

## Magnetism in Multiferroic BiFeO<sub>3</sub>

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# Outline

- Reborn of BiFeO<sub>3</sub>
- Magnetic Properties
  - Magnetoelectric effect
  - Exchange coupling
- Electrical control of Ferromagnetic domains and device applications
- Conclusion and Outlook
- References



# Reborn of BiFeO<sub>3</sub>

- High quality single crystal thin films
- G-type Antiferromagnetic Ferroelectric at RT
  - $T_C \sim 870^\circ\text{C}$  and  $T_N \sim 370^\circ\text{C}$
- Rhombohedral R3c

## Epitaxial BiFeO<sub>3</sub> Multiferroic Thin Film Heterostructures

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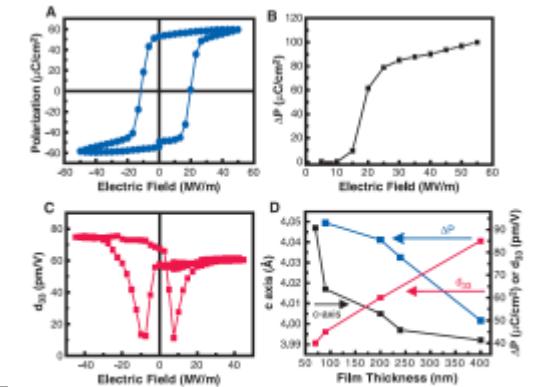
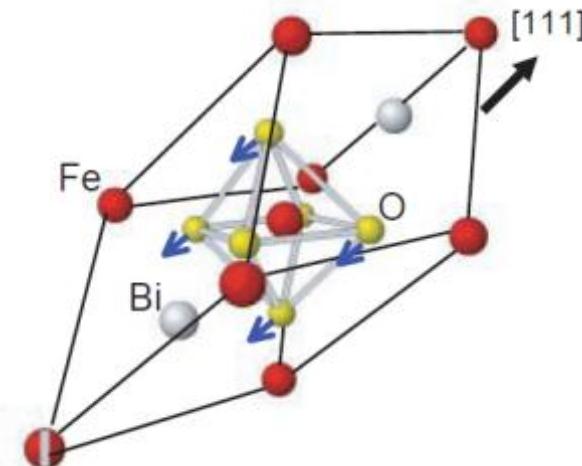


Fig. 2. [A] A ferroelectric hysteresis loop measured at a frequency of 15 kHz, which shows that the film is ferroelectric with  $P \sim 55 \mu\text{C}/\text{cm}^2$ . [B] Pulse polarization  $\Delta P$  versus electric field measured with electrical pulses of 10-μs width. [C] A small signal  $d_{33}$  for a 90-μm capacitor. [D] A summary of the thickness dependence of out-of-plane lattice parameter, polarization, and  $d_{33}$ . The small signal dielectric constant [27] follows the same trend as the  $d_{33}$ .



# Reborn of BiFeO<sub>3</sub>

- Magnetic moment detected (?)

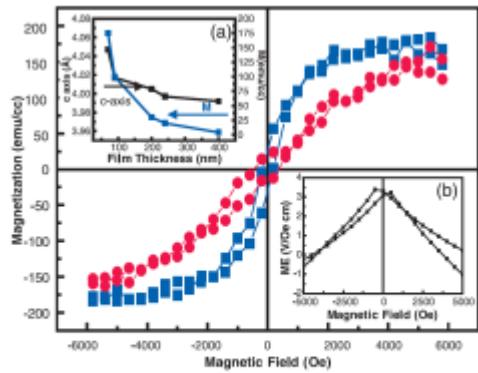
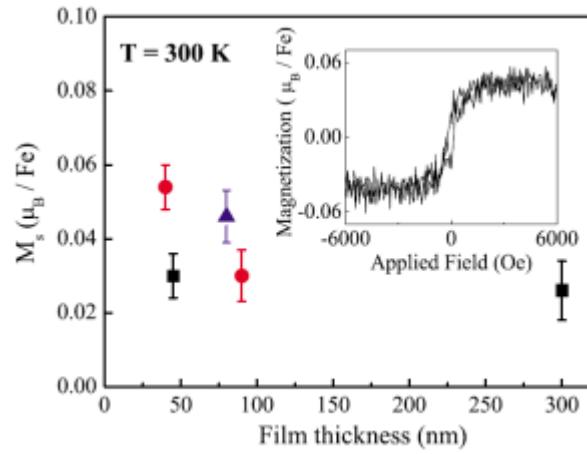


