Piezoelectrically-Enhanced Exchange Bias in Multiferroic Heterostructures

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Piezoelectrically-Enhanced Exchange Bias in Multiferroic Heterostructures.

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We propose a multiferroic tri-layer structure in which two magnetic layers are epitaxially constrained on a bottom piezoelectric substrate. In this structure, the exchange bias is observed due to interface spin coupling between the two magnetic layers. We also show that the exchange bias is significantly modulated by the application of an external electric field at room temperature, and the modulation in exchange bias is reproducible and reversible.

Spintronics is the area that studies the spin and charge degrees of freedom.[1] Most solid-state spintronic devices utilize artificially-constructed heterointerfaces and thus a control of interfacial spins is of scientific importance.[2] Exchange bias is an effect of spin coupling that relies on the interface magnetism across the ferromagnetic and antiferromagnetic or two ferromagnetic interfaces.[3] The spin coupling at the interface tends to keep spins in adjacent layers parallel to each other, resulting in a shift of the magnetic hysteresis loop.

Multiferroics are spintronic materials that exhibit two or more ferroic properties: ferromagnetism, ferroelectricity and/or ferroelasticity. This definition is often extended to antiferromagnetism, because the ferroelectric antiferromagnets are more abundant.[4-6] They have been a subject of intensive scientific investigation due to the advantage of multiple degrees of freedom. In multiferroics, the ferroelectric polarization can be induced or modified by the magnetic order[7] and an external electric field can induce changes in magnetization.[8] However, there are few multiferroic systems that exist in nature at room temperature because transition metal d electrons reduce the tendency of an off-centering ferroelectric distortion.[4,9] Moreover, the existing room temperature multiferroics show only weak magnetoelectric (ME) effects. The rareness of room-temperature multiferroics[5] and the weak ME coupling effects have led many researchers to combine ferroelectric (FE) materials with ferromagnetic/antiferromagnetic (FM/AFM) phases at microscopic or nanoscopic scales such as, nanoparticulate composite films, multilayered thin films, and nanopillar or columnar film structures.[10-15] Intensive research on the electric control of exchange bias has also been focused on the multiferroic heterostructures where individual multiferroic and magnetic layers are coupled to electrically enhance the exchange bias via interfacial spin interaction. For example, a combination of multiferroic hexagonal manganites, such as $YMnO_3$[16] and $LuMnO_3$[17], (FE/AFM) and Py (FM) layers was designed to electrically control the exchange bias and the magnetotransport properties. The field-effect device with multiferroic $BiFeO_3$ (AFM/FE) and $La_{0.7}Sr_{0.3}MnO_3$ (FM) layers[18] were also fabricated to achieve the reversible electric control of exchange bias. In the above multiferroic heterostructures, the electric field can be used to tune the exchange-bias coupling in AFM/FM heterostructures and eventually enable the magnetic switching of the FM layer. Although this is a significant progress, the ME coupling is still weak and practicable mostly in the low temperature region. Recently, a magnetoelectric Cr_2O_3 bulk[19,20] with ferromagnetic Co/Pd multilayer films was refocused as a candidate for reversible electric control of magnetism at room temperature, thanks to the roughness-insensitive ferromagnetic spin state at the surface of Cr_2O_3.[21]

Here, we propose a piezoelectrically-enhanced exchange bias in the multiferroic tri-layer structure where two magnetic layers are epitaxially constrained to the bottom piezoelectric substrate. In this structure, the electric control of the exchange bias is possible at room-temperature and significantly enhanced by in-plane compressive strain that stems from the piezoelectric substrate.

Figure 1(a) schematically depicts the asymmetric tri-layer structure in which $NiFe_2O_4$ (NFO) and $CoFe_2O_4$ (CFO) are employed to accommodate the exchange bias effect. NFO has a very small coercive field.[22] On the other hand, CFO has a relatively high coercive field of ~5 kOe and strongly resists demagnetization.[23] Therefore, CFO is a harder magnet than NFO and will act as a pinning layer in this structure. Due to this large difference in magnetic coercivity, a strong exchange bias effect is expected at the NFO-CFO interface. The $0.72Pb(Mg_{1/3}Nb_{2/3})O_3$ – $0.28PbTiO_3$ (PMN-PT) substrate is adapted as a bottom electrode by virtue of a giant piezoelectric response (1700 pC /N)[24] at this stoichiometric composition. The PMN-PT substrate also brings compressive strain into the upper ferrite layer due to their lattice mismatch. According to recent results,[25,26] the epitaxial strain incorporated in the thin films can favor one easy axis by the modification of magneto-crystalline anisotropy. For NFO and CFO epitaxial films, compressive strain favors a magnetic easy-axis in the in-plane direction while tensile strain favors it in the out-of-plane direction. Accordingly, the magnetic easy axis in the NFO/CFO layers can be shifted into the in-plane orientation by utilizing the compressive strain arising from the PMN-PT substrate. As a result, one would expect the magnetic spins in both layers to be coherently aligned along the in-plane direction and hence the spin interaction at the NFO-CFO interface can be effectively improved.

