Room temperature exchange bias and spin valves based on $BiFeO_3/SrRuO_3/SrTiO_3/Si$ (001) heterostructures

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We report the growth and characterization of exchange bias and spin valve heterostructures based on the multiferroic antiferromagnet $BiFeO_3$ on Si (001) substrates. Using $Co_{0.9}Fe_{0.1}$ as the ferromagnet, we demonstrate heterostructures with large negative exchange bias and negligible training (or a decrease in exchange bias field as a function of repeated magnetic cycling) at room temperature. We additionally report the manufacture of spin valve structures that have been found to have current in-plane magnetoresistance of over 2.25% at room temperature. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2801695]

Devices based on having the ability to electrically control exchange bias have been proposed;[1] however, an understanding of the appropriate materials necessary to make this a reality did not exist until very recently. With the rebirth of interest in multiferroic materials,[2–5] especially magnetoelectric materials, where there is coupling between magnetic and electronic order parameters, much attention has been given to understand how to integrate these materials into devices. Central to these studies are materials such as the magnetoelectric antiferromagnetic $BiFeO_3$ (BFO),[6] whose high ordering temperatures [Néel temperature of ~640 K (Ref. 7) and ferroelectric Curie temperature of ~1100 K (Ref. 8)] have made it a prime candidate for device integration. Furthermore, recent experiments have demonstrated a direct interaction between the magnetic and ferroelectric order parameters in BFO and the ability to electrically switch the nature of the magnetic domain structure in this material.[9] At the same time, much work has been completed to understand how to grow high quality, fully epitaxial, single phase thin films of BFO on various substrates, including Si.[10] This has in turn, opened a possibility for creating functional devices. By understanding how the interesting functionality of multiferroic materials can be used to achieve goals such as electrically controlling magnetism, we offer a pathway to logic, memory, and spintronic devices.

One avenue with which this may be achieved is through the creation of an exchange coupled heterostructure based on multiferroics. Exchange bias, or a unidirectional exchange anisotropy which is associated with an anisotropic exchange interaction that occurs across the interface between a ferromagnet and an antiferromagnet, has been the focus of much research since its discovery in 1956.[11] The formation of a unidirectional anisotropy and exchange bias can intuitively be explained by thinking of the ferromagnetic layer behaving as if it had and extra (internal) biasing field. Thus, the energy required to switch the magnetization antiparallel to the imaginary internal biasing field is larger than the energy required to switch the magnetization parallel to the imaginary internal biasing field (an excellent treatment of exchange bias can be found in Nogués and Schuller).[12] To date, exchange bias remains a static property, but the combination of traditional magnetic materials with multiferroics could be one pathway to realize electrically controllable exchange bias systems. At the heart of this concept are two types of coupling: *intrinsic* and *extrinsic*. The intrinsic coupling refers to the coupling between order parameters within a multiferroic material, such as BFO, where previous studies have shown that the application of an electric field, which changes the ferroelectric polarization can also change the nature of magnetism in the material.[9] The extrinsic coupling refers to the exchange coupling between magnetic order in the multiferroic material and the magnetic order in a traditional ferromagnet. Implied in this is that electric fields applied to the multiferroic material will effect changes on the magnetic order of the coupled ferromagnet. Taking full advantage of the intrinsic coupling between order parameters in a multiferroic and the extrinsic coupling between the magnetic order in the multiferroic and the coupled ferromagnet layers could lead to intriguing functionalities.

To date there have been only a few studies investigating exchange bias with multiferroic materials including $YMnO_3$ (Refs. 13 and 14) and BFO (Refs. 15–17) that have shown exchange bias with such systems can be demonstrated in a static manner. Dynamic switching of the exchange bias field with an applied electric field, however, had remained elusive until a recent report by Laukhin *et al.* focusing on $YMnO_3$ at very low temperatures.[18] Despite such promising results, however, no researchers have demonstrated this functionality at room temperature or integrated these structures on Si substrates to pave the way for device trials.

