Title
Overcoming the limits of exchange bias effect in the magnetic thin films by introducing nanostructured internal interfaces

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Title : Overcoming the Limits of Exchange Bias Effect with Nanostructured Internal Interfaces between FM and AFM

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Abstract

Single layer film with 3-dimensional distribution of internal interfaces between ferromagnet and antiferromagnet could be achieved through the inhomogeneous distribution of oxygen atoms within the ferromagnetic transition metal films. Exchange bias properties of this phase nano-mixture film including both exchange and superexchange couplings in the layer were investigated under various conditions. Single magnetic nanostructured film exhibited large exchange bias field regardless of the layer thickness, which violates the known relationship of inverse proportionality between the exchange bias field and the thickness of the magnetic layer in conventional FM/AFM bilayer systems. Furthermore, it was found that the exchange bias can be set in any direction between in-plane and out-of-plane directions, overcoming the influence of magnetic shape anisotropy of thin film structure. In addition, a limitation of phase mixture film which has low blocking temperature is overcame with bottom of AFM layer. Thus, the present work demonstrates that the proper application of nanostructure can overcome the limit of conventional materials to extend the potential applications of exchange bias effect.

Introduction

Strong inter-atomic coupling at the interface between ferromagnetic (FM) and antiferromagntic (AFM) materials causes the hysteresis loops of FM to shift along the field axis breaking the symmetry of the hysteresis response, which is called exchange bias effect.[1] The discovery of exchange bias effect itself by Meiklejohn and Bean was with CoO/Co nanoparticles,[2] and it has been heavily studied and found in various systems with FM/AFM interfaces.[3,4,5,6,7] With the development of thin film technologies, among the many exchange bias systems, Co and CoO thin film layers have continued to be an exemplary system with their well-known large coercivity and exchange bias.[1,8] Furthermore, the Neel temperature of CoO is close to room temperature that provides experimental convenience to study the temperature dependence of exchange bias effect.[9] However, it also present a limitation for application at room temperature due to the low Neel temperature of CoO. Addition of Ni in the places of Co to form $Co_{1-x}Ni_xO$ is known to increase the Neel temperature in proportion to the Ni concentration, x.[10] In the present work, we use $Co_{0.7}Ni_{0.3}O$ for AFM, which has Neel temperature approximately 360 K [1,10] so that the exchange bias at room temperature can be investigated.

In general, the amount of shift is represented with the exchange bias field (H_E), and is correlated with the amount of uncompensated interfacial spins on the AFM interface.[11] Through the more than 50 years of study, research on the exchange bias (EB) effect of bilayers of FM and AFM has made considerably progresses driven by not only scientific but also industrial interests with wide uses in many devices.[12],[13],[14],[15],[16],[17] Additionally, the ability to control the material characteristics with external environment factors has always been a major spotlight issue that many researches has been trying to expand this capacity to control these property which is expected to add rich functionalities for the development of especially spintronics device applications involving both ferromagnetic and antiferromagnetic materials.[18,19] ~~However, despite many efforts, it still have several limitations to use application devices.~~

Being the interface effect in its nature, EB effect is known to be inversely proportional to the thickness of FM in the bilayers, which impose the limit on the thickness of exchange biased FM with a sufficiently large H_E.[11] In detail, H_E follows this simplified equation; $H_E \propto \frac{1}{t_{FM} M_{FM}}$, where t_{FM} is thickness of FM and M_{FM} is saturation magnetization of FM material. And, anisotropy of the ferromagnetic film is usually takes either in-plane or out-of-plane directions as its easy axis, so that exchange bias anisotropy shows different behaviors depending on the direction although AFM spins are aligned by the applied field during the 'field cooling' procedure.[20],[21] Therefore, with the layered structure in the exchange bias system, these obstacles still exist, thereby much effort in research has been trying to overcome them. We hereby present the modified interface structure between FM and AFM system to lift off the limitations of conventional flat two-dimensional interfaces in the thin film layers and possibly extend the applications of the exchange bias effect.