Fig. 4. Magnetic hysteresis loops measured by vibrating sample magnetometry for a 70-nm-thick BFO film, showing an appreciable saturation magnetization of  $\sim 150$  emu/cm<sup>3</sup> and a coercive field of  $\sim 200$  Oe. The in-plane loop is shown in blue, and the out-of-plane loop is in red. Inset (a) shows the thickness dependence of saturation magnetization, illustrating the effect of heteroepitaxial constraint. Inset (b) is a preliminary ME measurement result showing a maximum value of  $\sim 3$  V/cm·Oe and hysteresis about 200 Oe.

vs.



Eerenstein et. al. *Science* 307, 1203 (2005)

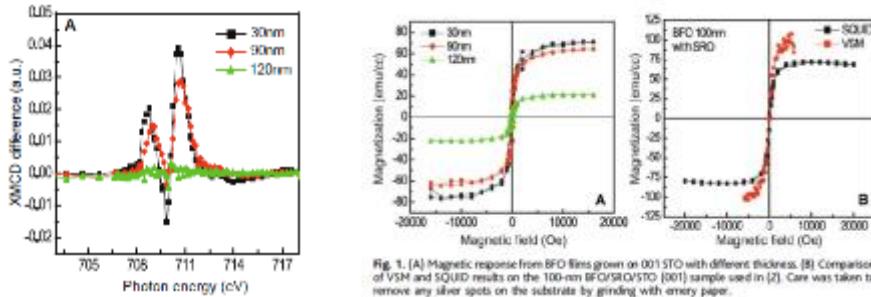


Fig. 1. (A) Magnetic response from BFO films grown on 001 STO with different thickness. (B) Comparison of VSM and SQUID results on the 100-nm BFO/SRO/STO (001) sample used in [2]. Care was taken to remove any silver spots on the substrate by grinding with emery paper.

# Magnetic Properties

- Ferromagnetism in ferroelectric domain walls of antiferromagnetic multiferroics

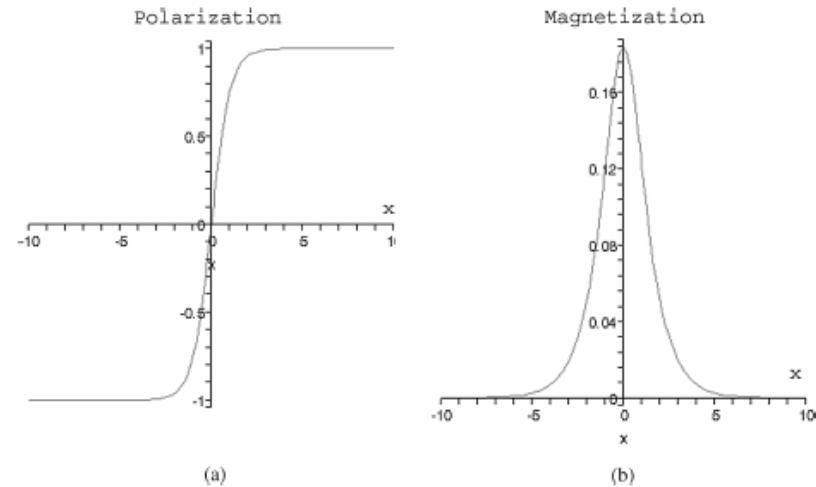
Ferroelectrics, 375:123–131, 2008  
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DOI: 10.1080/00154010802437969



## Landau Theory of Ferroelectric Domain Walls in Magnetoelectrics

M. DARAQTCHIEV,\* G. CATALAN, AND J. F. SCOTT

$$\begin{aligned}G_{MP} &= G_0 + \frac{\kappa}{2}(\nabla P)^2 + \frac{\lambda}{2}(\nabla M)^2 + L_{MP}(P, M) \\&= G_0 + \frac{\kappa}{2}(\nabla P)^2 + \frac{\lambda}{2}(\nabla M)^2 + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\eta}{6}P^6 + \frac{a}{2}M^2 \\&\quad + \frac{b}{4}M^4 + \frac{n}{6}M^6 + \frac{\gamma}{2}P^2M^2\end{aligned}$$



**Figure 3.** Shape of the ferroelectric polarization and magnetization across the domain wall. A net magnetization appears in the centre of the domain wall even though the domains themselves are still paramagnetic. (See Color Plate IX)