Growth of thin films of BFO and the bottom electrode $SrRuO_3$ (SRO) were completed by pulsed laser deposition at 700 °C in 100 mTorr partial pressure of oxygen and cooled in 1 atm of oxygen. The films are grown on $SrTiO_3$ (STO) buffered Si (001) substrates. The substrates are produced by growing a high quality, strained 20 Å layer of STO on a Si

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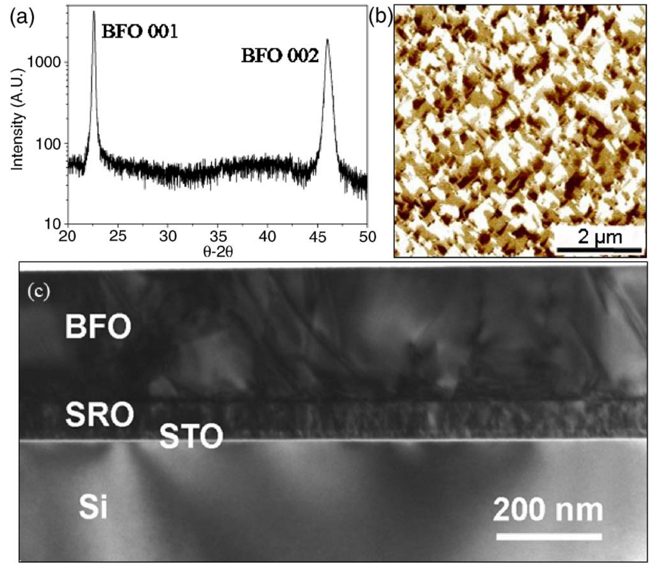

FIG. 1. (Color online) Structural analysis of typical $BiFeO_3$ films on Si (001) substrates. (a) X-ray diffraction. (b) In-plane piezoforce microscopy image shows the presence of all four in-plane polarization variants in these BFO films. (c) Transmission electron microscopy image.

(001) wafer using molecular beam epitaxy. X-ray diffraction analysis of a BFO/STO/Si (001) structure [Fig. 1(a)] shows high quality, single phase, 00*l* films of BFO. Previous studies have shown that the pseudocubic lattice of BFO is rotated by 45° in-plane relative to the underlying Si substrate leading to the following epitaxial relationships (using the pseudocubic notation for BFO): $[100]_{BFO} \| [110]_{Si}$, $[010]_{BFO} \| [-110]_{Si}$, and $[001]_{BFO} \| [001]_{Si}$.[10] The ferroelectric domain structure of the BFO/SRO/STO/Si (001) heterostructures was imaged using piezoforce microscopy (PFM). The in-plane PFM contrast [Fig. 1(b)] shows the presence of a four-variant "mosaic-like" domain structure. Because BFO is a rhombohedrally distorted perovskite ferroelectric material with the polarization lying along the pseudocubic ⟨111⟩ we can interpret the three colors seen in the image as arising from polarizations pointing along all of the possible [111]. The out-of-plane component of the image (not shown) is consistent with a fully downward polarized (pointing toward the bottom electrode) film. PFM imaging reveals that these films exhibit a mixture of all four-possible downward pointing, in-plane polarization variants which we call a "mosaic" domain structure. This complicated domain structure may be the result of the tensile stress due to thermal mismatch between Si ($\alpha_{Si} \sim 3 \times 10^{-6}\ \text{deg}^{-1}$) and many oxides ($\alpha_{BFO} \sim 1 \times 10^{-5}\ \text{deg}^{-1}$).[10] The large thermal stress during growth and cooling of the film may result in the formation of the highly complex domain structure observed in PFM which may help accommodate this stress. Additionally, previous reports have shown that similar films have good ferroelectric properties[10] and these samples behave similarly. *Z*-contrast transmission electron microscopy (TEM) images reveal that smooth interfaces extend through the films over large areas [Fig. 1(c)]. Furthermore we can identify the presence of both ferroelectric domain walls running throughout the BFO layer as well as dislocations in the BFO film arising from the mismatch between BFO and Si substrate. Despite the presence of defects in the films as imaged via TEM, both the SRO and BFO films are fully epitaxial on the STO buffer layer, which serves as an excellent template for the integration of complex oxides on Si wafers, and rotated by 45° from the underlying Si substrate.

