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Absence of strain-mediated magnetoelectric coupling at fully epitaxial Fe/BaTiO$_3$ interface (invited)

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Interfacial MagnetoElectric coupling (MEC) at ferroelectric/ferromagnetic interfaces has recently emerged as a promising route to achieve electrical writing of magnetic information in spintronic devices. For the prototypical Fe/BaTiO$_3$ (BTO) system, various MEC mechanisms have been theoretically predicted. Experimentally, it is well established that using BTO single crystal substrates MEC is dominated by strain-mediated mechanisms. In case of ferromagnetic layers epitaxially grown onto BTO films, instead, no direct evidence for MEC has been provided, apart from the results obtained on tunneling junction sandwiching a BTO tunneling barrier. In this paper, MEC at fully epitaxial Fe/BTO interface is investigated by Magneto-Optical Kerr Effect and magnetoresistance measurements on magnetic tunnel junctions fabricated on BTO. We find no evidence for strain-mediated MEC mechanisms in epitaxial systems, likely due to clamping of BTO to the substrate. Our results indicate that pure electronic MEC is the route of choice to be explored for achieving the electrical writing of information in epitaxial ferromagnet-ferroelectric heterostructures. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4870915]

I. INTRODUCTION

MagnetoElectric materials (MEs), i.e., single phase materials and composites, exhibiting the coupling between the electric and magnetic degrees of freedom, have recently received a great deal of attention. In fact MEs offer the possibility of switching the magnetization with an electric field, which would represent a major achievement for information storage applications. For instance, it would allow to remove the main obstacle in the miniaturization of magnetic random access memories (MRAMs), where the writing operation requires magnetic fields or large currents. Another possibility is the development of multiple-state data storage elements. However, a single phase material showing a sizable coupling between ferromagnetism and ferroelectricity at room-temperature is still missing. A promising approach to circumvent the lingering scarcity of single-phase room-temperature multiferroics is combining ferroelectric (FE) and ferromagnetic (FM) materials with high Curie temperatures to design interfacial multiferroics. In these systems, the couple of the ferroic orders (magnetoelectric coupling, or MEC) is achieved at the interface between a FM and a FE. Among many FM/FE heterostructures, Fe/BaTiO$_3$ (BTO) has emerged as prototypical system. These materials possess robust ferroic orders at room temperature and a negligible lattice mismatch (~1.4%) which favours epitaxial growth of Fe/BTO interfaces. Two kinds of MEC have been predicted at this interface: (i) direct coupling, owing to interfacial electronic effects, and (ii) indirect coupling, mediated by strain. The first ones, leading to changes in the Fe surface magnetization and surface magneto-crystalline anisotropy, have been theoretically predicted based on bond-reconfiguration driven by ionic displacement or spin dependent screening mechanisms. Experimentally, it has been demonstrated that for Fe thin films deposited on BTO single crystals the ME coupling is strain-mediated. Large magnetic anisotropy and coercivity changes in the Fe layer have been reported in response to FE switching of a BTO crystal controlled by applied electric fields. However, fully epitaxial Fe overlayers on BTO films grown on other substrates are definitely more interesting in view of integration in practical devices. Recent experimental reports suggest the presence of pure electronic interfacial MEC mechanisms in these systems. Garcia et al. demonstrated the nonvolatile electrical control of the tunnel magnetoresistance (TMR) in artificial Fe/BTO/La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) multiferroic tunnel junctions (MFTJs) after switching the electrical polarization of the tunnel barrier, reflecting the modulation of the carriers spin polarization by the direction of FE polarization. In addition, experimental evidence of remanent induced magnetic moments on Ti and O atoms coupled with those of Fe was more recently observed in analogous Fe/BTO/ LSMO MFTJs by means of X-ray resonant magnetic scattering measurements. On the other hand, in the case of Fe/BTO fully epitaxial systems, mechanical clamping from the substrate could largely suppress the strain-mediated MEC, but so far a clear experimental demonstration of the impact of this clamping effect does not exist.