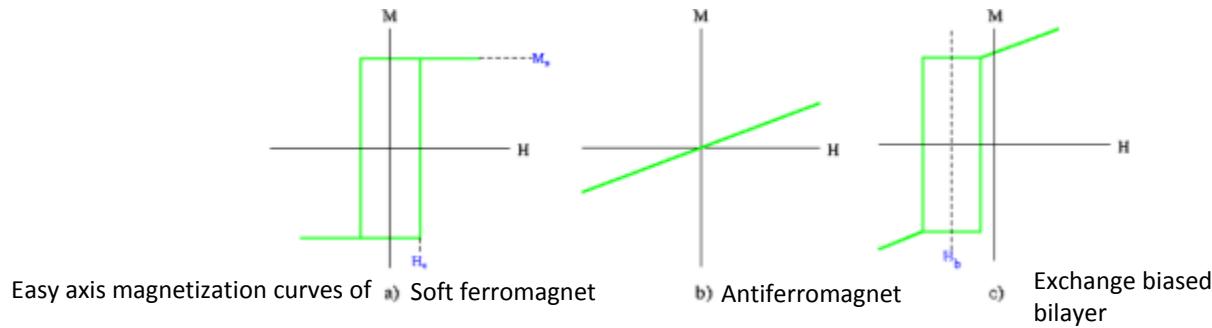
# Magnetic Properties

- Magnetoelectric effect

$$P_i = \sum \alpha_{ij} H_j + \sum \beta_{ijk} H_j H_k + \dots$$

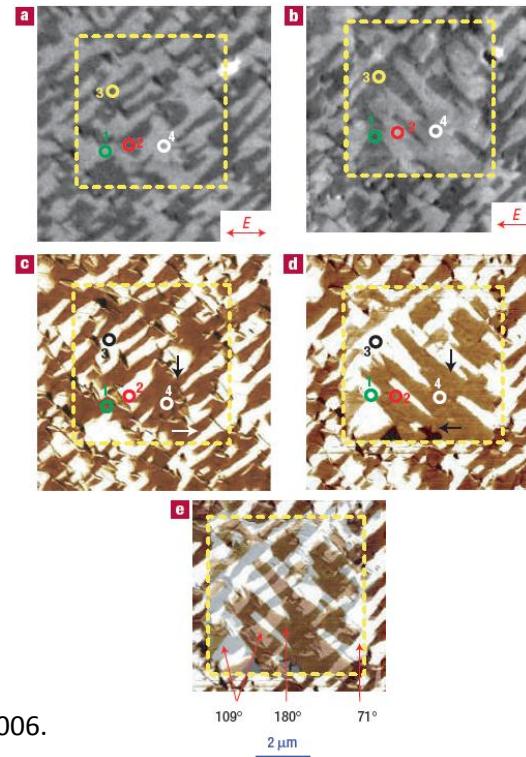
$$M_i = \sum \alpha_{ij} E_j + \sum \beta_{ijk} E_j E_k + \dots$$

- Exchange bias



# Magnetoelectric effect in BFO

- Coupling between the ferroelectric and antiferromagnetic domains via ferroelasticity



Zhao et al. *Nat. Mater.* 5, 2006.

**Figure 5** PEEM and In-plane PFM Images of the same area of a  $\text{BiFeO}_3$  film before and after electrical poling. a,b, PEEM images before (a) and after (b) poling. The arrows show the X-ray polarization direction during the measurements. c,d, In-plane PFM images before (c) and after (d) poling. The arrows show the direction of the in-plane component of ferroelectric polarization. Regions 1 and 2 (marked with green and red circles, respectively) correspond to  $109^\circ$  ferroelectric switching, whereas 3 (black and yellow circles) and 4 (white circles) correspond to  $71^\circ$  and  $180^\circ$  switching, respectively. In regions 1 and 2 the PEEM contrast reverses after electrical poling. e, A superposition of in-plane PFM scans shown in c and d used to identify the different switching mechanisms that appear with different colours and are labelled in the figure.