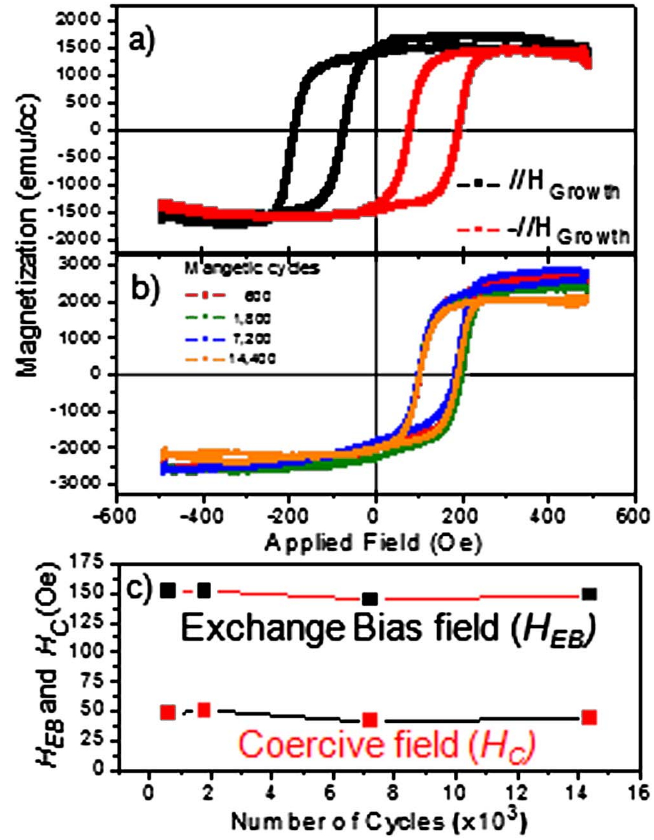

FIG. 2. (Color online) Typical magnetic properties for bilayer CoFe/BFO heterostructures. (a) Magnetization hysteresis loops reveal large negative exchange bias. (b) Repeated magnetic cycling results in very little change in the magnetic properties. (c) Exchange bias field and coercive field as a function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

Following the growth of the BFO/SRO/STO/Si (001) heterostructures the samples were transported to a vacuum sputtering system with a base pressure of 5×10^{-9} Torr, where the ferromagnetic metal—$Co_{0.9}Fe_{0.1}$ (CoFe) and capping (Ta) layers were grown. Growth of the CoFe films was completed in an applied magnetic field, $H_{growth} = 200$ Oe, which allows us to induce a uniaxial anisotropy in the films. Both bilayer CoFe (2.5 nm)/BFO (100–200 nm) and asymmetric spin valve structures CoFe (2.5 nm)/Cu (2 nm)/CoFe (5 nm)/BFO (100–200 nm) were grown and characterized. Previous analysis has demonstrated that there is no evidence for the oxidation of the CoFe films following the growth.[19]

Magnetic measurements were completed on both bilayer and spin valve structures using a loop tracer, vibrating sample magnetometer, and SQUID magnetometer. Magnetization hysteresis loops for the bilayer structures [Fig. 2(a)] reveal classic exchange bias behavior. We have measured negative exchange bias fields (H_{EB}) between 135–165 Oe in magnitude. Rotation of the sample and measurement antiparallel to the applied growth field direction reveals the corresponding shift of the hysteresis loop in the opposite direction and points to a ferromagnetic alignment between the pinned, uncompensated spins in BFO and the CoFe spins. Measurement along the direction perpendicular to the applied growth field directions reveals a hard axis for the sample. Additionally, exchange bias systems have traditionally suffered from something known as the training effect.[12] Training refers to a

