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Hypo-Ferromagnetic State at the Diffuse Internal Interface between Ferromagnet and Antiferromagnet

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Abstract: Magnetic properties are determined by collective behaviors of spin configuration in a material, which is then affected significantly by the nature of the couplings among atoms. At the interface between ferromagnetic and antiferromagnetic phases, higher degree of variation in the spin configuration can be derived with the consideration of diverse interface atomic structures. In the present work, interfacial configuration was further extended by establishing the gradient of oxygen concentration across the diffuse interface region between ferromagnetic metallic and antiferromagnetic oxide phases with nanoscale inhomogeneity. With mixed ferromagnetic and antiferromagnetic couplings among atoms in the interface sub-oxide state, novel magnetic behaviors can be induced. We report here, for the first time, a significant increase of saturation magnetization with temperature over a broad temperature range, which is against the conventional expectation for any generally known magnetic materials. The unusual temperature behavior is understood as the combined effects of competing ferromagnetic and antiferromagnetic couplings acting on atoms near the interface region.

One Sentence Summary: Ferromagnetic and antiferromagnetic couplings can be mixed to form a ‘hypo-ferromagnetic’ state at the diffuse interface region with incomplete oxidation between metallic ferromagnetic and oxide antiferromagnetic phases.

Magnetic properties of ferromagnetic (FM) or antiferromagnetic (AFM) material are considered mostly in terms of well-known simple parallel or antiparallel alignments of atomic magnetizations. More complex spin configurations including magnetic domains (1), domain walls (1,2), vortices (3), as well as skyrmions (4), can also be established depending on the nature of the couplings between atoms. Alteration of spin configurations from the usual alignments in FM or AFM phases (5,6) can often be facilitated at the interface between FM and AFM because the atoms around the interface are under the influences of exchange interactions with neighboring atoms belonging to both either FM and AFM sides (7-13). Furthermore, magnetic coupling across the interface is generally regarded to play an essential role to determine the overall magnetic behaviors of coupled FM-AFM systems (6). These couplings have been recognized to cause the exchange bias effect (6,14,15), which has been employed in the spin valve structure (16,17) in combination with giant-magnetoresistance effect (18) to make critical contribution on the growth of modern information (19) and sensor technologies (20). Added to their technological implications, academic interests to fully understand the couplings between AFM and FM have driven many researches for several decades (6,10,14,15,21-24). Additional chances to derive novel magnetic properties from nonconventional spin arrangement (7,13) still exist with interfaces, and the interface effect can be dominantly manifested by the formation of magnetic phase consisting of coexisting FM and AFM orderings. Their combined effects allow a prospect for new magnetic materials with unprecedented magnetic effects.

Although the technological application of AFM has traditionally been rather limited, with the recent reconsideration of high anisotropy energy of AFM (25) and zero apparent magnetization (25), AFM is gaining new attentions with the realization of its enhanced stability against thermal and field perturbations in comparison to FM (5,26). Therefore, engineering capability to tune, modify, or extend the functionalities of AFM is desirable for the advancement of spin-based technologies with extended base of magnetic materials. In this regard, we speculate that the utilization of FM/AFM interface to functionalize AFM could be an effective approach with the potential to take advantage of interface structures. Accompanied with novel atomic configuration, magnetic structures at the interface (27) of nanostructured magnetic multi-phases bring wealthy possibilities of new magnetic materials and correspondingly new magnetism. Magnitude of these interface effects can be effectively amplified in proportion to the areal interface density by the formation of fine nanogranular mixtures of AFM and FM. In-depth understanding for the collective effects of FM and AFM as well as the superparamagnetism in the nanoscale structures need to be taken into consideration for the full understanding of magnetic nano-mixtures.