# Exchange coupling in BFO heterostructures

APPLIED PHYSICS LETTERS 89, 242114 (2006)

## Tunnel magnetoresistance and robust room temperature exchange bias with multiferroic $\text{BiFeO}_3$ epitaxial thin films

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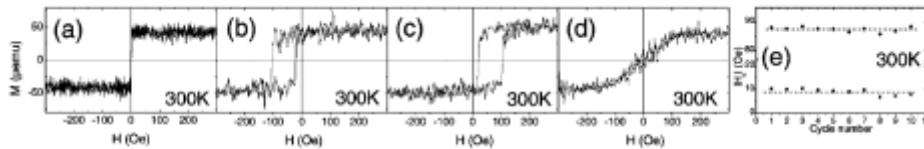


FIG. 4. (a) Hysteresis loop along the [100] direction of CoFeB (5 nm)/Si layer. Hysteresis loops along (b) the [100] direction, (c) the [-100] direction, and (d) the [010] direction of CoFeB (5 nm)/BFO (35 nm)/STO bilayer. (e) Coercive fields of a similar sample for successive  $H$  cycles (up to  $\pm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

## CoFe/Si and CoFe/BFO/STO/Si

APPLIED PHYSICS LETTERS 91, 172513 (2007)

## Room temperature exchange bias and spin valves based on $\text{BiFeO}_3/\text{SrRuO}_3/\text{SrTiO}_3/\text{Si}$ (001) heterostructures

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# MESA+

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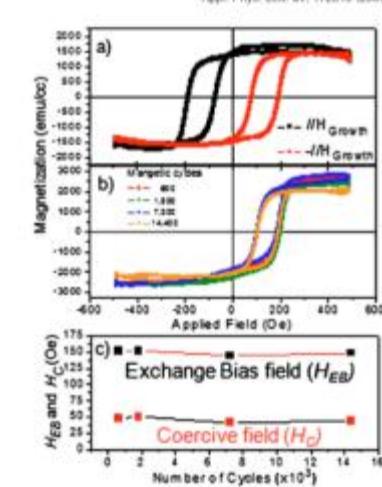
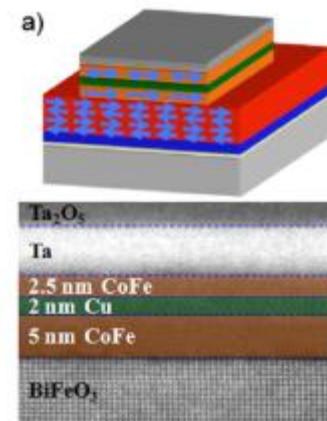


FIG. 2. (Color online) Typical magnetic properties for bilayer CoFe/BFO heterostructures. (a) Magnetization hysteresis loops reveal large negative exchange bias. (b) Repeated magnetic cycling results in very little change in the magnetic properties. (c) Exchange bias field and coercive field as a function of magnetic cycle—no training effect is observed.



# UNIVERSITY OF TWENTE.

# Nanoscale Control of Exchange Bias with BiFeO<sub>3</sub> Thin Films

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2050-2055

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Pu Yu,<sup>§</sup> Shu-Jen Han,<sup>||</sup> Donkoun Lee,<sup>||</sup> Shan X. Wang,<sup>||</sup> and R. Ramesh<sup>†,‡</sup>