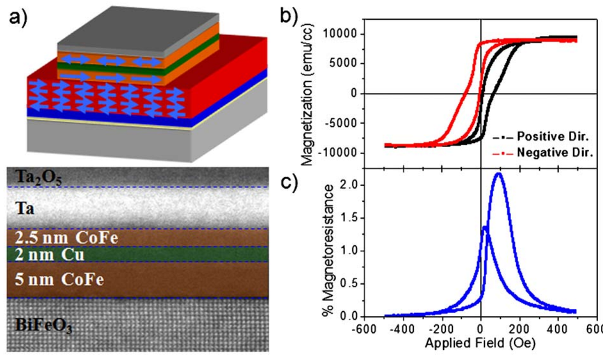

FIG. 3. (Color online) Spin valve structures based on CoFe/Cu/CoFe/BFO heterostructures. (a) Schematic illustration and scanning transmission electron microscopy image (b) Magnetic hysteresis loops of spin valve structures. (c) Current-in-plane magnetoresistance measurements.

systematic decrease in the magnitude of H_{EB} with repeated magnetic hysteresis often within the first few magnetic cycles. We have completed over 14 000 magnetic cycles on our bilayer structures and have observed very little change in the magnetic properties. Figure 2(b) shows snap shots of magnetic hysteresis loops taken after various lengths of time (measurements were completed antiparallel to the applied growth field direction). In all cases the shape and shift of the magnetic hysteresis loop remain nearly identical. Both the magnitudes of H_{EB} and the coercive field (H_C), defined as the width of the hysteresis loop a zero magnetization divided by 2, are found to be nearly constant even after 14 000 magnetic cycles [Fig. 2(c)]. This analysis points to the strong nature of the coupling between the BFO and CoFe layers and the robust nature of the anisotropy in this system.

The asymmetric spin valve structures studied consist of the following: (5 nm)Ta/(2.5 nm)CoFe/(2 nm)Cu/(5 nm)CoFe/(150 nm)BFO/(50 nm)SRO/(2 nm)STO/Si (001) [Fig. 3(a)]. Through the use of scanning transmission electron microscopy (STEM) we can investigate the high quality nature of the heterostructure. The interfaces between both the BFO and the CoFe and between the various metallic species (Cu and CoFe) are very smooth and show very little interdiffusion. Metallic layers (Cu and CoFe) appear to be either amorphous or nanocrystalline. This, in turn, provides us with an excellent system to probe the possibility for creating spin valve devices with multiferroic antiferromagnets. Magnetic measurements reveal that there are two switching events coming form the thin and thick layers of CoFe as well as a negative shift of the hysteresis loop by 40–50 Oe [Fig. 3(b)]. The magnitude of this shift is typical for single layer 5 nm CoFe films grown on BFO. A maximum current-in-plane magnetoresistance of ~2.25% was measured in these spin valve structures; however, the double peak structure of the magnetoresistance would likely make this system unsuitable for devices. Previous studies[17] suggest that the growth of a top BFO layer might lead to better performance in such structures, but the high temperature epitaxial growth of BFO films is unlikely on metallic layers and will, therefore, limit this undertaking.

This work demonstrates that exchange bias with multiferroic materials and the construction of simple device structures, such as spin valves, can be integrated with Si. The next step is to determine the best process to achieve electrically tunable properties in such systems. Previous work has demonstrated the capability to manipulate the magnetic domain structure of BFO using applied electric fields. The combination of this capability with traditional exchange interactions between an antiferromagnet and ferromagnet can serve as a pathway to functionality and device capabilities. Currently research is underway to investigate the possibility of dynamically switching and controlling the nature of the coupled ferromagnet by applying electric fields to the underlying BFO film.