In the present work, granular AFM phases of transition metal oxide were formed within the FM phase by reactive sputtering, and magnetic properties related to the interface were explored. $\text{Co}_{0.7}\text{Ni}_{0.3}$ alloy and Co metal were used as the FM phase material and controlled amount of AFM oxides of $\text{Co}_{0.7}\text{Ni}_{0.3}$ and Co were introduced in the metal phase whose grain widths are in the order of a few nanometers. We report an exotic behavior of magnetization in metal oxide AFM phase triggered by non-trivial arrangement of spins around the interface. As the temperature increased, saturation magnetization was found to increase significantly, as opposed to the traditional expectation that magnetization of ferromagnet should decrease with temperature due to the excitation of thermal magnons (1,28). This unanticipated behavior is interpreted to be the result of spin canting and incomplete compensation of magnetic moments at the interface, where incomplete oxidation causes atoms to be under the simultaneous actions of coexisting FM and

AFM couplings with the neighboring atoms. Relative strengths of those couplings determine the degree of apparent magnetization released from incomplete AFM couplings, and they behave as coupled to the nearby ferromagnetic moments. Temperature dependence of measured total magnetization depends on the temperature dependence of those acting couplings between atoms.

Depositions of phase mixture films were carried out at room temperature by reactive sputtering. With the oxygen concentration in the atmosphere, oxide contents in the deposited film could be fully controlled. The degree of oxidation in the deposited film was estimated from the measured saturation magnetization (M_s) of the composite films compared with the M_s of purely metallic film with identical thickness. Crystal structures of the films were verified with x-ray diffraction (XRD). Diffraction peaks corresponding to metallic and oxide phases were identified with their relative intensities and peak shapes varying with O_2 partial pressure (Figure 1A). Grain sizes in the film can be estimated from the analyses of XRD peak widths to be approximately 10 nm for purely metallic or completely oxidized films. On the other hand, when the films were deposited with partial oxidation, grain sizes ranged from 3 to 5 nanometers in widths. Reduced grain sizes can be understood considering the oxidation mechanism of the deposited metal atoms. Oxidation of metal atoms by the oxygen atoms in the atmosphere is expected to occur randomly at the surface of deposited film, effectively dividing the metallic grains into *subgrains* of oxides and metals resulting in the average grain sizes of 3-5 nm's. Transmission electron microscopy (TEM) of the films also confirmed the estimation of the grain size variations depending on the degree of oxidation (see Supplementary Information, SI).

Formation of nanoscale network of phase mixture was further verified by directly imaging the spatial distributions of metal and oxygen atoms in the Co - O mixture film with the oxidation degree of approximately 43 % using the atom probe microscopy technique. Atoms were individually dissociated from the specimen and their initial locations and species were determined to identify the original atomic distributions within the specimen. Fig. 1B shows reconstructed 3D distribution structure of internal interfaces, in which the yellow surface structure represents the oxygen isoconcentration surfaces defined with 20% of local oxygen concentration. Red and blue dots represent the spatial distributions of oxygen and Co atoms measured as they are taken away from specimen. Gradual change of atomic concentrations across the interface is shown in Fig. 1C, in which concentrations at all the locations in the specimen volume at the same distance from the isoconcentration surface was averaged and plotted as a function of distance. Therefore, this profile represents the average concentration distribution over the entire volume shown in Fig. 1B. Width of interface region varies at various locations in the specimen that the average oxygen concentration plotted in Fig. 1D can not reach 0 or 50 at.% corresponding to 0 and 100% oxidations, respectively. Randomly mixed network configuration of the constituting phases is clearly revealed, and the fraction of interface region in the entire specimen volume reaches approximately 70% considering that the width is ~4nm and the measured surface density of 0.173 nm^{-1} . Cross-sectional view of the phase mixture for the slab indicated in Fig. 1B is displayed in Fig. 1D, where spatial distribution of detected Co atoms, O atoms, and Co-O-H atomic clusters were mapped and local chemical concentrations were obtained and displayed in blue, red, and green, respectively, corresponding to metallic cobalt, oxide, and sub-oxide regions. Co-O-H cluster was assumed to represent Co-O as hydrogen atoms were added to the Co-O clusters from the specimen during the measurement procedure. Degree of oxidation was represented with color concentration. It is noted again that these regions of various oxygen concentrations formed from the spatially inhomogeneous incorporation of

