Exchange bias and spin glass behavior in biphasic NiFe₂O₄/NiO thin films

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Abstract

Magnetic exchange bias and coercivity of nanogranular NiFe₂O₄/NiO thin films, prepared using flow-stabilized microplasmas and post-deposition annealing, have been investigated as a function of ferrimagnet/antiferromagnet phase fraction, grain size, and temperature. Exchange bias (EB) and vertical shifts in hysteresis loops observed in the as-deposited and low-T annealed (≤ 600 °C) films were attributed to exchange coupling between nanocrystalline NiFe₂O₄ (~8-10 nm) and a structurally-disordered spin glass (SG)-like phase. At higher annealing temperature (850 °C), the observed EB was found to arise from exchange coupling between NiFe₂O₄ and NiO, rather than a SG phase, most likely due to reduction of structurally-disordered interfaces and a substantial increase in NiFe₂O₄ grain size (~26 nm).

Keywords: exchange bias, spin glass, microplasma, thin film deposition

1 Introduction

The exchange bias (EB) effect, due to electronic exchange interactions at the interface between a ferromagnet (FM) and antiferromagnet (AFM), results in a horizontal shift of the FM hysteresis loop (H_{EB}) after field cooling (FC) through the Néel temperature (T_N) of the AFM. This effect originates from pinning of unpaired electron spins at the FM/AFM interface where the irreversible spins of the AFM impart a supplementary unidirectional anisotropy to the system along the FC direction, effectively resisting the reversal of the FM moment with applied field.^{1,2} Although EB was first discovered in core@shell (Co@CoO) nanoparticles by Meiklejohn and Bean nearly six decades ago,³ much of the research in the field has focused on layered systems for their use in spintronic devices,⁴ magnetic sensing (read heads),⁵ random-access memories (M-RAM),⁶ and transistors.^{7,8} More recently, there has been a resurgence of interest in exchange biasing of magnetic nanoparticles to overcome the superparamagnetic limit, i.e., the size limit below which particle magnetization becomes unstable at room temperature, which is hampering the advancement of ultra high-density data storage technologies.⁹

Traditionally, core@shell (FM@AFM) structures are realized by chemical modification where a transition metal-based FM core is oxidized^{3,10} or sulfidized¹¹ to form the AFM shell. This technique is somewhat limited as it can only make a narrow suite of material combinations, and it is difficult to independently control the sizes of the core and shell, interfacial structure, and shell crystallinity. A variety of solution-based techniques¹²⁻¹⁴ have also been employed to overcome some of these shortcomings, as well as offer access to EB using ferrimagnet (FiM)/AFM coupling. In addition to core@shell arrangements, promising EB results have been obtained with FiM nanoparticles dispersed in an AFM matrix, where the connectivity (continuity) of the AFM phase has been shown to enhance exchange coupling at FiM/AFM

interfaces.¹⁵⁻¹⁸ The strength of this coupling is quite complex and has been shown to depend on several variables, including particle size, chemical intermixing, and interfacial strain, contact and structure.

Moreover, the situation becomes more complicated if a spin glass-like (SG) phase is present, which is often the case in nanoparticle or nanogranular EB systems synthesized by mechanical¹⁹⁻²⁰ (ball milling) or wet-chemical methods.²¹⁻²² In these cases, spin disorder in the spin glass phase can couple to the reversible phase at low temperatures, yielding EB and anomalous vertical shifts of hysteresis loops. Generally speaking, formation of the SG phase is due to atomic rearrangement at surfaces, or from finite size effects where the increase in surface/volume ratio induces structural disorder at the particle surface. For example, the EB effect has been seen separately in oxide spinels (e.g., NiFe_2O_4 ²³⁻²⁴ and CoCr_2O_4 ²⁵) and AFM (e.g., NiO ²⁶) nanoparticles where the structural disorder at the surface leads to the formation of random, non-collinear surface spins, which either couple to or change the magnetic order of the particle at low temperatures. Although the EB effect is rather profound in SG systems, the effect does not persist up to room temperature, making these systems undesirable for data storage. As such, it is of great technological interest to find new approaches to engineer the magnetic behaviour of nanogranular EB systems.