In conclusion, bilayer CoFe/BFO and asymmetric spin valve CoFe/Cu/CoFe/BFO structures have been produced in which the application of an applied magnetic field during the growth of the ferromagnetic films results in the formation of exchange anisotropy on Si substrates. Exchange bias fields over 150 Oe in magnitude (the largest to date) have been observed and no reduction in the magnitude of the exchange bias has been observed with over 14 000 magnetic cycles at room temperature. Additionally, spin valve structures have also been shown to exhibit ~2.25% magnetoresistance (the largest to date in a BFO based structure) at room temperature. Finally, these results are promising for the continued study of BFO and multiferroic based magnetic devices and for the eventual production of an electrically tunable magnetic device.

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[1]C. Binek and B. Doudin, J. Phys.: Condens. Matter **17**, L39 (2005).
[2]M. Fiebig, J. Phys. D **38**, R123 (2005).
[3]N. A. Spaldin and M. Fiebig, Science **309**, 391 (2005).
[4]W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature (London) **442**, 759 (2006).
[5]R. Ramesh and N. A. Spaldin, Nat. Mater. **6**, 21 (2007).
[6]J. Wang, J. B. Neaton, H. Zheng, V. Nagaranjan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Science **299**, 1719 (2003).
[7]J. R. Teague and R. Gerson, Solid State Commun. **8**, 1073 (1970).
[8]S. V. Kiselev, R. P. Ozerov, and G. S. Zhdanov, Sov. Phys. Dokl. **7**, 742 (1963).
[9]T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M. P. Cruz, Y.-H. Chu, C. Ederer, N. A. Spaldin, R. R. Das, D. M. Kim, S. H. Baek, C. B. Eom, and R. Ramesh, Nat. Mater. **5**, 823 (2006).
[10]J. Wang, H. Zheng, Z. Ma, S. Prasertchoung, M. Wuttig, R. Droopad, J. Yu, K. Eisenbeiser, and R. Ramesh, Appl. Phys. Lett. **85**, 2574 (2004).
[11]W. H. Meiklejohn and C. P. Bean, Phys. Rev. **102**, 1413 (1956).
[12]J. Nogués and I. K. Schuller, J. Magn. Magn. Mater. **192**, 203 (1999).
[13]J. Dho and M. G. Blamire, Appl. Phys. Lett. **87**, 252504 (2005).
[14]X. Marti, F. Sánchez, D. Hrabovsky, L. Fàbrega, A. Ruyter, and J. Fontcuberta, J. Appl. Phys. **99**, 08P302 (2006).
[15]J. Dho, X. Qi, H. Kim, J. L. MacManus-Driscoll, and M. G. Blamire, Adv. Mater. (Weinheim, Ger.) **18**, 1445 (2006).
[16]H. Béa, S. Fusil, M. Bibes, S. Cherifi, A. Locatelli, B. Warot-Fonrose, G. Herranz, C. Deranlot, E. Jacquet, K. Bousehouane, and A. Barthélémy, Appl. Phys. Lett. **89**, 242114 (2006).
[17]X. Qi, H. Kim, and M. G. Blamire, Philos. Mag. Lett. **87**, 175 (2007).
[18]V. Laukhin, V. Skumryev, X. Martí, D. Hrabovsky, F. Sánchez, M. V. García-Cuenca, C. Ferrater, M. Varela, U. Lünders, J. F. Bobo, and J. Fontcuberta, Phys. Rev. Lett. **97**, 227201 (2006).
[19]Y.-H. Chu, L. W. Martin, M. B. Holcomb, S.-J. Han, Q. Zhan, P.-L. Yang, K. Lee, A. Fraile-Rodriquez, A. Scholl, S. X. Wang, Z. Q. Qiu, and R. Ramesh, "Controlling exchange interactions with a magnetoelectric multiferroic" Nat. Mater. (submitted).