oxygen atoms (during the film deposition). This random network structure of irregular shapes of grains with their widths in the order of a few nanometers warrants the significantly increased internal interface density within the specimen. The interface density in the film would be maximized for the sample with approximately equal proportions of two phases, and the interface related properties would most distinctly be revealed at the concentration of approximately 50 %. The interface is found to be rather diffuse in their chemical composition as noted above. Across the interface, oxygen and cobalt concentrations were found to gradually change over the length of 3-4 nm, which means the interface is diffuse and that the boundary between the metal and oxide phases in the film is ambiguous. Considering the average grain sizes determined from x-ray diffractions and the diffuse interface, it is noticeable that the majority of the specimen volume belongs to this diffuse interface region, in which the oxidation progressed insufficiently (not enough) to form a fully oxidized monoxide structure, thereby resulting in an oxygen deficient oxide state of ‘sub-oxide’ or ‘intermediate’ state between metal and oxide phases. In this sub-oxide phase, Co atom is neighbored by both O and Co atoms, while a metal cation in the oxide phase is surrounded by oxygen atoms only. Therefore, for any given Co atom in the sub-oxide phase, O atom mediated super-exchange couplings and direct ferromagnetic couplings between Co atoms would coexist depending on its immediate neighbor atoms. Neither full ferromagnetic couplings nor antiferromagnetic couplings with the surrounding atoms can be established in this configuration, hence partial ferromagnetism and antiferromagnetism are expected to exist simultaneously.

Of the many magnetic properties related to the presence of interfaces, saturation magnetization and exchange bias effect are directly related to the arrangement of magnetic spins with respect to the atomic arrangements. The spin arrangements under the influences of competing and/or combinatorial FM and AFM exchange interactions can vary significantly depending on the strengths of those couplings, and should be reflected in the measurement of magnetic hysteresis loops. Therefore, hysteresis loops were measured at various temperatures ranging from 10 K to 325 K to confirm the temperature dependence of spin coupling behaviors of the sub-oxides. Fig. 2A shows the measured M-H loops for the sample with 48 % of oxidation. Surprisingly, the measured M_s was found to increase with the measurement temperature. We emphasize that this trend is opposite of what is normally expected from a conventional ferromagnetic material, with which M_s should decrease continuously with temperature and eventually reaches zero at Curie temperature (1).

From the hysteresis loops measured with composite films of various oxidation degrees, change of M_s as compared to the value at 10 K ($\Delta M_s(T)/M_s(10\text{ K}) = [M_s(T) - M_s(10\text{ K})]/M_s(10\text{ K})$) was obtained as a function of temperature, and plotted in Fig. 2B. Both pure FM metal and nearly fully oxidized films exhibited no appreciable changes in the measured M_s as the temperature increased, while all the phase mixture films exhibited increasing saturation moment with temperature. In particular, up to 26 % increase of M_s with temperature was measured for the film prepared from $\text{Co}_{0.7}\text{Ni}_{0.3}$ with 48 % of oxidation, which is expected to have nearly the maximum internal interface density. When either FM or AFM phase is dominantly present, the amount of interface should decrease accordingly and the change in M_s should also decrease as shown in Fig. 2C, in which $\Delta M_s(325\text{ K})/M_s(10\text{ K})$ was shown as a function of AFM oxide concentration. These results support a strong correlation between the interface and the M_s increase. Additionally, considering the nanoscale dimensions of the granular network structure as shown in Fig. 1B, blocking temperatures of the AFM grains should be taken into consideration to

understand the temperature dependence of M_s . When two-phase mixture has similar relative ratio in the film, the grain size of AFM is a few nanometer and its blocking temperature is about 250 ± 30 K (29) owing to grain size distribution. As shown in Fig. 2B, the amount of released saturation moment radically increase with temperature in this range. In other words, coupling strength between AFM spins weaken and become unsteady as the temperature approaches the blocking temperature and its spin behavior follows FM spin in the interface and contributes to the increased magnetization moment.