Herein, we present a high-pressure microplasma (MP)-based deposition technique²⁷⁻³⁴ to synthesize nanogranular EB films to study how annealing influences morphology, structure, and exchange bias coupling characteristics. Specifically, biphasic $\text{NiFe}_2\text{O}_4/\text{NiO}$ films, deposited at 175 °C using MPs, were annealed at 400, 500, 600, and 850 °C, and were studied under field cooled (FC) and zero field cooled (ZFC) conditions. Results showed that exchange bias (H_{EB}) in as-deposited and low temperature annealed films (≤ 600 °C) was due to exchange coupling involving a structurally disordered spin glass (SG) phase, while at higher temperatures (850 °C), H_{EB} appears to originate from direct coupling between NiFe_2O_4 and NiO crystalline phases.

2 Materials and Methods

2.1 Microplasma deposition

Nanogranular $\text{NiFe}_2\text{O}_4/\text{NiO}$ thin films were spray deposited onto 300 nm thick SiO_2 layers on (100) Si substrates using the DC microplasma (MP) deposition system shown in Fig. 1 and detailed elsewhere.³⁵ The MP source consists of a stainless steel capillary tube (i.d. = 500 μm) operating as the cathode and a grounded ring as the anode with Macor insulator. A flow-stabilized, hollow-cathode discharge is struck and maintained inside the end of the capillary tube using a current-regulated, high voltage power supply (0-25 mA, 0-5 kV). The SiO_2/Si substrates are positioned ~ 1 cm downstream of the plasma jet on an electrically floating, raster-scanning stage equipped with a cartridge heater (RT-600 °C). The entire assembly is housed in a vacuum chamber with roughing pump and maintained at 10-100 Torr.

Organometallic precursors (nickelocene, $\text{Ni}(\text{Cp})_2$, and ferrocene, $\text{Fe}(\text{Cp})_2$; STREM) were sublimed in separate temperature-controlled cells ($T_{\text{cell}} = 25$ °C), mixed with 9:1 Ar: O_2 gas flow and delivered to the hollow-cathode discharge ($I = 8$ mA, $V = -500$ V) with a total flow rate of 200 sccm. Nickel-iron oxide nanoparticles/clusters formed in the hollow-cathode region of the plasma were spray-deposited onto SiO_2/Si substrates at 175 °C; the substrate was raster-scanned in a serpentine fashion at 0.3 mm/s underneath the jet to create large area films ($\sim \text{cm}^2$). Argon makeup gas (100 sccm) was also introduced into the chamber background, and the chamber was regulated at 20 Torr for the duration of the experiment. After deposition, the

large area $\text{NiFe}_2\text{O}_4/\text{NiO}$ film ($X_{\text{Ni}} = 0.76$, metals basis) was cut into multiple pieces, with each piece separately heat-treated at 400, 500, 600, or 850 °C for 4 hours in air. The samples obtained are denoted as AsDep, S400, S500, S600, and S850, respectively.

Fig. 1 Schematic of the microplasma deposition system. A direct-current Ar/O₂ plasma jet is struck inside a stainless steel capillary tube (i.d. = 500 μm) using a high voltage power supply (HVPS). Volatile Ni and Fe organometallic precursors are delivered to the plasma jet, react to form nickel-iron oxides, and spray deposited on a raster-scanned substrate to form large area $\text{NiFe}_2\text{O}_4/\text{NiO}$ nanogranular films. A photo of an Ar microplasma jet operating at 14 Torr is shown on the right.

2.2 Materials Characterization

Film morphology and atomic composition (i.e., X_{Ni} , metals basis) was analyzed using an FEI XL30 SEM equipped with an EDX detector. A PANalytical Empyrean X-ray diffractometer (Cu K α radiation) was used to obtain ω -2 θ scans, with a -4° offset to suppress the (004) Si peak of the underlying substrate at ~69° 2 θ . Rietveld refinement of the resulting XRD spectra in the 33-40° 2 θ range was performed using HighScore Plus software to calculate $\text{NiFe}_2\text{O}_4/\text{NiO}$ phase fractions and grain sizes from the (311) NiFe_2O_4 and (111) NiO reflections.[#] The Scherrer equation³⁶ was used for grain size calculation after calibrating the diffractometer with a sintered alumina plate standard (SRM 1976a; NIST) to account for instrument broadening and measurement geometry.