In the present work, a single layer film was fabricated by reactive magnetron sputtering in a controlled atmosphere, where oxygen gas concentration was set for incomplete oxidation of deposited metallic $Co_{0.7}Ni_{0.3}$ layer resulting in the two phase mixture of $Co_{0.7}Ni_{0.3}$ and $Co_{0.7}Ni_{0.3}O$ with controlled volume ratio within the film. In this phase mixture film, we have found notable differences compared with conventional FM/AFM bilayers and confirmed the removal of limitations commonly found in the bilayers through the use of single layered phase mixture film with nano-crystalline grain structure. In phase mixture film, we also demonstrated that the magnitude of exchange bias effect is significantly increased without the limit of FM thickness dependence. Therefore, the saturation magnetization can be independently manipulated in the device application without an accompanied change of exchange bias field (H_E) and coercivity (H_C). Furthermore, it was found that the exchange bias can be established (set) along any arbitrary direction between in-plane (IP) and out-of-plane (OOP) directions as desired. However, the blocking temperature of the phase mixture single layer film was found to be much lower than T_N of bulk $Co_{0.7}Ni_{0.3}O$ due to the nanometer scale grains sizes[22], hence the exchange bias effect is not measured at room temperature. Thus, an AFM (fully oxidized $Co_{0.7}Ni_{0.3}O$) layer was inserted at the bottom of phase mixture layer film in order to improve the limitation of phase mixture film in exchange bias effect. This is because the blocking temperature of $Co_{0.7}Ni_{0.3}O$ (AFM) film is nearly same with the Neel temperature of the bulk and exchange bias can be exhibited at room temperature. In bilayer structure with phase mixture for FM layer, we confirmed that large exchange bias also shows at room temperature simultaneously with overcoming the limitations which is compared with conventional bilayer film with permalloy ($Ni_{0.8}Fe_{0.2}$) in exchange bias system.

Sample fabrication and experimental methods

The film was fabricated by using reactive sputtering of the $Co_{0.7}Ni_{0.3}$ target in an argon and oxygen atmosphere of 2 mTorr total pressure. Oxygen partial pressure needed to be carefully controlled during the deposition to achieve an incomplete oxidation of deposited metal layer resulting in the mixture of $Co_{0.7}Ni_{0.3}$ and $Co_{0.7}Ni_{0.3}O$ (hereafter, CoNi-CoNiO) phases whose volume ratio is decided by the oxygen partial pressure during the deposition. The single layer film consisting of 50 % metal and 50 % metal oxide was selected to maximize the density of phase interface, which was confirmed with the magnitude of saturation magnetization as measured by Quantum Design Magnetic Property Measurement System (MPMS). Bilayers films of AFM ($Co_{0.7}Ni_{0.3}O$, 20 nm)/FM (*t* nm)/SiO_2 (3 nm) stacks were also prepared in order to compare as well as to modify the exchange bias effects. Permalloy (Py, $Fe_{0.2}Ni_{0.8}$) and mixture phase (CoNi-CoNiO) was used as FM material and FM thickness (*t*) was varied from 2 to 10 nm (*t* =

2, 3, 5 and 10 nm). [Brief summary of internal structure of the CoNi-CoNiO with reference to your Nanoscale paper]

Hysteresis loops were measured after field cooling from 380 K to 10 K in the applied field of 5 T along the measurement directions. In order to eliminate the training effect, field sweeping from 5 T to -5 T was carried out 10 times before starting the measurements of M-H loops at various temperatures ranging from 10 K to 370 K.

Results and Discussions

Overcoming the limits of exchange bias effects in conventional 2D interface system.