The observed interesting phenomenon of magnetic moment generation by temperature increase in the FM/AFM mixture can be understood with the altered spin structures around the interface (30). Schematic diagram in Fig. 2D illustrates the expected interface spin configuration around the FM and AFM interface region with their coupling strengths depending on the ambient temperature. At a sufficiently low temperature, individual magnetic moment on and/or around the interface follows parallel FM or antiparallel AFM orderings depending on the local atomic configurations of neighboring atoms. Long range FM or AFM ordering forms in the pure metal or fully oxidized phases, but the ordering becomes short ranged at the interface *sub-oxide* region where oxygen atoms are distributed inhomogeneously over the few nanometer widths. Therefore, this interface region is neither FM nor AFM, but an atomic scale mixture of both. FM couplings and AFM couplings coexist in random mixture. As the interface phase occupies significant fraction of the specimen volume, overall magnetic properties of the entire film is significantly affected by the properties of this interface spin structure. In addition to the mixed FM-AFM spin configuration, it is also noted that T_C of FM is much greater than T_N of monoxide AFM. As the temperature increases, AFM couplings between the atoms weaken (26) while the FM couplings remain relatively strong and stable (1), thereby atomic magnetic moments in the sub-oxide interface may tilt to form twisted alignments with neighboring atomic moments that exerts FM and AFM couplings simultaneously depending on the local atomic configurations. Misalignment from AFM ordering should give rise to net magnetic moment and they should behave following the FM phase effectively exhibiting additional ferromagnetic saturation moments in the measured hysteresis loops. In other words, AFM spins at the interface region follow the order of FM spins as their AFM couplings get weaker due to the temperature increase. This effectively reduces moment compensations of in AFM and accordingly increases the apparent M_s of the overall film as temperature increases. The trend is expected to continue up to the Neel temperature of the AFM phase, which is ~ 370 K for $\text{Co}_{0.7}\text{Ni}_{0.3}\text{O}$.

The feasibility of spin misalignments in the spin structure with randomly distributed FM and AFM couplings was tested with the use of the atomic scale magnetic simulation code Vampire. Increasing spin twisting effect with temperature was displayed in Fig. ?? based on the simulation results. Depending on the magnitudes of atomic moments and exchange coupling energies, spin alignments can vary to give rise to various degree of M_s increase with temperature. Further details on the simulation are included in the SM.

Increased interface density with inhomogeneous nanostructures accompanied with the reduced thermal stability of AFM in the nanometer scale granular film is reflected in the measurement of exchange bias field as a function of temperature in Fig. 2E. Extremely high exchange bias field greater than 1 kOe at 10 K was measured due to the high interface density derived from the nanoscale network structures. It is notable that the high value of exchange bias field is more than an order greater than is usually expected from the bilayer films of comparable magnetic

component materials. Nanometer scale structure also exhibits the suppression of exchange bias field, H_E , starting at much lower temperature than T_N of AFM, which is in contrast to the prior results with bilayers (26). Moments at the AFM with smaller widths would be released at lower temperatures than those belonging to the grains with greater sizes (28,29). Therefore, it is thought that the detailed temperature dependence of M_S is related with the geometrical characteristics of the network nanostructure and the nature of spin canting for AFM couplings. Upon continuous heating above Neel temperature, AFM would eventually become paramagnetic and AFM would not be able to contribute to M_S . Effect of Neel temperature can be confirmed by comparing analogously structured oxide phase mixture films fabricated from Co and $\text{Co}_{0.7}\text{Ni}_{0.3}$ as the Neel temperature of CoO is 293 K, which is within the measurement range of the magnetometer used in the present study. M_S of the composite film exhibited continuous increase with temperature up to 300 K and began to decrease above T_N of CoO (Fig. 3). Smaller ΔM_S of ~5 % for the CoO as compared to 26 % of ΔM_S for $\text{Co}_{0.7}\text{Ni}_{0.3}\text{O}$ is thought to be due to the stronger exchange couplings between Co atoms compared with couplings between Co and Ni atomic moments. The deflection or tilting of atomic moment in CoO is believed to be more difficult than in the $\text{Co}_{0.7}\text{Ni}_{0.3}\text{O}$ (6,31), hence the coupling of AFM moments in CoO with FM should be weaker resulting in lesser ΔM_S in CoO.

