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Abstract:

We measure the magnetotransport properties of individual 71º domain walls in multiferroic $BiFeO_3$ by means of conductive – atomic force microscopy (C-AFM) in the presence of magnetic fields up to one Tesla. The results suggest anisotropic magnetoresistance at room temperature, with the sign of the magnetoresistance depending on the relative orientation between the magnetic field and the domain wall plane. A consequence of this finding is that macroscopically averaged magnetoresistance measurements for domain wall bunches are likely to underestimate the magnetoresistance of each individual domain wall.

Introduction

The field of domain wall nanoelectronics[1] owes to Ekhard Salje many of its foundation stones, and in particular the realization that domain walls offer extremely thin and yet topologically-protected percolative paths for charge transport, with additional functionality enabled by their controllable positioning [2]. Experimentally, Aird and Salje were the first to report a different transport regime in these extended nanostructures when they discovered evidence for superconductivity inside the ferroelastic twin walls of sodium-doped WO_3.[3]

Later, scanning probe investigation of transport properties in undoped multiferroics led to the first direct observation of enhanced conductivity on artificially written DW's in thin films of $BiFeO_3$ (BFO) by Seidel et al.,[4] while Chiu et al.[5] showed that enhanced conductivity existed not only in artificially written DW's but also in the walls of spontaneous epitaxially-induced twins. Farokhipoor and Noheda [6] reported the same finding and showed, in addition, that the magnitude of the current does not significantly depend on the type of ferroelastic domain walls (109^o or 71^o types) and that the conduction level is determined by the defect content.[7]

Even though different conduction mechanisms have been put forward by different works [5],[6],[8] enhanced conductivity appears in fact to be a fairly common effect not limited to multiferroic BFO; enhanced DW conductivity has also been reported in thin films of $Pb(Zr,Ti)O_3$ [9], or $BaTiO_3$ [10]; in improper ferroelectric single crystals of $ErMnO_3$[11] and $HoMnO_3$[12]; as well as in single crystals of $LiNbO_3$.[13]

The influence of magnetic field on the transport properties of domain walls of BFO has also been studied, not by direct local-probe techniques, but by spatially-extended measurements where large electrodes connect arrays of DW's. The first report, by He et al.,[14] demonstrated a significant magnetoresistance assigned to 109º ferroelectric DW's at temperatures below 200 K and under fields of up to 7 T. The magnetoresistance exhibited anisotropy as a function of the direction of the applied magnetic field, being negative when both magnetic field and transport are parallel to the DW's, and zero otherwise. More recently, Lee et al.,[15] also reported anisotropic magnetoresistance (AMR) on lithium-doped BFO films at low temperatures. They performed the measurements in capacitor-like structures and observed a unidirectional anisotropy accompanied by hysteresis. The peak in magnetoresistance coincided with the peak in displacement current during ferroelectric switching, consistent with magnetoresistance arising from domain walls, whose concentration is indeed biggest half way through the switching process. On the other hand, since all evidence to date is based on macroscopically averaged measurements, there is no indication of how (or whether) each individual domain wall, with its own particular orientation with respect to the external field, contributes differently to the total measured MR.

In this work we report the first attempt to directly measure the magnetoresistance at room temperature of individual ferroelastic 71º BFO DW's, using conductive - atomic force microscopy (C-AFM) under the presence of external applied magnetic fields up to one Tesla. The 71º DW's of BFO were found to display an anisotropic MR and, importantly, the sign of the MR in these walls appears to be positive or negative depending on the relative orientation between field and wall. This is in contrast with the MR of 109º domain walls which is always negative or zero.[14] While the generality of these results needs to be tested in different samples and geometries; if confirmed, these results would imply that macroscopically averaged measurements can underestimate the magnitude of the local MR at domain walls, and that optimization of device response must therefore include engineering of the DW's so that they are all of the same type and aligned in the same direction with respect to the external magnetic field.