In this study, we investigate MEC mechanisms at fully epitaxial Fe/BTO interfaces. By means of magneto-optical Kerr effect (MOKE) we show that, in case of fully epitaxial Fe/BTO heterostructures grown on crystalline templates, no coercivity or magnetic anisotropy changes are detected. This demonstrates that strain-mediated MEC, previously seen on Fe films grown on BTO single crystal, is suppressed by clamping to the substrate. Magnetoresistance measurements...
on fully epitaxial Fe/MgO/Fe/BTO tunneling junctions also
do not display any sizable ME effect on the Fe film (3 nm\ thick) in contact with BTO. This is coherent with the absence of
strain-mediated coupling but also confirms that predicted
direct MEC mechanisms at the Fe/BTO interface are
strongly localized and cannot propagate to the upper
interface with MgO, which is the relevant one for spin dependent

II. EXPERIMENTAL DETAILS

Thin film growth and \textit{in-situ} characterization have been
carried out in an ultrahigh vacuum (UHV) system equipped
with a molecular beam epitaxy (MBE) apparatus, a chamber
for pulsed laser deposition (PLD) and one for electron spectrosco-
copies, as described elsewhere.\textsuperscript{17} BTO and LSMO layers
have been grown by PLD using a quadrupled Q-Switched
Nd:YAG laser (266 nm) providing pulses 7 ns long with a
fluence of 2.2 J/cm\(^2\) (for BTO deposition process) and 5.2 J/cm\(^2\)
(for LSMO deposition process). It was operated at a repetition
frequency of 2 Hz to generate a plasma from stoichiometric
targets placed in front of the substrate at a distance of 30 mm
(for BTO deposition process) or 40 mm (for LSMO deposition
process). Before the growth, an annealing of the substrate up
to 730 °C is performed for cleaning and ordering the surface.
The temperature is controlled by a pyrometer. LSMO films
have been grown at a deposition temperature of 730 °C and
an oxygen pressure of 0.02 Torr. The growth of BTO films
has been performed at 640 °C with an oxygen pressure of
0.02 Torr. The deposition rate in these conditions is
0.15 Å/pulse for LSMO and 0.18 Å/pulse for BTO, as deduced
from RHEED oscillations and confirmed by X-ray reflectome-
try (XRR) measurements (data not shown). Growth paramet-
ers for BTO have been optimized following indications of
previous work,\textsuperscript{18} in order to obtain high quality epitaxial ferroelectric films with low surface roughness. Fe, Co, MgO, and
Au layers have been grown by MBE in UHV conditions (dur-
ing deposition pressure has always been kept in the range of
10\(^{-10}\)Torr) with the substrate kept at room-temperature (RT).
After the deposition of the Fe layer, a 20 min post-annealing at
200 °C has been performed in order to improve the struc-
tural quality of Fe. In the case of Fe/MgO/Fe junctions
growth, an annealing of 40 min at 200 °C has been performed
after the deposition of the second Fe layer in order to achieve
MgO crystallization. The deposition rates for Fe, Co, MgO, and
Au have been calibrated with a quartz microbalance and
then checked by \textit{in situ} X-ray photoemission spectroscopy
(XPS).