It is well known that one of the major factors to determine the magnitude of exchange bias effect in the conventional magnetic thin film is the thickness of the ferromagnetic layer coupled to the neighboring antiferromagnetic layer (as formulated by the inverse proportionality). In order to confirm the exchange bias effect of phase mixture single layer film itself, we measured hysteresis loops of the film. First, we confirmed large magnitude exchange bias field in the single layer film itself. More specifically, we carried out the measurements to specifically obtain the dependence of exchange bias effect on the thickness of the film. Prepared phase mixture film consisted of approximately equal ratio of FM and AFM phases with two different thicknesses of 5 and 10 nm. They were confirmed to be nearly identical in the structural and magnetic characteristics except for the thicknesses. In the general layered thin film bilayers, exchange bias field is inversely proportional to the FM thickness.[23] However, as shown in figure 1a, H_E of the two films in the present study remained essentially the same ; H_E's of both films were 1.75 kOe. Hence, the general relationship between H_E and FM thickness does not apply in the single layer phase mixture films. This is understood to originate from the 3-dimensional internal interface nanostructure within the entire body of the layer, which essentially keeps all the FM component in the film exchange coupled to the nearby AFM component within the film regardless of the total thickness of the mixture layer.[24] Therefore, FM layer thickness dependence in the exchange bias bilayer system could be lifted through the use of nanostructured phase mixture layer.

Furthermore, exchange bias of layered thin film system usually exhibits preferred bias direction along the easy axis of FM layer which is typically fixed to either in-plane or out-of-plane direction depending on the magnetic anisotropy of thin film. Figure 1b shows the exchange biased hystereses at 10 K measured with the phase mixture film with 40 % oxidation and 10 nm thickness after it was field cooled in various directions including both in-plane (0 degree) and out of plane (90 degree) directions. It is remarkably noted that the exchange bias could be set along any directions as confirmed by the nearly the same profiles of all the M-H loops in figure 1b, which is in quite contrast to the behavior of conventional FM/AFM film system[25,26] in exchange bias. The H_E and H_C of the film for IP is 1.7 kOe and 9.1 kOe, respectively, and the H_E and H_C of the film for OOP is 1.4 kOe and 10.0 kOe at 10 K. This result can be interpreted that shape anisotropy is nearly suppressed even if the hysteresis loops shows gradually change in direction because of remaining shape anisotropy caused by extremely thin thickness with 10 nm. This is because the nano-size grains of FM and AFM are randomly distributed in single layer film and interface between FM and AFM which is caused exchange bias effect is constructed with 3D structure like bulk as opposed to bilayer, 2D structure. Therefore, FM spins can be coupled with aligned AFM spins regardless of direction and exchange bias is implemented in field cooling directions. Furthermore, temperature tendency of H_E depending on field direction also indicates same behaviors which are gradually decrease with temperature as seen in figure 1c. Therefore, we can establish large exchange bias field regardless of thickness and direction of the phase mixture single layer film at low temperature.

Phase mixture film has large magnitude of both H_E and H_C at low temperature. The exchange anisotropy only appears to 220 K and vanishes above 240 K, which is so-called blocking temperature (T_B), where it is lower than the Neel temperature of the bulk $Co_{0.7}Ni_{0.3}O$ (T_N ~360K). As same with previous study,[22, 24] we also observed that phase mixture film has low blocking temperature because it is consist of phases with a few nano-meter grain size. Therefore, we prepared fully oxidized Co0.7$Ni_{0.3}O$ (AFM) layer at the bottom of phase mixture film, which can be expected to implement exchange bias at room temperature by fastening disordered AFM spins in phase mixture,

Exchange bias behaviors depending on FM materials and film structure

One of major characteristics of the phase mixture film is the significantly increased magnitude of the exchange bias field as shown in figure 1, and the H_E of phase mixture single layer film with 5 nm shows 1.75 kOe at 10 K. Despite large H_E, the film has a thermal limitation to use for devices at the room temperature because it has low blocking temperature compared with bulk $Co_{0.7}Ni_{0.3}O$ (AFM) due to nano-size grain of phases as shown in blue line of figure 2. To improve the thermal limitation, AFM layer is deposited below phase mixture layer to fasten disordered AFM spins within phase mixture film at the interface. Consequently, exchange bias effect is held up to 350 K in AFM/Mixture (5nm) bilayers film, which is different result from phase mixture single layer film. In other words, we slightly overcome the thermal limitation of the mixture single layer film in exchange bias effect, which shows 420 Oe due to uncompensated spins of AFM at the interface between phase mixture layer and AFM layer at room temperature. In addition, exchange bias field is increase for 2.66 kOe at 10 K which is higher than phase mixture single layer, 1.75 kOe. In addition to film structure, in order to compare with H_E behaviors depending on FM materials, we also prepared bilayers film with Py for FM material. Exchange bias field of mixture and Py is 2.66 kOe and 0.27 kOe, respectively, at 10 K, which is 10 times larger. Also, at room temperature, H_E of mixture and Py is 0.42 kOe and 0.12 kOe, respectively. We confirmed that large exchange bias also exhibit not only low temperature but also room temperature in bilayers system with phase mixture compared with permalloy for FM material.

