Controlling disorder-mediated exchange bias in $(\text{Mn,Zn,Fe})_3\text{O}_4$ thin films

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ABSTRACT

We report exchange bias in $(\text{Mn,Zn,Fe})_3\text{O}_4$ thin films that are compositionally homogeneous. We show that exchange bias in these Mn-Zn ferrite (MZFO) films can be tuned quite easily through annealing of the as-deposited films. The annealing process increases the crystallinity, as measured by x-ray diffraction (XRD). This improvement in crystallinity is accompanied by lower coercive fields, lower exchange bias fields, and higher saturation magnetizations. Exchange bias in these nominally homogeneous ferrite films is correlated with the degree of both structural and magnetic disorder. Based on the annealing experiments, we believe that these MZFO films may consist of crystalline regions that are separated from one another by disordered regions of the same nominal composition. The disordered regions serve to exchange bias the more structurally and magnetically ordered crystalline MZFO grains, leading to a shift of the magnetic hysteresis loop. Together these results indicate that the magnitude of the exchange bias can be controlled by tuning the degree of crystallinity in the system.

Exchange bias has been discovered in a wide variety of systems containing at least one interface between a ferromagnet (FM) and an antiferromagnet (AFM)[1–5]. A shift of the magnetic hysteresis loop that induces an asymmetry about the field-axis of a magnetization versus magnetic field curve is the hallmark of exchange bias, also termed exchange anisotropy. Utilization of this unidirectional anisotropy to stabilize magnetic domains in the development of reliable read heads and for applications in high-density recording media has revolutionized technology and paved the way for future progress of magnetoresistive random-access memory (MRAM)[6–9]. Yet, despite the enormous amount of research on these systems, the details governing exchange bias remain unclear[10,11]. Investigations into alternate pathways for achieving this phenomenon can provide important insight into the intricate mechanism of exchange bias and how it can be controlled.

While there is a rich history of studies on exchange biased AFM-FM interfaces, the presence of an antiferromagnetic phase is not essential for generating a shift of the magnetization loop with respect to the field axis. In addition to the well-studied antiferromagnet-ferromagnet interface, exchange bias has been observed in spin glasses, systems containing only hard and soft ferri- or ferro-magnets, and sometimes even in ferrimagnets that are biased by their own amorphous microstructural phases[12–15]. In particular, ferrimagnetic spinel-structure oxides have been studied as model systems for this type of exchange bias[16,17]. Previously, Venzke *et al.* demonstrated that a nanocrystalline thin film of NiFe_2O_4 exhibited exchange bias even without an external biasing layer. They attributed this behavior to possible clustering of antiferromagnetic or spin-glass-like regions in their material. Upon annealing their sample, they found that the exchange bias vanished and the magnetic hysteresis loop became symmetric about the origin, indicating that disorder may have been responsible for the asymmetric hysteresis[17]. Also with NiFe_2O_4 films, Korenivski *et al.* effectively simulated the interface between a single crystallite in contact with a disordered region of the same composition. They showed that an epitaxial film of NiFe_2O_4 with a symmetric magnetic hysteresis loop could be exchange biased by depositing on it an amorphous layer of NiFe_2O_4 [15]. A handful of studies on other ferrites and chromites have followed, each demonstrating that the formation of submicron magnetic grains embedded in a disordered non-antiferromagnetic matrix can lead to unidirectional anisotropy in the presence of a cooling field[18–20].

There have been numerous theoretical explanations of exchange bias that aim to explain the mechanisms and predict the magnitude of the exchange bias field across a variety of systems. Still, the magnitude of the exchange field is often overestimated[2,4,10,21–23]. Explanations of the discrepancies between theory and experiment have included random interface roughness between the biased (FM) and biasing (AFM) layers and domain formation in the AFM, both yielding partial spin compensation and suppressed exchange coupling between the FM and AFM[4,21,22]. This has led to efforts to perfect the flatness of interfaces and to minimize defects in the materials in order to achieve the maximum possible exchange bias[21,24]. Yet given the results on spinel ferrite and chromite systems,

we propose that disorder can be a valuable tool for engineering exchange bias in certain materials systems.