MOKE experiments have been performed on epitaxial
Au(3 nm)/Fe(6 nm)/BTO(50 nm)/LSMO(50 nm)//STO(001)
(STO stands for SrTiO\(_3\)) heterostructures grown \textit{in-situ},
as described above. A shadow mask has been used during Au/Fe
deposition in order to define macroscopic circular areas with
1 mm diameter. This structure, schematized in Fig. 2(a),
allows to perform MOKE experiments under electric-bias
conditions. The bias voltage to control the BTO dielectric
polarization has been applied between the Au/Fe electrode and
the conductive LSMO layer. The laser beam was focused on
the same Fe area. In-plane magnetic hysteresis loops have
been collected in the longitudinal configuration for different
angles (\(\theta\)) between the applied magnetic field and the
BTO[100] direction. Note that this corresponds to the
Fe[110] axis since Fe epitaxially grows on BTO with 45°
rotation of its cubic lattice with respect to that of BTO, in
order to reduce the lattice mismatch.\textsuperscript{19} MOKE measurements
have been performed using the polarization modulation tech-
nique: a photoelastic modulator, working at a frequency of
50 kHz, has been employed in order to increase the signal-
to-noise ratio.\textsuperscript{20} For each value of \(\theta\), loops have been col-
clected under different electric-bias conditions: from −7.5 V
up to +7.5 V. Polar plots of the coercive fields collected at
RT have thus been obtained for each poling condition of the
Fe BTO layer.

Epitaxial magnetic tunnel junctions (MTJs) on BTO
have been fabricated using Au(3 nm)/Co(20 nm)/Fe(5 nm)
/MgO(3 nm)/Fe(3 nm)/BTO(150 nm)//Nb:STO(001) samples
(Nb:STO stands for conductive 1.0% wt. Nb doped STO
single-crystal substrates) grown \textit{in-situ} by combined use of
PLD and MBE techniques, as previously described. After dep-
oosition of the stack, micrometric tunneling junctions
(Fe/MgO/Fe), with area ranging from 16 to 1600 \(\mu\)m\(^2\),
have been fabricated using optical lithography and ion milling.
This device, schematized in Fig. 3(a), allows measuring the MTJ
for different BTO electric-bias conditions. The voltage to con-
trol the FE polarization in the BTO layer has been applied
between the bottom Fe layer and the conductive Nb:STO sub-
strate. Tunneling magnetoresistance (TMR) has been measured
between the top Co/Fe electrode and the bottom Fe layer,
which is connected to ground. TMR measurements have been
carried out at various temperatures from 50 to 350 K, with the
dc four-probe method and magnetic field applied along both
the Fe [100] and [110] axes. TMR curves have been collected
for different voltages applied across BTO: from −10 V up to
+10 V in ascending steps and then descending back to −10 V.

III. RESULTS AND DISCUSSION

A. MOKE

In-plane magnetic hysteresis loops from Fe/BTO/LSMO
//STO samples have been measured at RT by MOKE for dif-
ferent angles (\(\theta\)) between the applied magnetic field and the
BTO[100] direction. In Fig. 1(b), we report the characteristic
loops obtained for \(\theta = 0°\) (blue empty circles) and \(\theta = 45°\)
(green full squares). The loop is square for \(\theta = 0°\) and
becomes stepped at \(\theta = 45°\), where two characteristic coercive
fields (H\(_1\) and H\(_2\) for positive fields) appear. Despite the
absolute values of H\(_1\) and H\(_2\) are both compatible with the
coercive field of thin single crystal Fe films and the stepped
loops could indicate the presence of some uniaxial anisot-
ropy,\textsuperscript{21} the analysis of the angular dependence of MOKE
loops reveals a different scenario. In Figure 1(a), we present the
polar plot of the two coercive fields (H\(_1\) and H\(_2\)) versus
magnetic field orientation \(\theta\). The values of H\(_1\) (black full
squares) are found to be almost constant along all \(\theta\) directions.
On the contrary, H\(_2\) (red empty circles) is strongly dependent
on \(\theta\): it is minimum at 45° and 135°, and then rapidly
increases going toward \(\theta = 0°\) (or 180°) and 90°. Surprisingly
enough, however, loops at 0° and 90° become squares again,
so that $H_{c2}$ cannot be defined. This suggests that our loops can be interpreted as the superposition of two loops. The first one comes from the LSMO bottom electrode, is connected to the coercive field $H_{c1}$, and presents very small anisotropy as expected for manganites.\(^{22}\) The second loop, instead, arises from the outer Fe electrode and displays the expected fourfold anisotropy, as seen from the evolution of $H_{c2}$. In fact $H_{c2}$ is minimum for $45^\circ/C14$ and $135^\circ/C14$, i.e., for the external field applied along the [100] and [0–10] easy axes of the Fe layer, while it increases when going towards $0^\circ$ or $90^\circ$ which would correspond to the Fe hard axes. At $0^\circ$ and $90^\circ$, however, the loop from the Fe layer is no more detectable in this kind of MOKE experiments where we sweep the external field from $/C0$ to $+/10$ Oe. By consequence, the loops taken at $0^\circ/C14$ and $90^\circ/C14$ simply reflect the LSMO magnetic behavior. From this analysis, we can then conclude that the Fe films epitaxially grown on BTO display the expected fourfold anisotropy,\(^{19,23}\) with easy axes rotated by $45^\circ$ with respect to the BTO[100] direction, according to the previously established epitaxial relationship.