Further confirmation and information on the magnitude of magnetization associated with irregular interface phase can be obtained by comparing the results from the sub-oxide mixture film in the present study and from the conventional bilayer films of FM $\text{Ni}_{0.8}\text{Fe}_{0.2}$ /AFM CoO with the flat interface. It is known that atomic intermixing at the interface occurs during the room temperature sputtering procedure (32). Although small depending on the degree of intermixing, the interface ferromagnetism should be present for the usual bilayers of FM/AFM as the metallic cations at the interface are coupled to both ferromagnetically and antiferromagnetically with neighboring atoms. As shown in Fig. 4, it was indeed confirmed in the measurement of magnetization with temperature. Magnetization of the bilayers is dominated by the moment from $\text{Ni}_{0.8}\text{Fe}_{0.2}$ FM exhibiting the typical trend of slight decrease with temperature. However, at temperatures around the Neel temperature of CoO, 293 K, bilayers exhibited small bump in magnetization. Magnitude of the bump was approximately about $\sim 2 \times 10^{-5}$ emu/cm² regardless of the FM layer thickness as they came from the interface region of AFM (see SI). When this magnitude of interface magnetization was applied to the case of Co-CoO random network structures as in Fig. 1B, ~8 % of M_S increase can be expected, which is of the same order as the experimental result obtained from Co-CoO mixture (See SM for details).

In summary, it was demonstrated that a random network structure consisting of nanoscale phases with varying oxidation degrees could be prepared with high density of interface between phases. Spatially inhomogeneous oxidation degrees within the nanostructure led to the formation of interface sub-oxide phases with the widths of a few nanometers, in which FM and AFM couplings were intermixed. The density of interface phase is significantly increased owing to the nanoscale dimensions of the internal structure, hence the magnetic properties of those internal interfaces become the representative properties of the composite structure. Within the interface phase, it was found that significant amount of magnetic moments could be drawn from the distortion of AFM antiparallel spin alignments resulting in incomplete moment compensations. The degree of distortion should depend on the exchange coupling strengths within the constituting phases, and the magnetic moment is derived from the weakened AFM couplings, increased ambient temperature results in more effective release of magnetic moments to yield the

increase of apparent M_s . As high as 26 % of M_s increase with increasing temperature was experimentally measured in the present report. Additionally, with the 3 dimensional nanostructures, exchange bias effect in the granular structure can also be improved by more than an order of magnitude. Therefore, fine-tuning of magnetic properties of AFM can be achieved via the nanostructural control of the phase mixture material. And it is demonstrated that the proper control of nanostructure of AFM and FM provides an effective route to fully exploit and extend the functionality of AFM materials as well as to overcome the thermal degradation of FM materials.