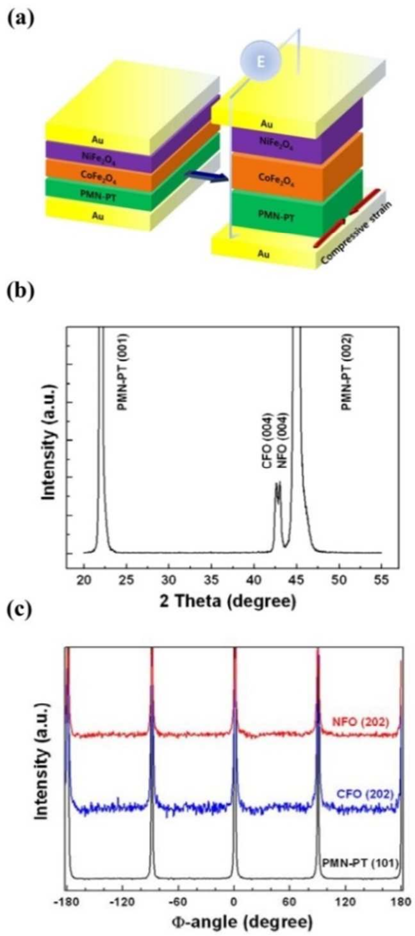

Fig. 1 (a) A schematic drawing of magnetic/piezoelectric tri-layer structure in which the exchange bias is controlled by the electric field. It illustrates that the piezoelectric substrate gives rise to compressive strain on the upper magnetic layers when applying an external electric field. (b) θ-2θ X-ray diffraction (XRD) pattern of the 20-nm-thick NFO and CFO thin films grown on a piezoelectric (001) PMN-PT substrate. (c) Phi (φ)-scan diffraction patterns of the tri-layer structure measured on (202) planes for NFO and CFO, (101) plane for PMN-PT.

20-nm-thick NFO and 20-nm-thick CFO layers were grown on a 5 mm by 5mm PMN-PT (001) substrate using pulsed laser deposition with a KrF excimer laser (wavelength 248 nm; Lambda Physik). The deposition was carried out at 700 ° C under partial O_2 pressure of 100 mTorr. The sample was in-situ post-annealed after the growth for 30 minutes. The laser energy density was ~1.5 J cm^{-2} and the repetition rate was 3 Hz. Sintered ceramic pellets of NFO and CFO were used as target sources for the PLD deposition. Non-magnetic Au films were coated on both the top and the bottom surfaces by employing a magnetron DC sputter. Figure 1(b) shows a typical θ-2θ x-ray diffraction pattern of the tri-layer structure indicating that the NFO layer is preferentially grown along (001). In order to examine the in-plane epitaxy and crystallographic relationship between the substrate and the ferrite films, we measured phi (φ)-scan spectrums of the tri-layer structure. These patterns were obtained by keeping the Bragg angle at (202) for CFO and NFO and (101) for PMN-PT. The four peaks that are 90° apart occur at the same azimuthal phi-angles for both CFO, NFO and PMN-PT, demonstrating a coherent epitaxial growth on the (001) PMN-PT substrate.

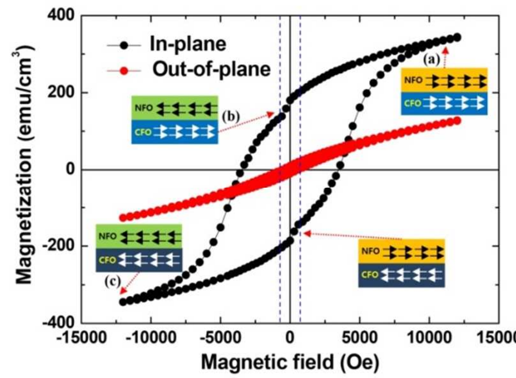

Fig. 2 Room-temperature magnetization-field hysteresis curves of the two magnetic layers measured along in-plane and out-of-plane directions. It shows the magnetic easy axis with in-plane direction. Abrupt change in magnetization near a zero magnetic field (blue dot-lines) arises from the rotation of spins in the NFO layer with keeping the spins in the CFO layer fixed. Schematic spin configurations for different states of a hysteresis are depicted in insets