In this study we demonstrate that exchange bias can be controlled systematically in room-temperature-deposited spinel ferrite thin films by tuning the degree of disorder. Specifically, we modify the crystallinity of disordered, ferrimagnetic $(\text{Mn,Zn,Fe})_3\text{O}_4$ (MZFO) thin films through a series of annealing experiments. As-deposited films appear to be "self-biased"—that is, we observe a shift of the magnetic hysteresis loop in the absence of an antiferromagnetic or otherwise distinct biasing material. This exchange bias can be decreased and even eliminated via annealing. Through structural and magnetic characterization of these films, we conclude that the magnitude of the exchange bias is correlated with the degree of crystallinity in the MZFO thin films. These results suggest that exchange bias originates from exchange coupling across interfaces between crystalline and defective MZFO regions in our room-temperature deposited MZFO films.

We used pulsed laser deposition (PLD) to grow MZFO thin films on (110) MgAl_2O_4 (MAO) substrates. Both MZFO ($a=8.510 \text{ \AA}$) and MgAl_2O_4 ($a = 8.083 \text{ \AA}$) crystallize in the spinel crystal structure, despite a large lattice mismatch of over 5%. MZFO of stoichiometry $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ is the optimal Zn-doping to maximize saturation magnetization[21,25,26]. Due to the volatility of Zn in the deposition process, we chose a slightly Zn-rich PLD target composition of $\text{Mn}_{0.5}\text{Zn}_{0.6}\text{Fe}_{1.9}\text{O}_4$, which was the source of all films in this study[27]. The target was synthesized via solid state reaction at 1050°C and pressed with 1250 psi in a hot press. Using PLD, we deposited MZFO thin films at room temperature in a background pressure of $\sim 10^{-7}$ Torr. A KrF excimer laser ($\lambda = 248 \text{ nm}$) operating at 10 Hz ablated the target surface with an energy density of $\sim 1.2 \text{ J/cm}^2$. For comparison, epitaxial MZFO films were also grown on (110) MgAl_2O_4 substrates. We deposited these epitaxial samples at 410°C and 18.2 mTorr in a mixture of 99% N_2 and 1% O_2 gas. We ascertained film thicknesses and stoichiometries from Rutherford backscattering spectrometry (RBS). For the annealing studies, separate room-temperature-deposited MZFO/MAO thin film samples were annealed in air for 2 hours each at 200°C , 400°C , 600°C , 800°C and 1000°C in a tube furnace. The temperature was increased at a rate of approximately $10\text{-}15^\circ\text{C/min}$, and all samples were cooled in the furnace in air. Film microstructure was analyzed using a Panalytical X'Pert Materials Research Diffractometer and a Digital Instruments Dimension 3100 atomic force microscope. A Quantum Design SQUID magnetometer (Magnetic Property Measurement System, or MPMS) was employed for studying magnetization as a function of applied magnetic field and temperature. Prior to all magnetization measurements, the samples were demagnetized at 360 K by oscillating the applied magnetic field from 5 T to zero field. The samples were then field cooled in a 5 T field from 360 K to the temperature of interest. All x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) measurements were conducted at Beamlines 4.0.2 and 6.3.1 of the Advanced Light Source at Lawrence-Berkeley National Laboratory. MZFO films were measured in $\pm 0.5 \text{ T}$ at room-temperature at a grazing incidence of 30° with circularly polarized light.

FIG. 1. Out-of-plane x-ray diffraction spectra of as-deposited and annealed MZFO samples using (a) θ - 2θ scans, and (b) ω rocking curves around the MZFO 440 reflection. In (a), points where the intensity is equal to zero have been omitted for clarity. (c) A comparison of the lattice constants among samples annealed under different conditions, as deduced from the MZFO 440 peak. The unique * marker plotted at 22 K refers to the as-deposited sample.

The room-temperature-deposited MZFO films (as-deposited MZFO) have film thicknesses of approximately 300 nm according to RBS. Despite using oxygen resonance techniques, it is difficult to extract the exact oxygen content of the films. We estimate with SIMNRA simulations for the RBS data that the Mn:Zn ratio for as-deposited MZFO is ~ 1.1 [28]. The epitaxial MZFO films were around 200 nm thick with an estimated Mn:Zn ratio of ~ 1.6 . The reason for this difference likely stems from the different sample deposition pressures; with higher pressures, the high vapor pressure of zinc can suppress its incorporation[27].