REFERENCES AND NOTES

1. S. Chikazumi, *Physics of Ferromagnetism* (Oxford University Press, UK, 1997); B. D. C. Cullity, C. D. Graham, *Introduction to magnetic materials*. (John Wiley & Sons. Inc., Hoboken, New Jersey, 2009).
2. G. Tatara, H. Kohno, J. Shibata, Microscopic approach to current-driven domain wall dynamics. *Phys. Rep.* **468**, 213-301 (2008).
3. T. Shinjo, T. Okuno, R. Hassdorf, K. Shigeto, T. Ono, Magnetic vortex core observation in circular dots of permalloy. *Science* **289**, 930-932 (2000).
4. S. Muhlbauer, B. Binz, F. Jonietz, C. Pfleiderer, A. Rosch, A. Neubauer, R. Georgii, P. Boni, Skyrmion lattice in a chiral magnet. *Science* **323**, 915-918 (2009).
5. F. Nolting, A. Scholl, J. Stohr, J. W. Seo, J. Fompeyrine, H. Siegwart, J.-P. Locquet, S. Anders, J. Luning, E. E. Fullerton, M. F. Toney, M. R. Scheinfein, H. A. Padmore, Direct observation of the alignment of ferromagnetic spins by antiferromagnetic spins. *Nature* **405**, 767-769 (2000).
6. A. E. Berkowitz, K. Takano, Exchange anisotropy – a review. *J. Magn. Magn. Mater.* **200**, 552-570 (1999).
7. V. Skumryev, S. Stoyanov, Y. Zhang, G. Hadjipanayis, D. Givord, J. Nogues. Beating the superparamagnetic limit with exchange bias. *Nature* **423**, 850-853 (2003).
8. T. C. Schulthess, W. H. Butler, Consequences of spin-flop coupling in exchange bias films. *Phys. Rev. Lett.* **81**, 4516-4519 (1998).
9. I. Groza, R. Morel, A. Brenac, C. Beigne, L. Notin, Electrical and magnetic properties of Co/CoO core-shell clusters. *IEEE Trans. Mag.* **47**, 3355-3357 (2011).
10. F. Radu, M. Etzkorn, R. Siebrecht, T. Schmitte, K. Westerholt, H. Zabel, Interfacial domain formation during magnetization reversal in exchange-biased CoO/Co bilayers. *Phys. Rev. B* **67**, 134409 (2003).
11. D. L. Peng, K. Sumiyama, T. Hihara, S. Yamamuro, T. J. Konno, Magnetic properties of monodispersed Co/CoO clusters. *Phys. Rev. B* **61**, 3103-3109 (2000).
12. S. H. Tsai, D. P. Landau, T. C. Schulthess, Effect of interfacial coupling on the magnetic ordering in ferro-antiferromagnetic bilayers. *J. Appl. Phys.* **93**, 8612-8614 (2003).
13. J. Eisenmenger, I. K. Schuller, *Nature Mater.* **2**, 437-438 (2003).

14. W. H. Meiklejohn, C. P. Bean, New magnetic anisotropy. *Phys. Rev.* **102**, 1413-1414 (1956).
15. J. Nogues, K. Schuller, Exchange bias. *J. Magn. Magn. Mater.* **192**, 203-232 (1999).
16. C. Y. You, H. S. Goripati, T. Furubayashi, Y. K. Takahashi, K. Hono, Exchange bias of spin valve structure with a top-pinned $\text{Co}_{40}\text{Fe}_{40}\text{B}_{20}/\text{IrMn}$. *Appl. Phys. Lett.* **93**, 012501 (2008).
17. Z. Wei, A. Sharma, A. S. Nunez, P. M. Haney, R. A. Duine, J. Bass, A. H. MacDonald, M. Tsoi, Changing exchange bias in spin valves with an electric current. *Phys. Rev. Lett.* **98**, 116603 (2007).
18. C. Reig, M. D. Cubells-Beltran, D. R. Munoz, Magnetic field sensors based on giant magnetoresistance (GMR) technology: applications in electrical current sensing. *Sensors* **9**, 7919-7942 (2009).
19. C. Chappert, A. Fert, F. N. V. Dau, The emergence of spin electronics in data storage. *Nature Mater.* **6**, 813-823 (2007).
20. Ito, M. Shinkai, H. Honda, T. Kobayashi, Medical application of functionalized magnetic nanoparticles. *J. Biosci. Bioeng.* **100**, 1-11 (2005).
21. X. Y. Lang, W. T. Zheng, Q. Jiang, Dependence of the blocking temperature in exchange biased ferromagnetic/antiferromagnetic bilayers on the thickness of the antiferromagnetic layer. *Nanotech.* **18**, 155701 (2007).
22. T. Yamauchi, K. Shiiki, Coercive force of Co-CoO thin films. *J. Appl. Phys.* **41**, 5982-5985 (2002).
23. M. Huijben, P. Yu, L. W. Martin, H. J. A. Molegraaf, Y. -H. Chu, M. B. Holcomb, N. Balke, G. Rijnders, R. Ramesh, Ultrathin limit of exchange bias coupling at oxide multiferroic/ferromagnetic interfaces. *Adv. Mater.* **25**, 4739-4745 (2013).
24. J. I. Hong, T. Leo, D. J. Smith, A. E. Berkowitz, Enhancing exchange bias with diluted antiferromagnets. *Phys. Rev. Lett.* **96**, 117204 (2006).
25. X. Marti, I. Fina, T. Jungwirth, Prospect for Antiferromagnetic Spintronics. *IEEE Trans. Mag.* **51**, 2900104 (2015).
26. K. Takano, R. H. Kodama, A. E. Berkowitz, Interfacial uncompensated antiferromagnetic spins: role in unidirectional anisotropy in polycrystalline $\text{Ni}_{81}\text{Fe}_{19}/\text{CoO}$ bilayers. *Phys. Rev. Lett.* **79**, 1130-1133 (1997).
27. C. A. F. Vaz, J. A. C. Bland, G. Lauhoff, Magnetism in ultrathin film structures. *Rep. Prog. Phys.* **71**, 056501 (2008).
28. S. Gangopadhyay, G. C. Hadjipanayis. Magnetic properties of ultrafine Co particles. *IEEE Trans. Mag.* **27**, 3174-3176 (1992).
29. P. J. van der Zaag, Y. Ijiri, J. A. Borchers, L. F. Feiner, R. M. Wolf, J. M. Gaines, R. W. Erwin, M. A. Verheijen. Difference between blocking and neel temperature in the exchange biased $\text{Fe}_3\text{O}_4/\text{CoO}$ system. *Phys. Rev. Lett.* **84**, 6102-6105 (2000).