A Quantum Design MPMS 5XL SQUID magnetometer was used to characterize the temperature and field-dependent magnetic behaviours of the films. Specifically, field cooled (FC) and zero field cooled (ZFC) M-T curves were measured in a 20 kOe field from 300 to 5 K. Hysteresis loops were measured across a range of temperatures between 300 and 5 K, where each measurement was preceded by field cooling in a 20 kOe field from 300 K to suppress the training effect.³⁷ ZFC hysteresis loops were also measured at 5 K.

3 Results and Discussion

3.1 Morphology and Structure

XRD spectra for the as-deposited and annealed samples are shown in Fig. 2(a). All samples have reflections that can be indexed to both rocksalt NiO (Fm3m) and inverse spinel NiFe_2O_4 (Fd-3m), confirming their biphasic nature. The broad hump centered at ~69° 2 θ is due to the underlying Si substrate and measurement geometry. The data suggest a substantial change in the $\text{NiFe}_2\text{O}_4/\text{NiO}$ phase distribution with annealing, as can be seen from the ratio between the (311) NiFe_2O_4 and (111) NiO intensities [Fig. 2(b)]. The phase fraction and grain size of the NiFe_2O_4 and NiO phases were extracted using Rietveld refinement analysis (fits are represented as the bold black lines in Fig. 2(b)) and are summarized in Figs. 2(c) and (d), respectively. The phase fraction for the AsDep film was estimated at 28/72 mol% $\text{NiFe}_2\text{O}_4/\text{NiO}$, which deviates

from the expected value³⁸ of 16/84 mol% for the $\text{NiFe}_2\text{O}_4/\text{NiO}$ system with a composition of $X_{\text{Ni}} = 0.76$ (metals basis, balanced by Fe). Based on the x-ray data, we hypothesize that this modest discrepancy may be due to the formation of Ni-rich amorphous regions during deposition, resulting in an 'observed' enrichment of NiFe_2O_4 compared to NiO in the film. Nonetheless, we would still expect the relative phase fraction of NiO to be much larger than NiFe_2O_4 , given the high Ni composition and the varying complexities of the two structures. That is, generally speaking, metal cations can more easily diffuse into the interstitial sites of the simple rocksalt structure of NiO (i.e., FCC packing of O^{2-} anions with the Ni^{2+} cations occupying the octahedral interstitial sites) than for the more complex inverse spinel³⁹ structure of NiFe_2O_4 (i.e., FCC packing of O^{2-} anions with all the Ni^{2+} and half of the Fe^{3+} cations situated in octahedral interstitial sites, and the remaining Fe^{3+} ions located in the tetrahedral sites).

The relative phase fraction changes substantially from 28/72 to 9/91 mol% $\text{NiFe}_2\text{O}_4/\text{NiO}$ after annealing at 400 °C for 4 hours. The data imply that the aforementioned Ni-rich amorphous regions are crystallizing into NiO and NiFe_2O_4 , with NiO forming at a more rapid rate. Additionally, there is likely to be conversion from metastable NiFe_2O_4 into NiO. As the annealing temperature increases, there is a concomitant increase in the rate of crystallization and we observe an increase in the relative amount of NiFe_2O_4 to NiO compared to the S400 sample [Fig. 2(c)]. This result can be interpreted in a multistep process: (i) in the early stages of heat treatment, Ni-rich amorphous regions crystallize to preferentially form NiO, and/or conversion of NiFe_2O_4 to NiO, and (ii) as crystallization proceeds, the amorphous regions become progressively more Fe-rich with the NiFe_2O_4 phase forming more rapidly than NiO at later times during annealing, leading to a relative increase in the NiFe_2O_4 phase. Moreover, small shifts of the NiO XRD reflections to lower 2θ (higher d-spacing) with increasing anneal temperature (see Supplementary Material Fig. S1) suggest that the initially deposited NiO rocksalt lattice is doped with Fe^{3+} ions (ionic radius: $\text{Fe}^{3+} < \text{Ni}^{2+}$). As the samples are annealed, we hypothesize that the Fe^{3+} ions diffuse out of the NiO lattice to form crystalline NiFe_2O_4 , resulting in a relative increase in NiFe_2O_4 mole fraction in agreement with Fig. 2(c).