To experimentally verify the effect of epitaxial strain on the magneto-crystalline anisotropy, we first examined the magnetization-field (M-H) hysteresis loop at room temperature along both in-plane and out-of-plane directions. As shown in Figure 2, the M-H hysteresis loop measured along the in-plane direction shows a nearly square-shaped saturated loop, while the loop measured along the out-of-plane exhibits a very slim and unsaturated loop. This indicates that the compressive strain from the PMN-PT substrate is likely to align the magnetic easy axis of the ferrites into the in-plane direction, in agreement with the previous results.[24,25] It is interesting to note that the hysteresis loop shows a rapid decrease in magnetization between -1 kOe and 1 kOe. Regarding to this phenomenon, the intuitive spin configurations are schematically shown as insets in Figure 2. The spins in both the NFO and the CFO layers lie parallel to each other at the interface (a). When the magnetic field is reversed, only the spins in the NFO layer start to rotate whereas the spins in the CFO layer remain fixed until the coercive field of the CFO is finally attained (b). As the magnetic field approaches the maximum, the magnetic spins in both the NFO and CFO layers are completely reversed keeping them parallel to each other again (c). Therefore, one can conclude that the steep incline near the origin in the hysteresis loop is attributed to the rotation of spins in the soft ferrite (NFO) layer.

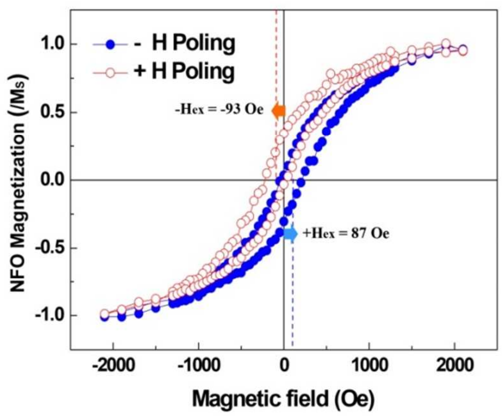

Fig. 3 Minor hysteresis loops extracted from the major hysteresis curve for magnetic fields in between +2 kOe and -2 kOe. The magnetization attributed to the CFO layer was subtracted from the data, and then normalized to the saturated magnetization. The magnetic shifts in these exchange biased loops are -93 Oe and +87 Oe, respectively, with respect to magnetic poling directions.

Figure 3 shows minor hysteresis loops of the NFO layer obtained at room temperature in the NFO/CFO/PMN-PT structure. For this measurement, the sample was initially magnetically poled along the in-plane direction up to 12.5 kOe, which is well above the coercive field of CFO. We then measured the hysteresis loop between -2 kOe and +2 kOe in order to isolate the NFO contribution from the major hysteresis loop (The minor hysteresis curve was obtained by subtracting the CFO moments from the raw data. Another CFO reference film with the same thickness on the PMN-PT substrate was used for this correction). In this field range, the magnetic spins in the NFO layer can be switched reversibly, whereas the others in the CFO layer keep frozen. Therefore, the CFO spins exert an additional torque on the NFO spins, trying to keep them in their original position. As a result, an extra magnetic field is required to overcome the microscopic torque and the coercive field in the NFO layer becomes higher. Conversely, the spins in the NFO layer are likely to return to the original state since the spin coupling with same direction is energetically more favorable. In this figure, the minor hysteresis loop shows a saturated shape with a very small coercive field, in comparison with typical hysteresis loops of NFO. Note that the exchange bias ($H_{ex,}$ shift of the magnetic hysteresis loop) is clearly seen with a shift of hysteresis loop as marked by red and blue dot-lines. The loop shifts are -93 Oe and 87 Oe with respect to positive and negative poling fields, respectively. This suggests that the spins in both layers strongly interact with each other at the interface, and the interaction is responsible for the exchange bias effect.

With the initial characterization of the minor hysteresis loops, we then studied the effect of an electric field on exchange bias. For this purpose, we measured the minor hysteresis loop under an electric-field and compared this with the hysteresis loop obtained without an electric field. The electric field was applied along the out-of-plane direction across the NFO/CFO/PMN-PT structure, which is perpendicular to the magnetic field direction. The electric-field-induced changes in the exchange bias are shown in Figure 4(a) and 4(b). Before applying the electric field, the minor hysteresis loop shows the shift to the left [Fig. 4(a)] or the right [Fig. 4(b)] due to the exchange bias coupling (black circles), depending on

