SrTiO₃/LSMO,¹¹ Co/LaAlO₃/LSMO,¹² Co/TiO₂/LSMO,¹³ and Co/Al₂O₃/LSMO (Ref. 11) have shown that the sign and amplitude of the TMR depend on the wave function matching at electrode-barrier interfaces and on the electronic structure of the barrier. The positive TMR we observe here could thus reflect the preferential transition of positively spin-polarized Co wave functions by the epitaxial BFO barrier (the complex electronic structure^{14,15} of which has not been calculated yet). Alternatively, it is possible that symmetry mixing occurs at the interfaces due to the presence of structural imperfections such as oxygen vacancies.

The TMR vanishes around $T^* = 200$ K [Fig. 2(b)], despite the rather high T_C of the LSMO electrode (330 K). This discrepancy between T^* and T_C in manganite MTJs is a long-standing issue.^{16,17} It was shown previously that the T_C of high quality manganite interfaces is around 300 K,^{18,19} i.e., lower than the bulk T_C by some 50 K. The lower value of T^* that we observe here can also signal a local deoxygenation of the LSMO surface during the low-pressure growth of the BFO layer (6×10^{-3} mbar vs 0.41 mbar for LSMO).

FIG. 2. (a) $R(H)$ curve of a Au/CoO/Co/BFO/LSMO//STO (001) junction. The arrows show the magnetic states of each layer for the different resistance states. (b) Evolution of the TMR with T .

FIG. 3. XAS spectra measured in BFO (70 nm)/LSMO (15 nm)//STO (001) with the linear polarization vector E oriented parallel and perpendicular to the sample plane (top) and the corresponding XLD spectra (bottom).

We conclude this part on BFO MTJs by noting that the maximum TMR value we have obtained is rather large [comparable in absolute value to those measured in Co/LaAlO₃/LSMO (Ref. 12) or Co/STO/LSMO junctions,¹¹ despite the AF nature of the tunnel barrier (see later). Previous measurements on MTJs with AF manganite barriers (e.g., La_{0.55}Ca_{0.45}MnO₃) had yielded rather low TMR.^{20,21} This can be due to either spin depolarization at interfaces (likely to present a large degree of spin disorder due to a competition between FM interactions—in the electrode—and AF interactions—in the barrier) or to spin depolarization during the tunneling process (e.g., via magnon excitation). Even though systematic studies on junctions with different barrier thicknesses are required to better understand these effects, our observation of a large TMR in the Co/BFO/LSMO system suggests that the spin disorder present at the BFO/LSMO interface is weak.

X-ray absorption spectroscopy (XAS) measurements have been performed on a BFO (70 nm)/LSMO sample with a photoemission microscope at SIM beamline at the Swiss Light Source in electron-yield mode at a grazing photon beam incidence (see inset of Fig. 3). We can exclude FM order in our BFO thin films as no circular dichroism has been observed (see also Ref. 22). Figure 3 displays two XAS measurements at the Fe $L_{3,2}$ edges obtained with E parallel and perpendicular to the sample plane (averaged over an area of $\sim 20 \mu\text{m}^2$). The XAS features are in good agreement with hematite ($\alpha\text{-Fe}_2\text{O}_3$) spectra²³ and are similar to the XAS measured for LaFeO₃.²⁴

While the magnetic origin of circular dichroism in a ferromagnet can be easily demonstrated, the magnetic attribution of linear dichroism (XLD) is more difficult as it can originate from either anisotropic charge distribution, crystal field, or antiferromagnetism.²³ However, from the similitude of the measured XAS features with the results obtained on $\alpha\text{-Fe}_2\text{O}_3$ with E applied parallel or perpendicular to the AF axis,²³ we conclude that the linear dichroism we observe here contains a strong contribution from the AF character of BFO. We also note that Zhao *et al.* have recently shown that in BFO XLD arises from both ferroelectricity and antiferromagnetism.²⁵ Finally, we point out that the AF character of our BFO films has been confirmed by neutron diffraction experiments.²⁶

To exploit the AF behavior of our BFO layers at room temperature, we have searched for an exchange bias (EB) effect between a BFO layer and a high T_C FM.²⁷ Following Dho *et al.*,²⁸ we have induced a uniaxial anisotropy in the FM by sputtering a 5 nm CoFeB layer on a BFO film at

FIG. 4. (a) Hysteresis loop along the [100] direction of CoFeB (5 nm)//Si layer. Hysteresis loops along (b) the [100] direction, (c) the $[-100]$ direction, and (d) the [010] direction of CoFeB (5 nm)/BFO (35 nm)//STO bilayer. (e) Coercive fields of a similar sample for successive H cycles (up to ± 300 Oe). Dashed lines are guides to the eyes.

room temperature in a magnetic field of about $H_{\text{growth}} = 200$ Oe applied in the [100] direction of BFO and a 10 nm Au capping layer.

Figure 4(a) shows the $M(H)$ cycle of a test sample of CoFeB Au (10 nm) / (5 nm) grown in the same conditions, on a SiO_2/Si substrate. As expected the CoFeB has a square and symmetric $M(H)$ loop with a low coercive field of ~ 1 Oe. Figures 4(b) and 4(c) show the $M(H)$ loop measured at 300 K with H either parallel or antiparallel to H_{growth} in the presence of a 35 nm BFO underlayer: the loop is enlarged and shifted along the field axis compared to that of Fig. 4(a), reflecting the presence of an EB at the CoFeB/BFO interface ($H_c = 42$ Oe, $H_{\text{EB}} = -62$ Oe). When H is applied perpendicular to H_{growth} [Fig. 4(d)], the $M(H)$ is typical of a measurement along a hard axis, indicating that an anisotropy has been created in the CoFeB layer. We note that we have observed this effect in several samples with different BFO and CoFeB thicknesses and with $\text{Ni}_{80}\text{Fe}_{20}$. Remarkably, the variation of H_{EB} as a function of the BFO thickness is in good agreement with what was found for the $\text{Ni}_{80}\text{Fe}_{20}/\text{FeMn}$ system.²⁷ This further confirms that BFO is responsible for the onset of EB in our CoFeB/BFO samples.

We note that EB has already been observed at low T with other AFMs, like in $\text{YMnO}_3/\text{SrRuO}_3$ bilayers.²⁹ Indications of RT EB have also been reported on $\text{Cr}_2\text{O}_3/\text{CoPt}$ samples³⁰ and $\text{NiFe}/\text{Cu}/\text{NiFe}/\text{BFO}$ spin-valve structures.²⁸ However, our results represent a direct observation of EB with a high T_N (640 K) AFM. Furthermore, we have verified that the EB effect is stable upon cycling the sample in a magnetic field and shows no training effect²⁷ [see Fig. 4(e)]. These are crucial points for the possible exploitation of this exchange bias effect in spintronics devices.

In summary, we have shown that very thin BFO films can be used as tunnel barriers between electrodes of LSMO and Co. This leads to a large positive TMR at low T . In addition, we have used the AF character of BFO to induce a robust EB on a CoFeB film at 300 K. The next step would now be to reverse the sign of the EB by applying an electric field at RT, via the magnetoelectric coupling existing in BFO.²⁵ This would provide an electrical control of the magnetization of the CoFeB and thus of the resistance of a MTJ using BFO as the pinning layer.

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