Fig. 2 (a) X-ray diffraction spectra of as-deposited and annealed $\text{NiFe}_2\text{O}_4/\text{NiO}$ films measured using Bragg-Brentano geometry with a -4° offset. (b) Overlay of raw x-ray data and the corresponding Rietveld refinement fits (black lines) in the $33\text{--}40^\circ$ 2θ range. (c) NiFe_2O_4 mol fraction (balanced by NiO), and (d) NiO and NiFe_2O_4 grain sizes obtained from Rietveld refinement of data presented in panel (b). AsDep, S400, S500, S600, and S850 refer to samples deposited at 175 °C (AsDep) and subsequently annealed at 400, 500, 600, and 850 °C for 4 h in air, respectively.

Plan and cross-sectional SEM micrographs for the AsDep sample indicate that the film is comprised of dense columnar structures where each individual column is composed of a fine distribution of particles that are < 50 nm [Figs. 3(a) and (b)]. We hypothesize that during the initial stages of thin film growth, a directed flux of activated species (e.g., Ar, Ni, Fe and O), clusters and/or nanoparticles of nickel-iron oxides impinge on the substrate surface, resulting in the nucleation and growth of small, randomly oriented oxide fibrils (~ 5 -10 nm). The evolution of these fibrils into tapered polycrystalline columns with faceted tops is characteristic of frequent renucleation and diffusion-driven growth where the incoming adatoms and/or nanoparticles from the gas phase deposit onto the growing film and locally rearrange along surfaces and grain boundaries to form crystalline phases. Interestingly, the as-deposited morphology appears to remain unchanged after annealing up to 600 °C [Fig. 3(c)]. However, after annealing at 850 °C, NiFe_2O_4 and NiO grains appear to sinter, as seen in Fig. 3(d). The NiFe_2O_4 and NiO grain sizes were obtained from the (311) NiFe_2O_4 and (111) NiO reflections using the Scherrer equation.³⁶ As shown in Fig. 2(d), the NiFe_2O_4 grain size remained relatively constant at ~ 8 -10 nm; however, at 850 °C, grain size increased substantially to 26 nm, in agreement with SEM. Conversely, the average grain size of NiO increased monotonically with anneal temperature from 22 nm for the AsDep sample to 35 nm for the S850 sample.

Fig. 3 Cross-sectional and plan SEM images of as-deposited and annealed (≥ 600 °C, 4 h in air) $\text{NiFe}_2\text{O}_4/\text{NiO}$ films grown via microplasma at 20 Torr: (a) cross-sectional view of the AsDep film, and plan views of the (b) AsDep, (c) S600, and (d) S850 films.

3.2 Growth Mechanism

Although a detailed study of microplasma growth dynamics is outside the scope of the present study, it is highly likely that 'activated' Ni and Fe species (e.g., ions, neutrals, etc.) formed in the hollow cathode region of the jet result in the formation of aerosolized clusters and/or small nanoparticles that are ultimately spray deposited on the substrate. Evidence for this stems from previous work with microplasmas operating at higher pressures (100's of Torr), where aerosolized nanoparticles in the 2-10 nm size range can be formed.^{28,34} Although pressures are lower in our case, it is still very likely that small clusters do form in the jet because gas phase collision frequencies are very high ($\sim 10^{10} - 10^{11}$ s⁻¹) at 20 Torr. Also, given that O_2 injected in the jet or chamber background results in oxide species and films would suggest that Ni/Fe species and/or aerosolized clusters/nanoparticles could react with active oxygen species both enroute to and at the substrate surface. Bombardment of the surface by charged species, which could enhance surface diffusion, may also assist in the formation of crystalline films at such low

substrate temperatures.⁴⁰ Systematic studies are currently underway to investigate the importance of these underlying effects, i.e., deconvoluting the role of gas-phase nucleation/growth versus surface diffusion-mediated processes, charged particle bombardment of the substrate, and determining the fundamental 'species' (e.g., ions/atoms, clusters, or nanoparticles) responsible for film growth at various pressures.