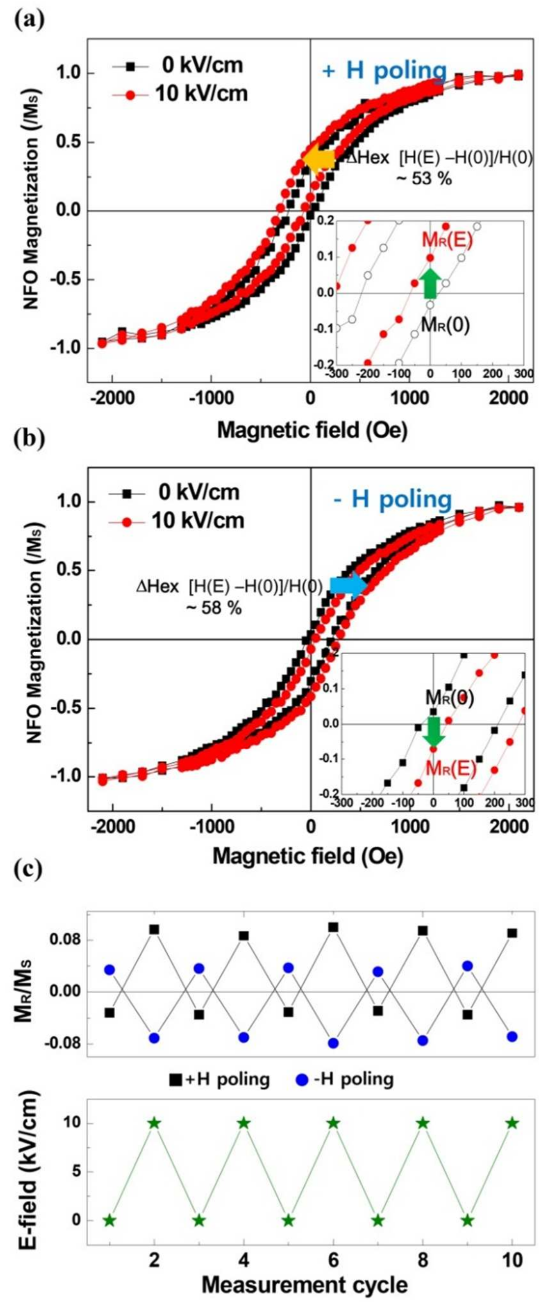

Fig. 4 The electric control of exchange bias in the NFO/CFO/PMN-PT tri-layer. The external electric field was applied with the out-of-plane direction which is perpendicular to the applied magnetic field direction. The exchange bias is significantly enhanced by the electric (E)-field of 10 kV/cm. Depending on the initial magnetic poling states, (a) positive poling and (b) negative poling of spins in the CFO layer, the hysteresis loop moves to the left (right) with ΔH_{ex} of ~53 % and ~58 % respectively. (c) Repeatable magnetization reversal as a function of measurement cycles, showing a reversible and reproducible control of exchange bias by the electric field.

the direction of the initial magnetic poling. By applying an electric field of 10 kV/cm, however, the hysteresis loop moves further to the left or right (red circles) of the 0 kV/cm loop with a significant additional change in the exchange bias and an enhancement of ~53% (~58%). Interestingly, the remnant magnetization (M_R) is electrically changed to a positive or negative branch with regard to the initial magnetic poling states in the CFO layer, as presented in the insets of Figure 4(a) and 4(b). In the case of the positive poling state, M_R in the negative branch is reversed under the electric field. Similarly, M_R in the positive branch is reversed by application of the same electric field in the negatively poled state, implying that the magnetic spins in the NFO layer are electrically controllable. Figure 4(c) shows a repetitive magnetization reversal of M_R in the NFO layer as a function of measurement cycle. Based on these results, we conclude that the exchange bias is considerably modulated by application of an electric field and the modulation is reproducible and reversible. The possible mechanism for the modulation is the piezoelectric strain incorporated in the CFO layer. Earlier work in our group shows that the electric field applied to the PMN-PT substrate along the c-axis produces compressive strain to the CFO films in the CFO/PMN-PT heterostructure.[22] In this study, the in-plane lattice parameter of the CFO film on the PMN-PT substrate is reduced with the electric-field strength as the applied electric field induces a compressive strain in the PMN-PT substrate along the in-plane direction. Accordingly, the piezoelectric strain generated from the PMN-PT substrate can be transferred to the upper CFO layer and the compressive strain incorporated in the CFO layer is likely to enhance the NFO-CFO spin coupling at the interface by fixing the CFO spins more strongly. As a result, much stronger magnetic field is required to entirely reverse the NFO spins, eventually leading to the enhancement of exchange bias. The value of enhancement in exchange bias was estimated using the following relation: $\Delta H_{ex} = [H(E) - H(0)]/H(0)$, where H(E) and H(0), respectively, are the exchange bias at the electric-field strength and under a zero-field condition. ΔH_{ex} of ~53 % and ~58 % were estimated for positive and negative poling, respectively.

Conclusions

We have presented a NFO/CFO/PMN-PT tri-layer structure in which an exchange bias is observed due to the spin coupling at the film interface. When the electric field is applied, the exchange bias is significantly enhanced by the piezoelectric compressive strain stemming from the PMN-PT substrate. Moreover, the modulation in the exchange bias is reversible and reproducible at room temperature, promising a new paradigm in next generation memory devices.

Notes and references

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The exchange bias is significantly enhanced by the piezoelectric compressive strain stemming from the PMN-PT substrate when applying the electric field, leading to reversible magnetic switches.