Furthermore, as generally known in permalloy bilayers film, exchange bias effect is maintained covering wide temperature range from low temperature and gradually decrease after 220 K due to thermal fluctuation of AFM spins near Neel temperature. However, bilayers film of phase mixture with FM material begin gradually decrease from 10 K to 175 K because of blocking temperature of phase mixture as shown in phase mixture single layer. From 175 K, the behavior of exchange bias effect shows same with Py bilayers.

From these results, we identify that thermal limitation of phase mixture film in exchange bias can be slightly lifted off through pinned layer of AFM on the bottom. Therefore, exchange bias exhibits above room temperature in mixture bilayers and the magnitude is much larger than Py bilayers film.

Thickness dependence of exchange bias with FM materials in bilayers system

Exchange bias field is directly affected by not only FM thickness but also saturation magnetization (M_S) of FM materials.[11] When we consider only saturation magnetization, magnetization of Py 3 nm film is almost same with mixture 5 nm film in square centimeter area. ($M_{S,Py}$: 840 emu/cm^3,

$M_{S,Mixture}$: 450 emu/cm^3) Therefore, this samples can be deserve to compare in exchange bias field in terms of saturation magnetization in exchange bias. In here, AFM layer is $Co_{0.7}Ni_{0.3}O$ with 20 nm. In the figure 3a, at 10 K, H_E of mixture film with 5 nm is 2.66 kOe which is 6 times larger than permalloy with 3 nm, 0.41 kOe. Also, in case of room temperature, the mixture even shows larger magnitude of H_E. ($H_{E,Mixture,300K}$: 0.42 kOe, $H_{E,Py,300K}$: 0.18 kOe). Therefore, we confirmed that phase mixture film shows large exchange anisotropy compared to the permalloy bilayers,though the samples have same saturation magnetization.

It is well known that exchange bias has linear relationship to t^{-1} in FM/AFM bilayers system. As shown in figure 3b-e, the relationship is perfectly consistent with permalloy bilayers across a wide range of temperature from 10 K to 300 K. However, this relationship deviates in phase mixture. (especially in thinner film.) It can be understood that internal interface between FM and AFM phases in phase mixture single layer film is dominant role in exchange bias effect at low temperature. On the other hand, this exchange coupling becomes weak with temperature increase due to low blocking temperature and thermal fluctuation, and interface between mixture and AFM layer is dominant role in exchange bias effect above blocking temperature.

Exchange bias with IP and OOP of bilayers with phase mixture for FM material

As shown in figure 1b and 1c, we already confirmed that the phase mixture single layer film overcomes direction dependence in exchange bias effect. This result is shown not only in the single layer film but also in bilayers of mixture/AFM. In general FM/AFM bilayer system, exchange bias field dominantly shows in preferred direction with FM anisotropy as shown in figure 4a. In-plane and out-of-plane are clearly distinguished easy and hard axis. However, in phase mixture bilayers film, shape anisotropy is suppressed same with the single layer as shown in figure 4b. There is a small gap (difference) in loop shape with azimuthal direction, and this is interpreted presence of in-plane magnetic anisotropy component in mixture/AFM film. These difference also appear in temperature dependence. Temperature trend of mixture bilayers in exchange bias with IP and OOP is slightly different from single layer film which shows similar behavior for direction. (It can be understood that $Co_{0.7}Ni_{0.3}O$ (AFM) has IP anisotropy due to thin film shape so that AFM spins are not aligned perfectly parallel for perpendicular.) However, note that direction dependence limitation in shape anisotropy also can be lifted off in bilayers system with phase mixture film, which shows large and similar magnitude both IP and OOP.