3.3 Magnetic Measurements

A magnetic hysteresis curve of the AsDep sample was obtained at 5 K after field cooling from 300 K in a 20 kOe field [Fig. 4]. The salient features of the M-H curve are the apparent negative shift of the hysteresis curve along the applied field axis, which is suggestive of the EB effect (H_{EB}), and the large vertical shift of the loop (i.e., $|M(+20 \text{ kOe})| \neq |M(-20 \text{ kOe})|$) in the field cool direction, where ΔM is twice the shift, as defined in Fig. 4. The EB effect corresponding to an exchange interaction between crystalline NiFe_2O_4 and NiO is only expected to appear if the sample is field cooled through the Néel temperature of NiO ($T_N \sim 525 \text{ K}$). In the present case however, EB was observed after the sample was field cooled through a much lower temperature of 300 K, and it is rather large ($H_{EB} = 2 \text{ kOe}$), suggesting that another magnetic phase is coupling to the reversible spins of NiFe_2O_4 . Furthermore, the openness of the M-H loop and the unsaturated behaviour at relatively high fields of 20 kOe are characteristic of coupling from a spin disordered or spin glass (SG)-like phase.⁴¹ It is well known that the surface layers of ferrites, when confined to the nanoscale, show SG behaviour at low temperatures due to finite size effects and/or structural disorder at the surface.^{23,24} Notwithstanding, we cannot discard the possibility that some portion of the large vertical and horizontal shifts may be attributed to minor loop effects that arise when the magnetic sample is not sufficiently saturated during the measurement (see discussion below and in Supplementary Material).²⁶

Fig. 4 Magnetic hysteresis loop of the $\text{NiFe}_2\text{O}_4/\text{NiO}$ AsDep film measured at 5 K after field cooling in a 20 kOe field from 300 K.

The FC and ZFC M-H loops measured at 5 K for samples annealed at different temperatures are displayed in Fig. 5. The important features to note are: (i) the ZFC curves are symmetric and centered about the origin (i.e., $H_{EB} = \Delta M = 0$), (ii) enhancement of coercivity (H_C) and the appearance of a horizontal shift (H_{EB}) of the M-H loops after FC, (iii) presence of a small vertical

shift of the hysteresis loop after FC for all but the S850 sample, (iv) significantly larger magnetic moments at higher fields compared to the AsDep film, which attests to the crystallization of NiFe_2O_4 from amorphous regions in the film, and finally (v) only the left branches of hysteresis curves widen after FC, indicating that exchange coupling only influences moment reversal in the negative field direction.

Fig. 5 Magnetic hysteresis loops measured at 5 K after ZFC (open symbols) and after FC in a 20 kOe field (closed symbols) from 300 K for the (a) S400, (b) S500, (c) S600, and (d) S850 $\text{NiFe}_2\text{O}_4/\text{NiO}$ annealed films. Insets show hysteresis curves over the full ± 20 kOe field range.

It has recently been demonstrated⁴², and mentioned elsewhere^{2,12,26,43}, that the same characteristics invariably associated with exchange bias (e.g., observations i, ii, and iii above), can also be consequences of minor loop phenomena, which manifest when the range of fields used in an M-H measurement are insufficient to effectively saturate the ferro- or ferrimagnetic phase. As such, it is imperative when studying exchange bias, or any other magnetic phenomenon that requires evaluation of magnetization curve parameters, to ensure formation of a major loop to unequivocally rule out minor loop effects. As proposed by Harres *et al.*⁴², one

method to identify a major vs. minor loop is to analyze the derivatives of both the descending and ascending branches of the hysteresis loop. If the derivatives of these branches coincide and overlap before the maximum field value of the measurement is obtained, then moment reversal has become a reversible process, and magnetic saturation achieved. This analysis was performed on the hysteresis loops shown in the insets of Fig. 5 (see Supplementary Material Fig. S2 for dM/dH analysis), confirming that the curves are major, and that the horizontal and vertical shifts in the hysteresis loops are in fact due to exchange coupling. The analysis was inconclusive for the as-deposited sample [Fig. 4] because of the low signal-to-noise ratio of the measurement, which can be attributed to relatively low magnetization from high structural disorder in the sample (i.e., when comparing the magnitude of magnetization between the AsDep and annealed samples in Figs. 4 and 5, respectively). Because exchange bias persists in the annealed samples, and minor loop effects are ruled out, it is reasonable to assume that exchange bias is likely responsible for the loop shifts in the as-deposited sample as well.