The as-deposited MZFO samples demonstrate a surprisingly high degree of order. Figure 1 shows (in blue) θ - 2θ and ω rocking curve x-ray diffraction (XRD) scans of the as-

FIG. 2. In-plane x-ray diffraction ϕ (phi) scans at the 404 MZFO and MAO reflections show that as-deposited MZFO is in registry with the underlying (110) MgAl_2O_4 substrate.

deposited MZFO thin films. Despite being grown at room-temperature, MZFO films diffract with exclusively $hh0$ type peaks in θ -2 θ XRD scans (Figure 1a). The full-width-at-half-maximum (FWHM) for a representative as-deposited MZFO film is $\Delta 2\theta_{440}=0.8^\circ$ on the 440 peak, compared to $\Delta 2\theta_{440}=0.4^\circ$ for the epitaxial MZFO film[16] The breadth of the as-deposited MZFO θ -2 θ peaks likely indicates a small particle size. While the superior crystalline quality in films grown at higher temperatures is expected, it is remarkable that MZFO can be deposited from a sintered powder at room-temperature and still nucleate with such strong crystallographic preference. The mosaic spread, as determined by FWHM of XRD rocking curves, naturally showed the same trend (Figure 1b): $\Delta\omega_{440}=1.6^\circ$ for as-deposited MZFO compared to $\Delta\omega_{440}=0.7^\circ$ for epitaxial MZFO. Phi (ϕ) scans were used to investigate the in-plane alignment of the film and substrate lattices. Remarkably, as-deposited MZFO samples exhibit in-plane ordering. ϕ -scans in Figure 2 reveal that there is an epitaxial relationship between as-deposited MZFO and the underlying MgAl_2O_4 substrates. Together with the out-of-plane XRD spectra, these results indicate that as-deposited MZFO is at least partially epitaxial and possibly nanocrystalline. That is, while there exist epitaxial regions in as-deposited MZFO, the samples are more disordered than the epitaxial films grown at higher temperatures as evidenced by broader XRD peaks.

FIG. 3. (a) Hysteresis loops measured at 10 K of as-deposited MZFO (blue), MZFO annealed at 600°C (orange) and MZFO annealed at 800°C (red) after field-cooling in +5 T (+50 kOe) in a SQUID magnetometer. The inset shows that the as-deposited MZFO loop is clearly shifted toward negative fields. Both the (b) exchange bias fields and the (c) coercive fields decrease overall as a function temperature in as-deposited MZFO.

SQUID magnetometry reveals negative exchange bias (Figure 3a); that is, a shift in the magnetic hysteresis loop toward negative fields when cooled in positive fields. The exchange field H_E (defined as the magnitude of this shift) is on the order of -200 Oe for as-deposited MZFO after cooling in +50 kOe (+5 T). (For comparison, the epitaxial film has an exchange bias field of -30 Oe at 10 K)[16]. As shown in Figure 3b, the magnitude of the shift decreases monotonically with temperature and disappears by 150 K. We have also plotted the coercive field as a function

temperature (Figure 3c) and found that the coercivity [$H_C=(H_+-H_-)/2$] similarly decreases in this range. It is important to note that comprehensive XRD studies show no compositional or structural phase segregation. That is to say, there are no detectable antiferromagnetic clusters, binary oxides, or other compounds. Thus, conventional models for exchange bias may not fully explain the observed behavior.

FIG. 4. Atomic Force Microscopy images for (a) as-deposited MZFO as well as films annealed at (b) 200 °C, (c) 400 °C, (d) 600 °C, and (e) 800 °C. Predictably, the films generally undergo an increase in root-mean-squared (RMS) roughness with higher annealing temperatures, as shown in (f). The unique * marker plotted at 22 K refers to the as-deposited sample. The films annealed at 1000 °C (*not shown*) are the only ones that show inhomogeneities, with buckling of the films due to apparent thermal stress..

To test whether disordered MZFO regions could be biasing magnetically and structurally ordered crystallites, we annealed the as-deposited MZFO films at different temperatures. After annealing, the saturation magnetizations are enhanced while the coercivities are strongly reduced (Figure 3a). All films remain highly textured in the out-of-plane direction, with no evidence of secondary phase growth or nucleation (Figure 1a). The out-of-plane lattice parameter decreases with increasing annealing temperatures (Figure 1c), which could be due to oxidation of the samples after annealing in air, leading to an overall reduction in defect density. Predictably, the surface roughens with increasing annealing temperatures, as shown in Figure 4. While the as-deposited films have root-mean-squared (RMS) roughnesses of less than 0.15 nm, after annealing at 800 °C the RMS roughness rises by an order of magnitude. Still, the samples are homogenous across the film surface up to 800 °C. However, after annealing at 1000 °C (*not shown*), there is a loss of structural integrity of the film as evidenced by apparent buckling of the sample, likely due to thermal stresses.