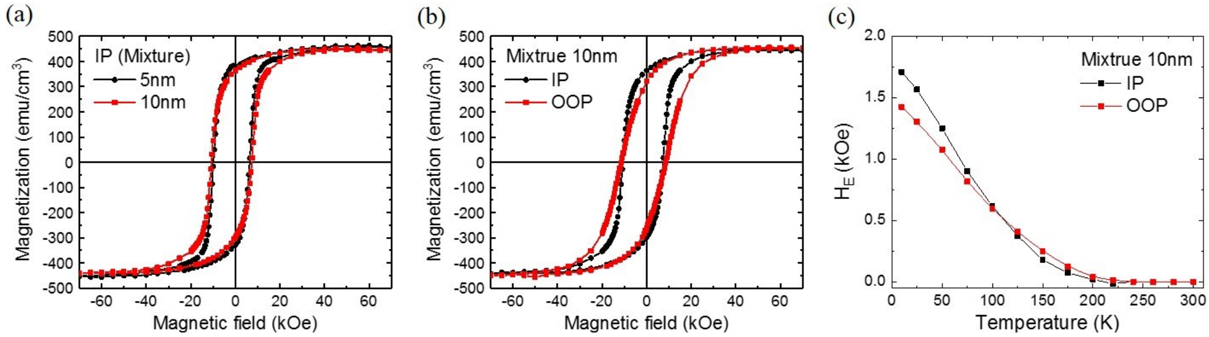
Conclusion

In summary, phase mixture single layer film shows maximized exchange bias effect and thickness and direction limitations in exchange bias effect can be lifted off in the film owing to 3-dimensional interface structure. In phase mixture film, interface density is equal regardless of thickness so that exchange bias field which is caused by interface between FM and AFM shows almost same magnitude without reference to thickness of the films. In addition, exchange anisotropy exhibits in all azimuthal direction, which is opposite to general exchange bias system. Furthermore, the limitation of phase mixture film which is low blocking temperature caused by nano-size grains is overcome by preparing AFM layer on the bottom of phase mixture film. Therefore, we suppose that phase mixture provides possibility of facility in application such as magnetic recording and storage devices by overcoming limitations in exchange bias effect.

Acknowledgements

Figures

Figure 1



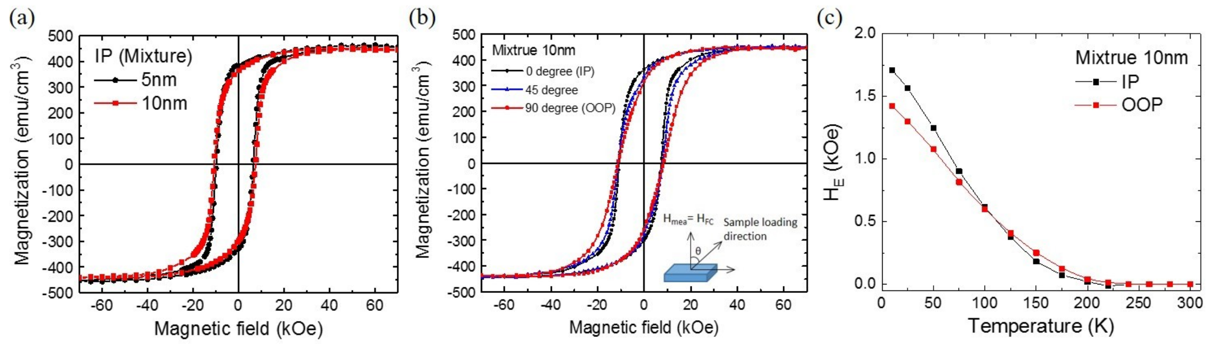


Figure 1. Hysteresis loops of phase mixture single layer films of (a) 5 and 10 nm thicknesses measured with applied field along an in-plane direction, and (b) direction dependence with 10 nm thickness (c) temperature dependence of exchange bias field depending on direction with 10 nm.