The existence of a horizontal shift after FC through a temperature (300 K) less than T_N (525 K) suggests that the T_N of NiO has been suppressed below 300 K due to finite size effects and/or there is an exchange interaction other than that between $NiFe_2O_4/NiO$. The EB phenomenon requires two exchange-coupled phases where one phase has a reversible magnetic moment and the other is fixed over fields used in the M-H measurement. Spin glasses have been reported in many cases to act as the fixed moment phase in core@shell nanoparticles,⁴⁴ as well as in mechanically-synthesized^{19,20} and co-precipitated nanogranular systems (e.g., FiM/SG).²² The non-collinear magnetic structure inherent in ferrite SG layers, due to finite size effects and broken exchange bonds at the FiM surface, can be biased using a magnetic field and frozen in this configuration upon cooling through its transition temperature (i.e., blocking temperature, T_B). The strong unidirectional anisotropy of the blocked SG phase effectively pins the moment of the reversible phase along the field cool direction, resulting in the EB effect (H_{EB}). In the present case, the unexpected horizontal loop shift, combined with small $NiFe_2O_4$ grains sizes ($\sim 8-10$ nm), supports the idea that SG phases may be present at $NiFe_2O_4$ surfaces, $NiFe_2O_4/NiO$ interfaces, and $NiFe_2O_4$ grain boundaries due to structural imperfections from grain refinement.

Anomalous vertical displacement of the hysteresis curves towards higher positive moments also accompanies the EB shift in all samples except S850; that is, the magnitude of the magnetic moment measured at the largest field in the FC direction is not equal to the moment measured in the opposite direction (i.e., $|M(+20 \text{ kOe})| \neq |M(-20 \text{ kOe})|$). This indicates that a fraction of the magnetic moments biased along the FC direction do not rotate with a reversing field. This simultaneous occurrence of both horizontal and vertical shifts of M-H loops at low temperatures is a reoccurring theme in spin glass systems.^{20,22,44} Here, the strong unidirectional anisotropy of the frozen spins (responsible for the EB effect) are pinned along the FC direction and do not rotate when the field is reversed, resulting in a larger magnetization in the FC direction.⁴⁵ Even with the strong evidence of SG coupling, we cannot discount the possibility that there is also direct coupling between $NiFe_2O_4$ and NiO in this sample, where the Néel temperature (T_N) of NiO has been suppressed below 300 K due to finite size effects. The extent to which T_N is reduced has been debated in the literature and the large variance in degree appears to stem from measurement technique (i.e., electron spin resonance⁴⁶, low field ZFC magnetic susceptibility⁴⁷, neutron diffraction⁴⁸ and muon spin relaxation/rotation⁴⁹), identity of the antiferromagnet, and particle size and shape.⁴⁹

To investigate the origin of this EB effect, the temperature dependence of the magnetic moment was measured for both ZFC and FC cases in a 20 kOe field [Fig. 6]. The ZFC M-T curves for all

annealed samples diverge from the FC curves at a characteristic “irreversibility” temperature, T_{irr} , defined as the temperature where $\Delta m = M_{FC} - M_{ZFC} \neq 0$ (denoted by arrows in Fig. 6). This divergence hints at the existence of exchange coupling in spin disordered systems.²⁰ The peak of the ZFC curve is the magnetic transition temperature (i.e., blocking temperature, T_B), below which the uncompensated spins in the SG layer are frozen into a glassy, metastable state. The broad ZFC curve indicates a wide distribution of transition temperatures, i.e., a broad energy barrier distribution between metastable spin configurations in the system that may be explained by varying SG layer thickness and exchange coupling energies. The irreversibility and blocking temperatures tend to lower temperatures when increasing the anneal temperature, which can be associated with a reduction of structural/magnetic disorder at interfaces. This conclusion is further supported by the reduction of the difference in moment at 5 K between the FC and ZFC curves (normalized by the ZFC moment) with annealing temperature (i.e., $(\Delta m / M_{ZFC})_{5K} = 0.18, 0.17, 0.10$, and 0.04 for S400, S500, S600, and S850 samples, respectively).

Fig. 6 Temperature dependent ZFC (open symbols) and FC (closed symbols) magnetic moments measured in a 20 kOe field for the (a) S400, (b) S500, (c) S600, and (d) S850 $\text{NiFe}_2\text{O}_4/\text{NiO}$ annealed films. Arrows denote the temperature at which the ZFC and FC curves diverge.