After investigation of the sample micromagnetic properties for un-poled BTO, we are ready to examine the effect of strain-mediated MEC at the Fe/BTO interface on the Fe magnetic anisotropy and coercivity. Figure 2(b) represents the in-plane magnetic hysteresis loops collected at $\theta = 68^\circ$ (where the Fe loop is visible) for un-poled BTO ($V^0$, black full squares) and BTO polarized up ($V^- = -7.5$ V, red empty circles) or down ($V^+ = +7.5$ V, blue empty triangles).\(^{24}\) No variations in the loops can be detected. The same result is obtained for loops collected along all other investigated $\theta$ directions, from $0^\circ$ to $180^\circ$ (data not shown). The absence of any influence of the application of electric fields to the BTO layer on the magnetic anisotropy and coercivity of the Fe layer clearly indicates that strain-mediated MEC, previously seen on Fe films grown on BTO crystals,\(^{13}\) is suppressed in the case of fully epitaxial Fe/BTO systems clamped by the substrate.

B. Fe/MgO/Fe tunneling junctions on BTO

The Au(3 nm)/Co(20 nm)/Fe(5 nm)/MgO(3 nm)/Fe(3 nm) /BTO(150 nm)//Nb:STO(001) heterostructure has been made to evaluate the magnetoresistance of the constituting Fe/MgO/Fe junction and its eventual variation upon polarization of the BTO layer. This architecture has been indeed proposed as an example of hybrid multiferroic device.\(^{5,25}\) The basic idea of these devices is that MEC at the interface between the FE layer and one of the FM layers in a spintronic device could be exploited to implement the electric control of the magnetization of said electrode, which corresponds to the “electric writing” of the information. The TMR curves shown in Fig. 3(b) have been recorded at 150 K (Ref. 26) for applied field along the Fe [110] axis and different BTO bias conditions. Curves taken with the field along the [100] Fe direction have been also measured but they are not reported here, because the best magnetization decoupling between the top and bottom layers has been found for field applied along the [110] direction. The low- and high-resistance states are those with parallel (P) and antiparallel (AP) magnetizations, with
the switching fields corresponding to the different coercivities of the two ferromagnetic electrodes. The top electrode switches at a higher magnetic field than the bottom one, because of the presence of the Co layer. For un-poled BTO (black full squares), the top and bottom Fe electrodes switch at 134 Oe and 28 Oe, respectively, and the TMR, defined as $(R_{\text{AP}} - R_{\text{P}})/R_{\text{P}} \times 100\%$, is about 0.1%. This value, very small if compared with giant TMR ratios experimentally found in fully epitaxial Fe(001)/MgO(001)/Fe(001) MTJs, arises from the very low thickness of the bottom Fe layer (just 3 nm thick) in contact with oxides (BTO and MgO). This thickness was chosen to maximize the possibility to propagate the perturbation from the bottom BTO/Fe interface to the Fe/MgO interface of the same film. However, this limited thickness revealed particularly challenging for the lithographic process. Furthermore, to avoid possible oxidation and interdiffusion at the Fe/BTO interface, we have lowered the annealing temperature required for the MgO crystallization down to 200°C, which is well below the optimized temperature for this system. Despite the limited value of TMR obtained in these prototypical devices, the TMR value was quite constant from 150 K to 300 K, and the signal to noise ratio good enough to investigate any possible variation of the TMR upon BTO polarization.