Figure 2

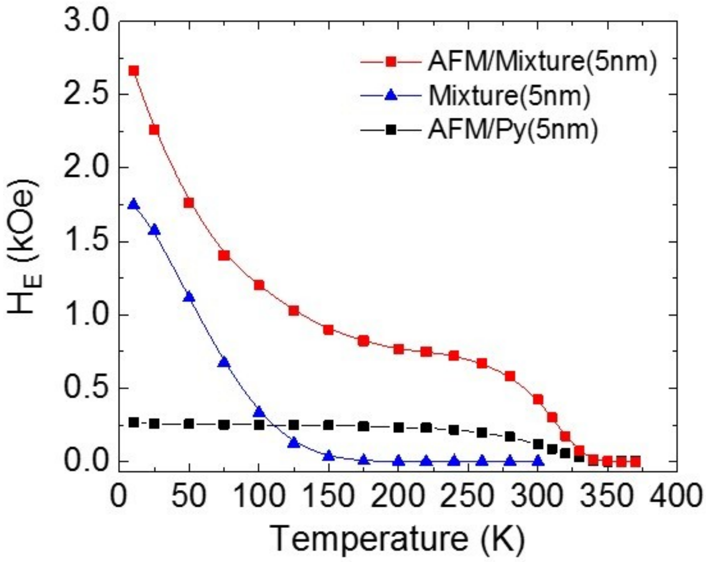


Figure 2. Temperature dependence of exchange bias field depending on FM materials (mixture and permalloy) and film structure (single and bi-layer).

Figure 3

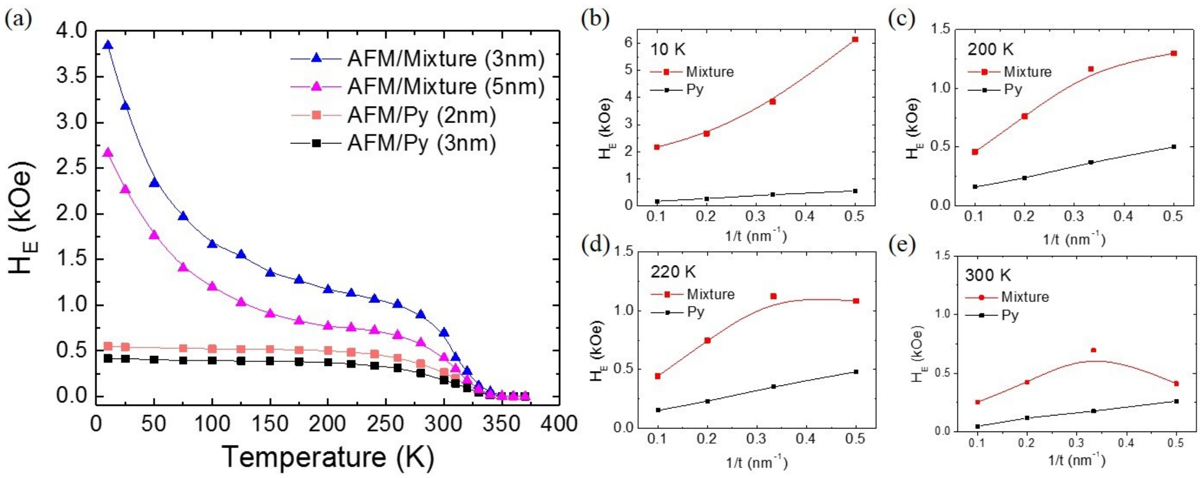
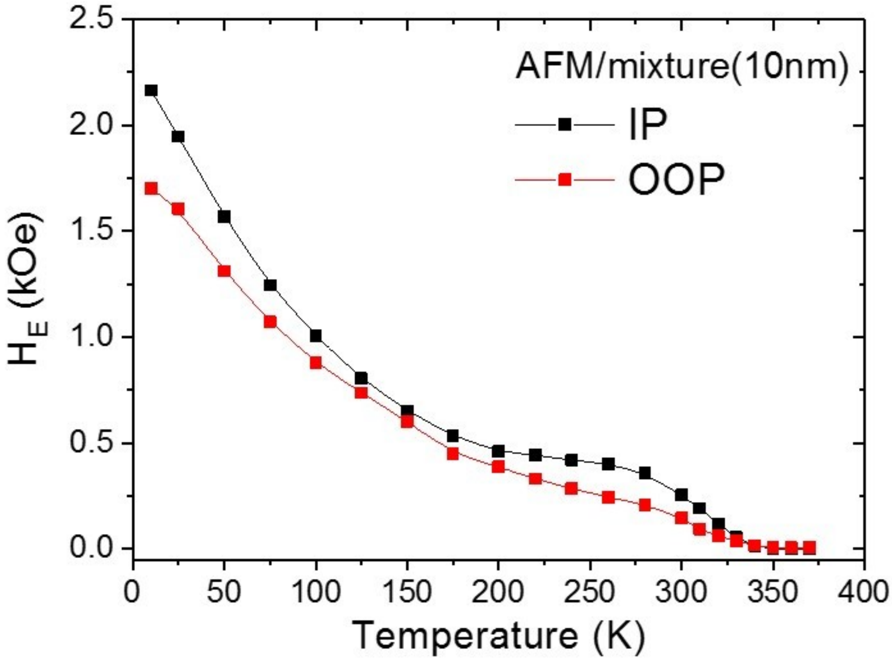