The temperature dependence of EB was studied by extracting H_{EB} from FC M-H curves measured at multiple temperatures between 300 K and 5 K [Fig. 7]. The EB effect is absent at higher temperatures, becomes observable at some lower temperature and then increases monotonically with decreasing temperature. The temperature at which the EB effect emerges for each annealed sample appears to correlate with the irreversibility temperature defined above, except for the S850 sample (indicated by arrows in Figs. 6 and 7). This result implies that the EB phenomenon in the S400 to S600 annealed samples can be explained by coupling between FiM NiFe_2O_4 grains and a SG layer at the interface. Multiple metastable configurations of the non-collinear magnetic structure of the SG phase can be accessed at higher temperatures where thermal energies are comparable to metastable energy barriers. This non-robust magnetic structure results in weak coupling between the FiM and SG. Once T_{irr} is reached, some of the uncompensated spins become frozen along the FC direction and couple to the reversible moment of the FiM, resulting in the EB effect. As the number of frozen spins along the FC

direction increase with decreasing temperature, there will be more FiM/SG coupling interactions at the interface, resulting in a larger loop shift.

Fig. 7 Temperature dependence of exchange bias (H_{EB}) in the (a) S400, (b) S500, (c) S600, and (d) S850 $\text{NiFe}_2\text{O}_4/\text{NiO}$ annealed films after FC from 300 K in a 20 kOe field. Arrows indicate the temperature at which H_{EB} becomes observable.

Moreover, a small vertical displacement of the FC hysteresis curves appears for the S400 to S600 annealed samples at temperatures below their respective T_{irr} . This observation is common in spin glass systems and suggests that there exists a relationship between EB and the vertical displacement of the loop.^{20,22} Zheng *et al.* have proposed a simple model to explain this relationship where H_{EB} is related to the pinning energy in the system and is given by $H_{EB} = \Delta E / 2M_R$.⁴⁴ Here, M_R is the saturation magnetization of the reversible spins, and ΔE is the energy barrier to overcome when M_R reverses with applied field. The magnitude of ΔE is dependent on the coupling strength between the frozen SG spins and those of the reversible phase, which increases with the number of exchange interactions. As such, ΔE scales with the number of frozen SG spins at the interface and can be directly measured by the vertical shift of the hysteresis loop, ΔM . Therefore, H_{EB} should be related to ΔM as $H_{EB} \propto \Delta M / M_R$. To test this, H_{EB} and ΔM were extracted from FC loops measured below T_{irr} for each annealed sample, and plotted against each other [Fig. 8]. The observed linear relationship demonstrates that the SG spins pinned along the FC direction are likely responsible for both the horizontal and vertical shifts observed for the hysteresis curves measured below T_{irr} .

Fig. 8 Correlation of horizontal (H_{EB}) and vertical (ΔM) hysteresis loop shifts for the (a) S400, (b) S500, and (c) S600 $NiFe_2O_4/NiO$ annealed samples, where H_{EB} and ΔM were obtained for each sample from the corresponding set of FC hysteresis loops measured at multiple temperatures. The solid lines demonstrate the linear dependence of H_{EB} with ΔM .

Conversely, the EB witnessed in the S850 sample does not appear to be from FiM/SG coupling, as evidenced by the lack of a vertical shift of the FC hysteresis loops and the lack of correlation between T_{irr} [Fig. 6(d)] and the onset of EB [Fig. 7(d)]. The apparent disappearance of the SG phase after 850 °C may be reasoned by the following: (i) all amorphous regions in the film crystallized, eliminating any spin-disordered phase, and/or (ii) the substantial size increase of $NiFe_2O_4$ grains from ~8 nm to 26 nm, which results in a large increase of the particle volume/surface ratio, effectively drowns out the effects of the interfacial FiM/SG coupling. As such, the origin of the EB effect in this case is most likely due to coupling between $NiFe_2O_4$ (FiM) and NiO (AFM). EB is unlikely to appear in a bulk system where NiO is the AFM without FC through T_N of NiO (525 K); however, when the NiO grains are confined to the nanoscale, a reduction in T_N may be observed.^{48,50}