Methods

For this study, an epitaxial BFO thin film on $SrRuO_3$ (SRO)-covered $DyScO_3$ (001) single-crystal substrates have been prepared by pulsed laser deposition (PLD). The BFO film was 50nm thick and the SRO bottom electrode 6nm. The $(110)_o$-oriented $DyScO_3$ single-crystal substrate was singly terminated ScO_2. The single termination of the substrate was achieved by thermally treating the substrate at 900^{o}C for 4 hours under 300 cc/min oxygen pressure.[16] This produces a surface with atomically flat vicinal terraces of c.a. 200nm width.

The base growth pressure of our PLD system is 10^{-7} mbar. The growth pressure and temperature are 0.3 mbar O_2 and 670^{o}C, respectively. A pulsed KrF excimer laser (wavelength of 248 nm) with a repetition rate of 0.5 Hz and energy density of 2 J/cm^2 was focused on the BFO target for 4 hours during the thin film growth. After deposition, the sample were annealed at 120 mbar oxygen ambient pressure with a cooling rate of 3^{o}C/min. The films are grown atomic-layer-by-atomic-layer, as observed by in-situ RHEED oscillations, and are atomically flat, following the also atomically flat terraces of the $DyScO_3$ substrate, as confirmed by AFM topographic measurements (Figure 1-b). The epitaxy and crystallography was examined by x-ray diffraction (XRD) using a Bruker x-ray 4-circle diffractometer (Figures 1-c and 1-d).

The ferroelectric configuration was probed by piezoresponse force microscopy (PFM) on an Asylum MFP3D in DART mode, by exciting the sample with a V_{ac} voltage applied to the sample at two different frequencies around the contact resonance frequency. Vertical and horizontal cantilever oscillation modes were used to characterize the orientation of the ferroelectric polarization, allowing to map the ferroelectric domain configuration, which consists of 71 degree domains as sketched in Figure 1-a.

The magnetotransport measurements at room temperature were done by C-AFM in the presence of an in-plane magnetic field applied in-situ at the same Asylum equipment. The current was measured using an ORCA tip holder with a current amplifier of $5\cdot10^9$ placed next to the grounded tip in combination with the Asylum's VFM-2 sample holder, which uses a permanent magnet placed under the sample that can be rotated within a horseshoe-shaped metallic structure to vary the in-plane magnetic field between 0 and 1 T at the sample position. For these measurements, mMasch NSC18 Pt tip were used, with conductive non-magnetic Pt coating.

After each measurement, PFM images were taken on the same area to confirm the stability of the DW and the absence of possible dynamic DW effects on the transport measurements. The applied voltage was kept limited to < 2 V (voltage applied to the bottom electrode) in order to avoid switching of the polarization, which would yield spurious displacement currents rather than true transport. Here it is worth noticing that although such events could also be avoided altogether by applying negative instead of positive voltages, there is a strong diode-like response of the domain walls, which show no appreciable current transport for negative biases.[6]

Results

X-Ray diffraction patterns confirm the fully coherent and epitaxial growth of the film with respect to the substrate (figures 1-c and 1-d). The off-specular reciprocal space map around the pseudocubic (103) reflection (figure 1-d) show that the film has the same in-plane lattice parameter and peak width as the substrate. Additionally, the film's peak-splitting shows the existence of ferroelastic domains, corresponding to the monoclinic r3 and r4 variants as defined by Chen *et al*.[17]

Because of the electrostatic boundary condition (bottom electrode and exposed top surface), there is a built-in field that favors downward polarization (see figure 2-b) and thus only 4 out of the 8 possible polarization orientations (figure 2-c). Therefore, only two types of domain walls can be present: those that separate polarization directions that differ by 109^o and those that separate polarization directions that differ by 71^o. However, as characterized by PFM, the great majority of domain walls are 71º DW parallel to the <100> or <010> directions. Vector PFM images (VPFM) in Figure 2 show the distribution of domains with alternating in-plane polarization, and uniform out of plane polarization.[18] The domains are of a fairly uniform width around 120±10 nm.