Figure 3. (a) Temperature dependence of exchange bias with various FM thickness. (b)-(e) thickness dependence of exchange bias effect depending on FM materials with temperature (10, 200, 220 and 300 K).

Figure 4



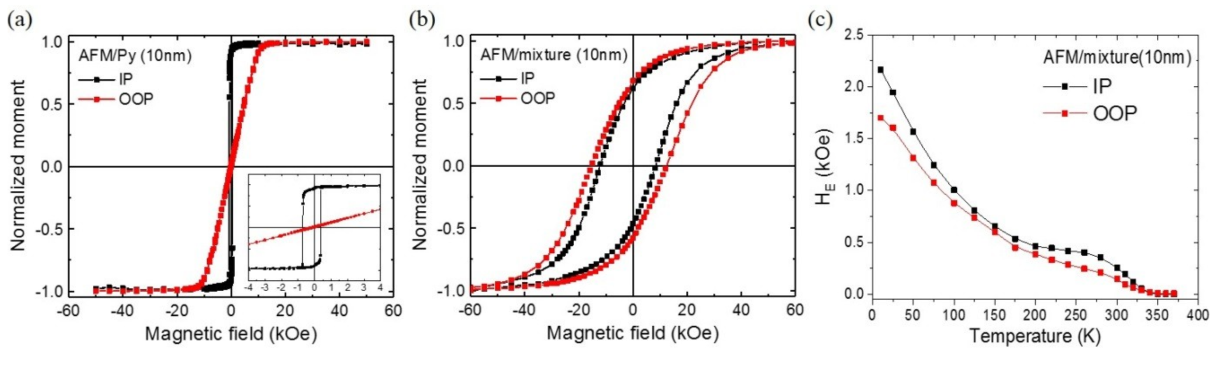


Figure 4. Exchange bias effect of direction dependence with (a) AFM ($Co_{0.7}Ni_{0.3}O$, 20nm) / Py (10nm) and (b) AFM ($Co_{0.7}Ni_{0.3}O$, 20nm) / Mixture

(10nm). (3) Temperature dependence of exchange bias effects after pinning the AFM ($Co_{0.7}Ni_{0.3}O$, 20nm) / mixture (10 nm) along the two different directions.