Variations in exchange bias (H_{EB}) and coercivity (H_C) at 300 and 5 K for all samples are summarized in Fig. 9. The large decrease in H_{EB} from the AsDep to S400 samples indicates a substantial improvement in crystallinity, diminishing the amount of spin disorder at $NiFe_2O_4/NiO$ interfaces and surfaces. Meanwhile, the drastic change in phase fraction with annealing seems to play a significant role in the amount of spin coupling at $NiFe_2O_4$ interfaces. Interestingly, H_{EB} and H_C increased with higher annealing temperature from 400 to 600 °C. It was found that the EB in these films was due to FiM/SG coupling, and that the thickness of the glassy layer decreased with higher annealing temperatures, which would instead suggest a trend opposing the one seen here. This surprising result may be due to more crystalline and smoother interfaces with higher heat treatment, where there is better connection between the SG and $NiFe_2O_4$ spins, resulting in stronger coupling at the interface with more FiM/SG spins participating in EB. Upon increasing the annealing temperature to 850 °C, EB becomes dominated by $NiFe_2O_4/NiO$ interactions (i.e., FiM/AFM) where the anisotropy, and thus the coupling, of the AFM is weaker than the SG phase. Furthermore, the much larger $NiFe_2O_4$ grain size in the S850 sample would tend to increase the FiM anisotropy energy, which requires higher pinning energy from interfacial exchange coupling to oppose moment reversal with field,

effectively lowering the observed H_{EB} . The H_C measured at both 300 and 5 K follow the same trend as H_{EB} measured at 5 K [Fig. 9], and can be interpreted using similar arguments as used for H_{EB} . Room temperature coercivity as high as 1100 Oe was realized for the S600 sample, which is significantly higher than what has been reported for the $\text{NiFe}_2\text{O}_4/\text{NiO}$ nanogranular or bilayer systems (see [22,51]). These results demonstrate the viability of using MPs as a deposition source to fashion biphasic, nanogranular films exhibiting EB and room temperature stability of nanoscale magnetic materials (< 20 nm) for potential data storage technologies.

Fig. 9 Coercivity (H_C) and exchange bias (H_{EB}) for the as-deposited and annealed $\text{NiFe}_2\text{O}_4/\text{NiO}$ films; H_C was measured at 300 and 5 K, and H_{EB} was measured at 5 K. Note: The signal-to-noise ratio of the AsDep sample at 300 K was extremely low and H_C could not be determined, suggesting that the AsDep film had structural and magnetic disorder.

4 Conclusions

In this work, we presented a detailed study of the EB effect in biphasic $\text{NiFe}_2\text{O}_4/\text{NiO}$ nanogranular films synthesized with high-pressure MPs and post-deposition annealing. The EB seen in the as-deposited and low-temperature annealed (≤ 600 °C) films was found to originate from coupling between nanocrystalline NiFe_2O_4 and a structurally-disordered SG-like phase. The EB effect became observable at and below the temperature where the ZFC and FC M-T curves diverge, i.e., the temperature where SG spins begin to freeze along the FC direction and pin the reversible NiFe_2O_4 spins, resulting in a horizontal shift of hysteresis loops. Furthermore, a concomitant vertical shift (ΔM) of the hysteresis loop was observed and found to be directly proportional to the magnitude of H_{EB} , indicating that the same SG-like spins are likely responsible. At higher annealing temperatures (850 °C), the observed EB was not accompanied by a vertical loop shift and is believed to be from direct exchange coupling between NiFe_2O_4 and NiO, where the SG-like phase is no longer present. The significant decrease in H_C and H_{EB} from the S600 to S850 samples was attributed to SG versus AFM pinning of FiM spins and a large

increase in NiFe_2O_4 grain size (~ 10 to 26 nm). The large room temperature H_c observed for samples S400 to S600 are noteworthy for applications requiring magnetic stability of magnetic nanostructures (~ 10 nm) at room temperature. Moreover, this work demonstrates the feasibility of using MP-based deposition to fashion a wider range of biphasic, nanogranular films to study exchange bias phenomena.

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6 Notes

‡ Because the x-ray beam length is a function of 2θ and the films are substantially thinner (~ 400 nm) than the penetration depth of the x-ray source (> 10 μm), the volume of material irradiated changes with 2θ , and phase fractions cannot be obtained. As such, the narrow 2θ region for Rietveld analysis was carefully chosen to estimate the NiFe_2O_4 and NiO phase fractions from the (311) NiFe_2O_4 and (111) NiO peaks at ~ 36 and 37.6° , respectively, which are close enough in 2θ to maintain the constant irradiated volume approximation. This analysis would break down if the films had a preferred orientation; however, the (111):(200) NiO and (220):(311) NiFe_2O_4 peak ratios of 0.61 and 0.30 (JCPDS file nos. 00-047-1049 and 01-086-2267), respectively, obtained using grazing-incidence XRD on a Rigaku diffractometer, suggest the films were indeed randomly oriented.

7 References

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