C-AFM was used to study the conductive properties of the DW following the sketch shown in Figure 3. The Pt-coated AFM tip was used as a top mobile electrode. The C-AFM image on the same area shown in Figure 2 shows a pattern of straight lines fully consistent with the presence of the DW as observed by VPFM, giving evidence of the enhanced conductivity of the domain walls. Single point C-AFM measurements allow obtaining of I(V) curves at different locations of the sample, with a lateral resolution of the order of few nanometers.

To analyse the magnetic-field dependence of the observed conductivity, in-plane magnetic fields of up to 1 T were applied parallel to the thin film plane in the (100) direction while measuring I(V) curves at different spots on the DW's. In order to account for the anisotropy of magnetoresistance effects, two different families of DW placed parallel and perpendicular to the applied magnetic field were analysed. When the magnetic field is parallel to the in-plane orientation of the DW, it is also fully perpendicular to the transport path (DW1, $H \perp I$). In contrast, when the magnetic field is perpendicular to the in-plane direction of the domain wall (DW2), the current transport path is inclined at 45 degrees with respect to the magnetic field (given the ~45 degree angle that this type of domain walls forms with the substrate) and, therefore, it includes two components: one with the field perpendicular both to the current direction ($H \perp I$) and the plane of the domain wall, and one with the field parallel to the current ($H // I$, see sketch in Figure 3).

I(V) curves were measured at different points on the sample, discarding any measurements where local ferroelectric switching (and thus ferroelectric displacement currents) had been induced by the external voltage. Over twenty such conductivity measurements with and without magnetic field were registered and compared; despite small quantitative differences between measurements, the qualitative behaviour was always the same, and representative examples of each type shown in Figure 4.

The results show two qualitatively different magnetoresistive responses: for the family of DW1 (field parallel to the in-plane direction of the wall), the magnetic field does not have a strong effect on transport, and appears to only slightly increase the conductivity, consistent with a small negative magnetoresistance as reported also for 109^o domain walls.[19]. In contrast, for the family of DW2, the magnetic field decreases the conductivity.

Discussion

It is noteworthy that the magnitude of the magnetoresistance at room temperature is larger than observed in macroscopically averaged measurements such as those of Lee *et al.*[15] The discrepancy is consistent with the observed magnetoresistive anisotropy: if walls with different orientation with respect to the magnetic field yield MR of different signs, their contributions can mutually cancel in macroscopically averaged measurements. An important lesson is therefore that macroscopically-averaged measurements can underestimate the local magnetoresistance of individual domain walls.

The other important result is of course the observation that magnetoresistance is anisotropic. This observation poses questions about the origin of the observed MR, and the cause of its anisotropy. Presently, we can only speculate: spin disorder in magnetic semiconductors is known to increase their resistivity and, conversely, magnetic fields increase spin alignment and thus cause negative magnetoresistance [20]. In some mixed valence perovskites, such as manganites, large negative magnetoresistance can also be induced by double-exchange [21, 22]. Either explanation requires a non-homogeneous ground state and would be consistent with an increased oxygen vacancy concentration at the domain wall (oxygen vacancies at the wall that change the local oxidation state of the Fe and its magnetic configuration), which in turn is also consistent with their conductivity mechanism [7].

In contrast, the positive MR for DW2, may be explained by a different mechanism that does not even require the domain walls to be magnetic to start with. Specifically, so-called geometric magnetoresistance is to be expected in a configuration with a magnetic field partially perpendicular to a transport plane. Such geometry induces a Lorenz force on the carriers that deviates their transport path, resulting in positive magnetoresistance.[23] This effect happens even in classic semiconductors such as silicon,[24] and is strongest in disordered systems.[25] Thus, while having fundamentally different origins, both negative and positive magnetoresistance can benefit from defect-induced disorder at the domain walls.