The magnetic coercive fields corresponding to the jumps in the resistance seen in Fig. 3(b) do not become significantly different once BTO is polarized. In particular, the coercive field of the bottom Fe electrode in contact with BTO (corresponding to the inner jumps in Fig. 3(b)) does not change at all. It stay fixes at 28 Oe both for $V^- = -10$ V and $V^+ = +10$ V. The minor changes seen on the switching magnetic fields for the top Fe layer hardened by the Co overlayer (140 Oe for $V^- = -10$ V (red empty circles) and 134 Oe for $V^+ = +10$ V (blue empty triangles) are not reproducible and can be ascribed to some instability of the micromagnetic configuration. This confirms the absence of any change in the bottom Fe layer magnetic anisotropy or coercivity induced by BTO polarization reversal. In agreement with MOKE experiments, our TMR data show that strain-mediated MEC is suppressed in the case of fully epitaxial Fe/BTO systems clamped by the substrate. On the contrary, TMR becomes slightly bigger once the BTO is polarized. An increase of $\sim 13\%$ (calculated as $(\text{TMR}_{V^-} - \text{TMR}_{V^0})/\text{TMR}_{V^0} \times 100\%$) is observed at both $V^-$ and $V^+$, as shown in Fig. 3(b). However, as the observed phenomenon does not depend on the sign of the applied voltage (i.e., on the direction of the BTO polarization), we cannot rule out spurious effect, such as heating due to the application of static voltages across the BTO during TMR measurements. Anyway, the limited entity of the effect we measured is in good agreement with the picture of pure-electronic MEC occurring at the Fe/BTO interface. Indeed, theoretical studies predicted a variation of the magnetic properties of the Fe within just the first atomic layers in contact with BTO. Our results confirm that any possible MEC, such as that experimentally seen in Ref. 14, cannot propagate up to the upper Fe/MgO interface which plays a crucial role in the spin dependent tunneling.

IV. CONCLUSIONS

In this paper, we have studied MEC mechanisms at fully epitaxial Fe/BTO interfaces. MOKE experiments under electric-bias conditions show no appreciable changes of Fe thin films magnetic anisotropy and coercivity upon reversal of the BTO polarization. This finding indicates that strain-mediated MEC is suppressed in fully epitaxial Fe/BTO systems. This result has been confirmed by TMR measurements on a hybrid multiferroic device, i.e., a fully epitaxial Fe/MgO/Fe tunneling junction fabricated on BTO. No sizable variations of the magnetic coercive fields or of the TMR have been detected upon reversal of the polarization of the BTO layer in contact with the Fe bottom electrode of the tunneling junction. Magnetoresistance measurements demonstrate the absence of sizable strain-mediated effect and also the strong localization at the Fe/BTO interface of predicted pure-electronic MEC. Our results thus indicate that, in case of fully epitaxial Fe/BTO heterostructures grown on crystalline templates, only direct MEC mechanisms can be exploited in spintronic devices. However, the device geometry must be compatible with the strong interfacial localization of these effects, as in the case of Fe/BTO/LSMO MTJs, where the Fe layer in contact with BTO is that directly involved in the spin dependent tunneling.

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24The voltage corresponding to the coercive field of 50 nm BTO is in the order of a few volts (see Ref. 18) so that we applied a voltage large enough to reverse the BTO polarization.
26150 K were chosen in order to minimize the leakage through the BTO films in order to make it three orders of magnitude lower than the current used to measure the TMR (50 μA).