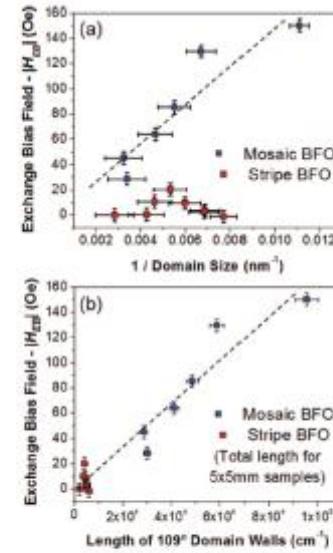
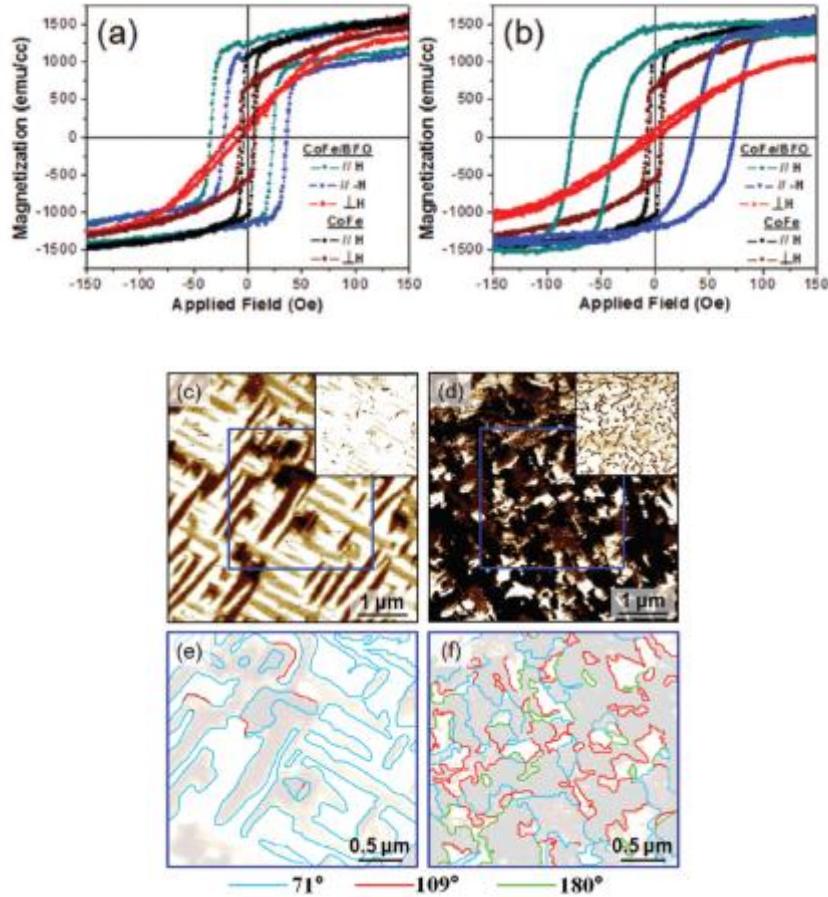
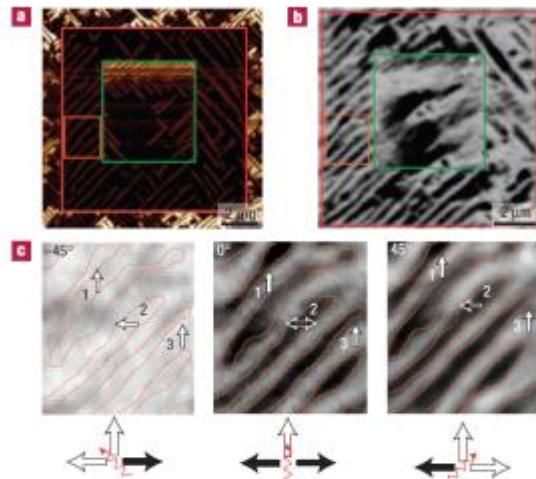


Figure 2. (a) Dependence of exchange bias field on domain size for CoFe/BFO heterostructures grown on mosaic-like (blue) and stripe-like (red) BFO films. (b) Exchange bias field of the same samples here graphed as a function of the total length of 109° domain walls/sample surface area in 5 × 5 mm samples.

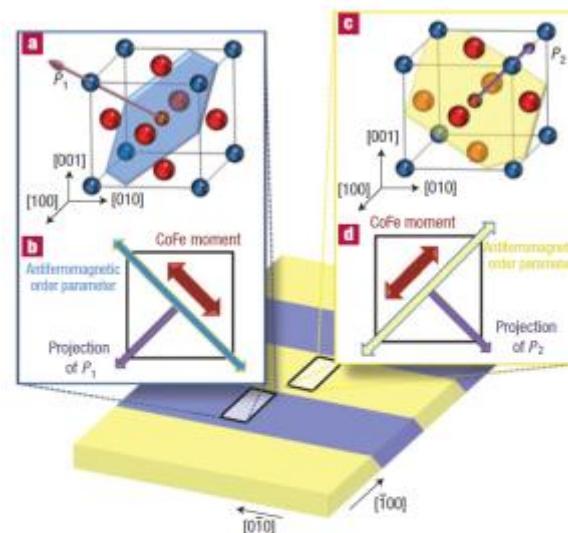
- 109° DWs are influential
- Might be the origin of uncompensated spin at the surface

# How to make more functional?

- Electrical control of Ferromagnetic layers by exchange coupling



**Figure 3** Microscopic evidence for coupling. **a**, In-plane PFM image showing the ferroelectric domain structure of a BFO film with a large ( $10\text{ }\mu\text{m}$ , red square) and small ( $5\text{ }\mu\text{m}$ , green square) electrically switched region. **b**, Corresponding XMCD-PEEM image taken at the Co L-edge for a CoFe film grown on the written pattern. Direct matching of domain structures is evident. Black contrast is interpreted as a spin pointing side-to-side in the image and grey as spin pointing up. **c**, Rotation of the sample in reference to the incoming right-circularly polarized light enables full determination of the nature of magnetism in the CoFe layer.