References

[1] J. Nogues, et. al. Exchange bias. J. Magn. Magn. Mater. 192 (1999)

[2] W. H. Meiklejohn, et. al. New magnetic anisotropy. Phys. Rev. 102 (1956)

[3] D. L. Peng, et. al. Magnetic properties of monodispersed Co/CoO clusters. Phys. Rev. B 61 (2000)

[4] F. Luis, et. al. Enhancement of the magnetic anisotropy of nanometer-sized Co clusters. Phys. Rev. B 65 (2002)

[5] R. L. Stamps, et. al. Application to Co/CoO Phys. Rev. B 54 (1996)

[6] T. Gredig, et. al. Magnetization reversal in exchange biased Co/CoO probed with anisotropic magnetoresistance. J. Appl. Phys. 91 (2002)

[7] R. Wu, et. al. Temperature dependence of exchnage bias and tranining effect in Co_CoO film with induced uniaxial anisotropy. J. Phys. D 48 (2015)

[8] F. Radu, et. al. Interfacial domain formation during magnetization reversal in exchange-biased CoO/Co bilayers. Phys. Rev. B 67 (2003)

[9] P. J. van der Zaag, et. al. Difference between blocking and neel temperatures in the exchange biased Fe3O4/CoO system. Phys. Rev. Lett. 84 (2000)

[10] M. J. Carey, et. al. Exchange anisotropy in coupled films of Ni81Fe19 with NiO and CoxNi1-xO. Appl. Phys. Lett. 60, 3060 (1992)

[11] A. E. Berkowitz, et. al. Exchange anisotropy. Magn. Magn. Mater. 200 (1999)

[12] K. Takano, et. al. Interfacial uncompensated antiferromagnetic spins:. Phys. Rev. Lett. 79 (1997).

[13] A. Hoffmann, et. al. Tailoring the exchange bias via shape anisotropy in ferromagnetic/antiferromagnetic exchange-coupled systems. Phys. Rev. B 67, 220406(R) (2003).

[14] V. Skumryev, et. al. Beating the superparamagnetic limit with exchange bias. Nature 423 (2003)

[15] H. Kanai, et. al. Spin-valve read heads with NiFe/Co90Fe10 layers for 5 Gbit/in2 density recording. IEEE Transactions on magnetics. 32 (1996)

[16] Y. Fan, et. al. Exchange bias of the interface spin system at the Fe_MgO interface. Nat. Nanotec. 8 (2013)

[17] S. M. Wu, et. al. Reversible electric control of exchange bias in a multiferroic field-effect device. Nat. Mat. 9 (2010)

[18] S. A. Wolf, et. al. Spintronics: A spin-based electronics vision for the future. Science 294 (2001)

[19] V. Baltz, et. al. Antiferromagnetic spintronics. Rev. Mod. Phys. 90 (2018)

[20] K. Gandha, et. al. Giant exchange bias and its angular dependence in Co/CoO core-shell nanowire assemblies. Phys. Lett. A 381 (2017)

[21] F. Radu, et. al. Quantitative description of the azimuthal dependence of the exchange bias effect. J. Phys. Condens. Matter 18 (2006)

[22] A. J. Devasahayam, et. al. The dependence of the antiferromagnet/ferromagnet blocking temperature on antiferromagnet thickness and deposition conditions. J. Appl. Phys. 85 (1999)

[23] A. E. Berkowitz, J. I. Hong, et. al. Refining the exchange anisotropy paradigm. Phys. Rev. B 81 (2010)

[24] M. Jung, et. al. Magnetism of the hypo-oxide state at the diffuse interface between the

ferromagnet and antiferromagnet phases. Nanoscale 9 (2017)

[25] H. Gao, et. al. Room temperature perpendicular exchange bias in CoNi/(Co,Ni)O multilayers with perpendicular magnetic anisotropy directly induced by FM/AFM interface. J. Magn. Magn. Mater. (2018)

[26] D. Kumar, et. al. Interface induced perpendicular magnetic anisotropy in a Co/CoO/Co thin-film structure: an in situ MOKE investigation. J. Phys. D: Appl. Phys. 47 (2014)