Of course, although our measurements are statistically robust and repeatable within our sample, it would be adventurous to assert the generality of the observed behaviour for other samples –particularly if, as discussed, it is likely to be influenced by defects. Extending these studies to different types of ferroelectric walls (109 degree, 180 degree) on films grown on different substrates and under different oxygen annealing conditions would be a helpful next step in that regard. Generally, however, domain walls are known to attract and be attracted to defects such as oxygen vacancies, and, in our case, the presence of such defects is consistent with the observed inhomogeneity in the domain wall current, as evidenced by alternating hotspots and darker regions in the conductivity profiles of the walls (Figure 3-c). Domain walls are also, due to their geometry, good candidates to display geometry-driven positive MR behaviour.

The two main lessons from this discussion are that (i) defects are likely to increase DW magnetoresistance (both positive and negative) by introducing disorder at the wall and (ii) since geometric magnetoresistance does not require the semiconducting material to be magnetic, it is possible that all ferroelectric domain walls, and not just those of $BiFeO_3$, be prone to MR effects. This latter hypothesis, however, remains to be tested.

Acknowledgements

GC., N.D and J. S. acknowledge funding from MINECO grant MAT2016-77100-C2-1-P and Generalitat de Catalunya grant 2014-SGR-1216. ND also acknowledges funding from "Ramon y Cajal" contract RYC-2010-06365 and FIS2015-73932-JIN from MINECO. ICN2 acknowledges support of the Spanish MINECO through the Severo Ochoa Centers of Excellence Program under Grant SEV-2013-0295.

Figure 1:

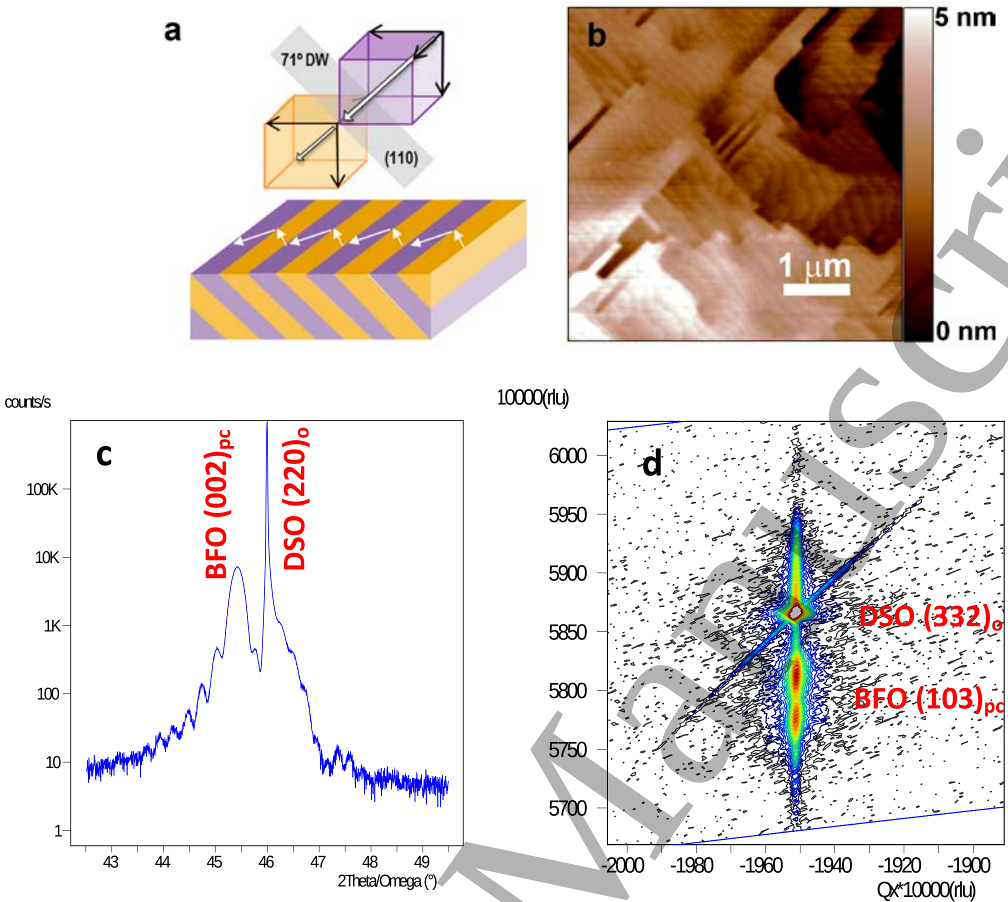

Figure 1. **a**, Configuration of as grown 71° ferroelectric DW's in BFO thin films, as characterized by PFM (see also Figure 2). **b**, Topography image obtained by AFM, showing atomically flat surfaces with unit-cell-high and 200-nm-wide vicinal steps. **c,** High resolution θ-2θ X-ray diffraction scan around the 002 diffraction peak, showing good crystallinity and interfacial sharpness, as indicated by the satellite peaks (oscillation fringes) around the film's diffraction peak. **d,** Off-specular reciprocal space map around the $BiFeO_3$ $(103)_{pseudocubic}$ diffraction peak and the $DyScO_3$ $(332)_{orthorhombic}$ diffraction peak. Notice that the in-plane lattice parameter and peak width of the film coincides with that of the substrate, indicating coherent epitaxial growth. The BFO peak-split in the out-of-plane direction corresponds to the two angular variants of the ferroelastic 71° domains.

Figure 2:

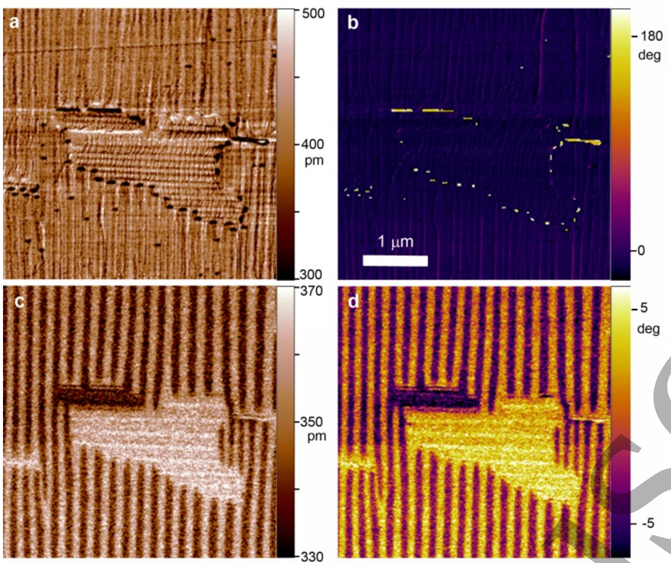

Figure 2. Vector PFM mapping: **a,** Vertical PFM amplitude and **b,** PFM phase. **c,** Lateral PFM amplitude and **d,** PFM phase. Together, the results indicate that all the domains have the same downward out-of-plane polarization, with the polarity alternating only in the in-plane direction, consistent with 71 degree domains. The domain width is 120±10nm.

Figure 3:

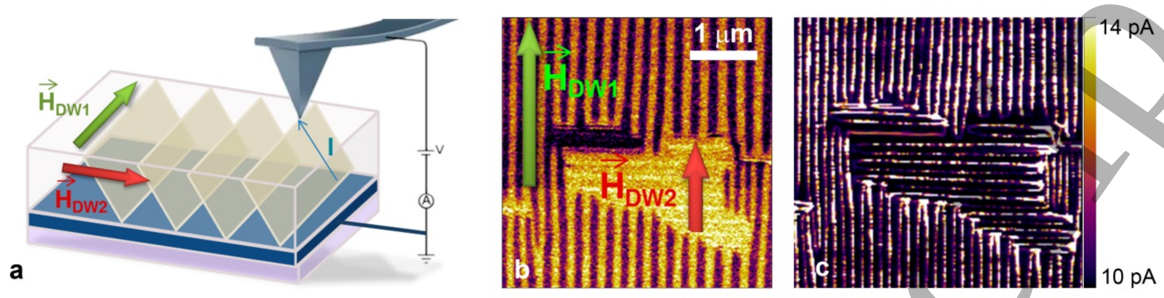

Figure 3. a, Scheme of the C-AFM configuration used for the magnetotransport measurements; it shows the relative orientations of the 71º DWs (shown in grey) with respect to the magnetic field in the two possible in plane directions (red and green arrows), and the transport path *I* between the tip and the substrate, shown as a blue vector lying within the plane of the DW. **b**, Lateral PFM phase image showing the two families of DWs used for the magnetoresistive measurements as described in the text, with different relative orientation of the magnetic field with respect to the DW, as sketched in **a** (note that from the experimental point of view, the direction of the in plane magnetic field is fixed and cannot be rotated). **c,** Current map measured with C-AFM prior to the application of any magnetic field. Notice that, while all the DW's are clearly conductive, the conduction is not homogeneous, as the lines show brighter "hotspots" of more intense current alternating with darker regions of weaker transport. This suggests that the conductivity is related to the presence of local defects at the walls.

Figure 4:

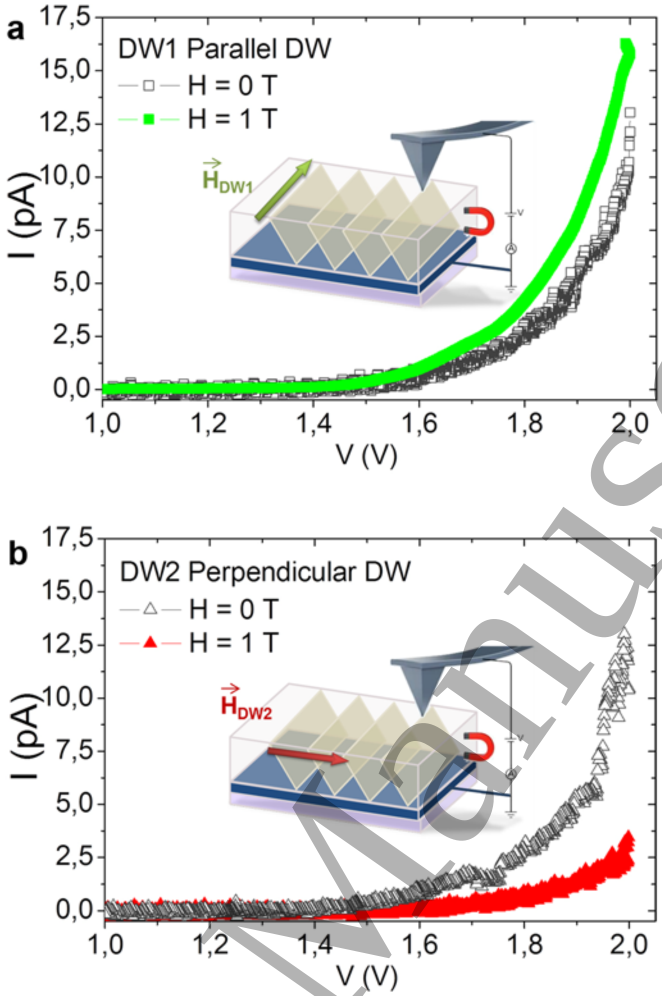

Figure 4. I(V) curves obtained for DW1 and DW2, without and with the presence of a magnetic field, with a grounded tip while applying the voltage to the sample. It is observed that the current levels are independent of the DW orientation since both curves overlap, but the presence of a magnetic field of 1T leads to behaviour coherent to AMR. The enhancement of conductivity levels with the presence of a magnetic field for the families of DW1 is also in agreement with the appearance of some degree of ferromagnetic order at the DW along the transport path, while the decrease of conductivity for the family of domains of DW2 can be correlated with a charge concentration at both sides of the DWs due to Hall effect.

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