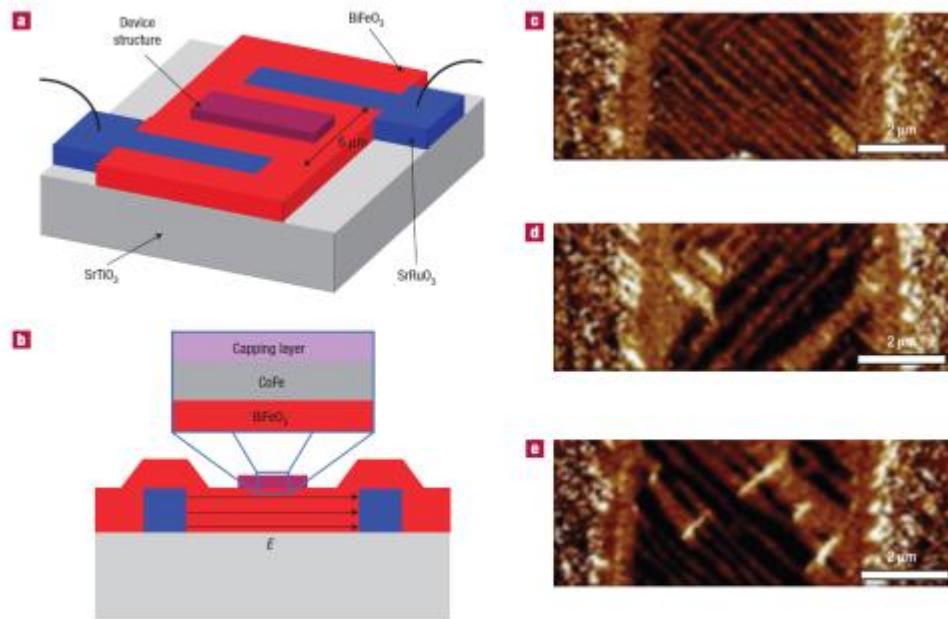
**Figure 4** Mechanism of coupling in CoFe/BFO heterostructures. **a-d**, Schematic diagrams of two adjacent domains in the [001]-oriented BFO crystal (a,c), in which the [111] polarization directions as well as the antiferromagnetic plane (that is perpendicular to this  $P$  direction) are identified, and the corresponding projections of the polarization direction, the antiferromagnetic plane onto the [001] and the corresponding  $M$ -directions in the CoFe layer (b,d).

## ARTICLES

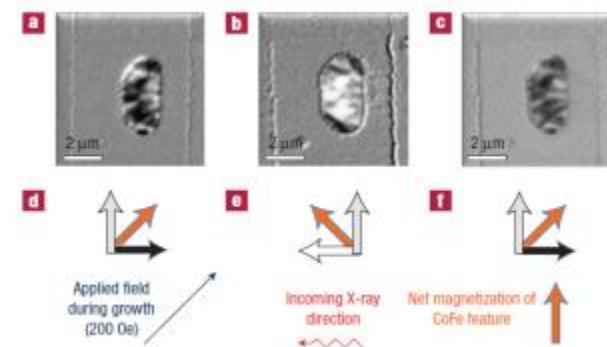
Electric-field control of local ferromagnetism using a magnetoelectric multiferroic

# How to make more functional?

- Electrical control of Ferromagnetic layers by exchange coupling



**Figure 5** Dynamic switching device structure. a,b, Three-dimensional (a) and cross-sectional (b) schematic diagrams of the coplanar epitaxial electrode device showing the structure that will enable controlled ferroelectric switching and electrical control of local ferromagnetism in the CoFe features. c–e, In-plane PFM images showing the ferroelectric domain structure for a device in the as-grown state (c), after the first electrical switch (d) and after the second electrical switch (e).