30. H. Ohldag, A. Scholl, F. Nolting, S. Anders, F. U. Hillebrecht, J. Stohr, Spin reorientation at the antiferromagnetic NiO(001) surface in response to an adjacent ferromagnet. *Phys. Rev. Lett.* **86**, 2878-2881(2001).
31. Schron, C. Rodl, F. Bechstedt, Crystalline and magnetic anisotropy of the 3d-transition metal monoxides MnO, FeO, CoO and NiO. *Phys. Rev. B* **86**, 115134 (2012).
32. J. I. Hong, S. Sankar, A. E. Berkowitz, W. F. Egelhoff Jr, On the perpendicular anisotropy of Co/Pd multilayers. *J. Mag. Mag. Mater.* **285**, 359-366 (2005).

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Figures

Fig. 1

A

B

C **D**

Fig. 1. Structure characterization of inhomogeneously oxidized film. (A) XRD patterns of phase mixture films with degree of oxidation varying from 0 to 97 %. (B) Random network internal structure of the comprising phases is represented by the spatial distributions of isoconcentration surface measured by atom probe tomography technique applied to the film with 43 % of oxidation degree. (C) Average atomic concentration profile of Co and O across the isoconcentration surface. (D) Sectional view of the phase distributions with various oxidation degrees including Co (blue), CoO (red), and interface suboxides (green) in the yellow slab indicated in (B).

Fig. 2

A

B

Fig. 2

C

D

Fig. 2

E

Fig. 2. Magnetic properties depending on $\text{Co}_{0.7}\text{Ni}_{0.3}\text{O}$ ratio in the films with temperature.

(A) Hysteresis loops of the film with 47 % oxide content at temperatures from 10K to 325K. The inset shows magnified view of the region indicated with blue shadow to highlight the change of M_s as the temperature increases. **(B)** The change of M_s depending on the temperature measured with the granular films with different oxide contents. $\Delta M_s(T) / M_s(10\text{K}) = [M_s(T) - M_s(10\text{ K})] / M_s(10\text{K})$, where $M_s(T)$ is saturation magnetization value at the temperature, T K. **(C)** The change of ΔM_s between 325 K and 10 K depending on the oxide contents. Black guide line is added for the relationship between the oxide content and ΔM_s . **(D)** Schematic view of the expected spin structures depending on temperature at interface between FM and AFM. **(E)** Temperature dependence on exchange bias, H_E , of the granular film with 47 % oxide concentration.

Fig. 3

Fig. 3. Comparison of M_s changes for AFM oxides with different exchange anisotropies. The change of M_s with temperature for two different AFM materials, $\text{Co}_{0.7}\text{Ni}_{0.3}\text{O}$ and CoO .

Fig. 4

Fig. 4. Influence of film structure on the increase M_s . Black closed square and red closed square exhibit the bilayer and granular (mixed phase) films, respectively. Inset shows magnified view of the moment change of bilayers around the Neel temperature of CoO.