**Figure 6** Electrical control of local ferromagnetism. a–c, XMCD-PEEM images taken at the Co  $L$ -edge revealing the ferromagnetic domain structure of the CoFe features in such a coplanar electrode device structure in the as-grown state (a), after the first electrical switch (b) and after the second electrical switch (c). d–f, Schematic descriptions of the observed magnetic contrast (grey, black and white) in the corresponding XMCD-PEEM images, respectively. Application of an electric field is found to rotate the net magnetization of the structures by 90°. The direction of the applied growth field and the incoming X-ray direction are labelled as well.



# Device Applications

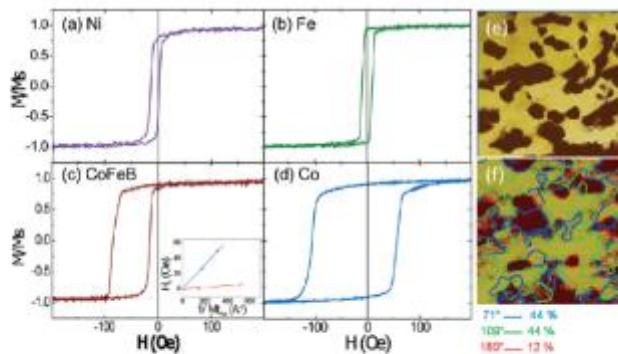


Figure 1. (a-d) Exchange bias for different 4 nm FM/BFO/BFO-Mn samples. Typical out-of-plane (e) and in-plane (f) PFM images of ferroelectromagnetic domain pattern and DW analysis of the BFO-Mn/BFO bilayer. The scan area is  $1 \times 1 \mu\text{m}^2$ . Inset: corresponding evolution of the exchange bias as a function of  $1/M_{\text{Fe}}$ .

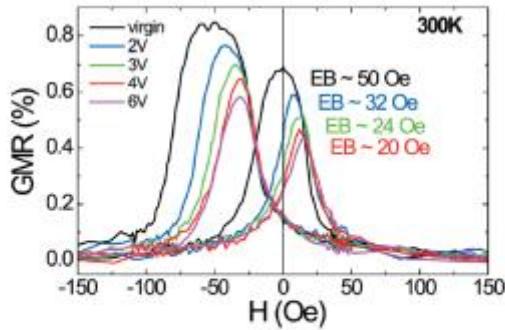


Figure 3. (a) GMR curves of a Au 6 nm/Co 4 nm/Cu 4 nm/CoFeB 4 nm spin valve after different poling events applied to the BFO/BFO-Mn bilayer. The stripe is 210  $\mu\text{m}$  long and 20  $\mu\text{m}$  wide.

## Room Temperature Electrical Manipulation of Giant Magnetoresistance in Spin Valves Exchange-Biased with BiFeO<sub>3</sub>

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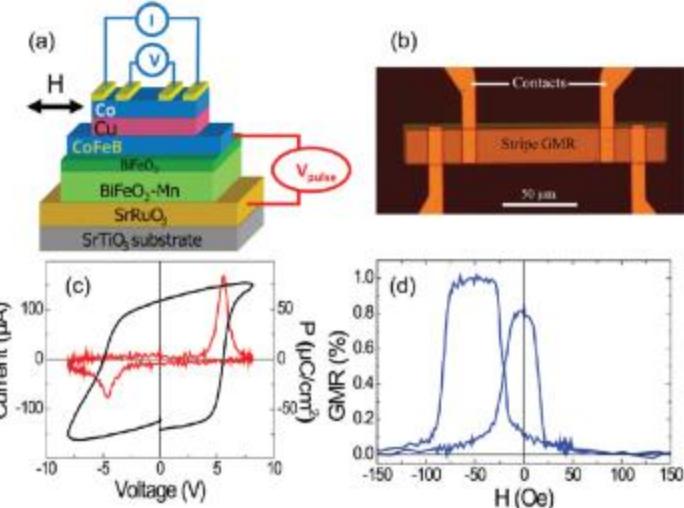


Figure 2. (a) Schematic of the device, (b) micrograph of the stripe with the electrical contacts, and (c) current and polarization versus electric field for a BFO/BFO-Mn bilayer. (d) Giant magnetoresistance of a Au 6 nm/Co 4 nm/Cu 4 nm/CoFeB 4 nm spin valve after patterning (30  $\times$  185  $\mu\text{m}^2$  stripe).

# Conclusions and Outlook

- Exchange coupling mechanism to be investigated more
- Possibility of BFO to be implemented in spintronics devices
- Increasing the efficiency of devices



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