Figure 5a shows the decrease in mosaic spread after a 2-hour anneal in air as a function of annealing temperature. Figures 5b and 5c demonstrate that annealing the as-deposited MZFO films at higher annealing temperatures results in increased saturation magnetizations and reduced coercivities. The 800 °C anneal yielded the highest magnetizations, with M_s of ~ 560 emu/cm³ and coercivities as low as ~ 90 Oe. This is more than double the magnetization value before annealing, and less than an eighth of the as-deposited coercivity. Annealing at progressively higher temperatures is also associated with a decrease in the exchange bias fields (Figure 5c). In fact, the samples annealed at 800 °C have both lower exchange bias fields and narrower rocking curves than the as-grown epitaxial films. Compared to the as-deposited case, H_E of an MZFO sample annealed at 800 °C is reduced from -200 Oe to just -10 Oe at 10 K after field-cooling in +50 kOe. So, with progressively higher annealing temperatures, we generally observe improved crystallinity, higher magnetizations, lower coercivities, and lower exchange bias fields.

Without the presence of compositionally distinct compounds that bias one another, we explain the shift of the magnetic hysteresis loop by considering the microstructure of the MZFO thin films. XRD results show that as-deposited MZFO samples are textured out-of-plane and are in-phase with the underlying substrate, indicating epitaxy and high structural order. However, we also observe broader rocking curve peaks in as-deposited MZFO as compared to the epitaxial and annealed samples. These broader peaks indicate that as-deposited MZFO films may consist of ordered crystalline regions or grains separated by grain boundaries. Given the alignment of the film and substrate peaks in the ϕ scans (Figure 2), we postulate that as-deposited MZFO samples are likely nanocrystalline

FIG. 5. Structural and magnetic changes as a function of different annealing temperatures for as-deposited MZFO. Each sample was annealed for two hours in air at the specified temperature. As-deposited RT-MZFO is plotted at 22 K and denoted with a unique * marker on the left-side of each plot. Parts (b), (c) and (d) represent data taken at 10 K after field-cooling in +5 T. (a) The FWHM of the rocking curve $\Delta\omega_{440}$ around the MZFO 440 reflection decreases monotonically with annealing temperature. (b) The magnetizations of annealed samples (M_{annealed}) at +5 T is given after normalization by their as-deposited magnetizations ($M_{\text{as-deposited}}$). This dimensionless number $M_{\text{annealed}}/M_{\text{as-deposited}}$ shows the ratio between annealed-MZFO and as-deposited MZFO magnetizations as a function of annealing temperature. (c) The magnitude of the exchange bias field H_E , like the mosaic spread as shown in part (a), decreases monotonically with annealing temperature. The coercivity H_C (d) follows nearly the same trend, though annealing at 200 °C does induce some widening of the hysteresis loop.

with grains (or crystallites) that are in-phase with the underlying substrate. These structurally and magnetically ordered MZFO crystallites likely coexist with more disordered MZFO regions near or at the grain boundaries. These disordered regions may serve to magnetically bias and pin the ordered regions, leading to a net shift of the magnetic hysteresis loop. Annealing as-deposited MZFO at sufficiently high temperatures improves the crystallinity of the disordered regions, leading to sharper peaks in the XRD θ - 2θ and ω rocking curve scans and decreasing both the exchange fields and coercivities.

It must be noted that post-annealing at 1000 °C for 2 hours results in significant interdiffusion at the substrate-film interface, as determined by RBS. Thermal stresses also cause significant buckling of the film as seen with atomic force microscopy (*not shown*). This increased disorder suppresses the overall magnetization (Figure 5b). Still, rocking curves continue to become sharper and exchange bias fields lower. Therefore, when determining the optimum annealing conditions for the improvement of both magnetic and structural properties, consideration of interdiffusion at the substrate-film interface cannot be neglected.

While both the exchange bias fields and the coercivities decrease as the MZFO films are annealed at higher temperatures, the coercivities do not decrease monotonically. The samples annealed at 200 °C show increased average coercivities with a lower exchange bias field. The exchange bias is lowered due to the overall improvement of the sample crystallinity and erosion of grain-boundary-like regions, as indicated by the FWHM of the rocking curves. But the non-monotonic behavior of the coercivity suggests that there may be two or more contributions to the coercive field. Enhanced coercivity can arise from an increase in the pinning site concentration (e.g., sample roughening), but may decrease as a result of lowering the overall defect density through annealing. The higher coercivity in the 200 °C annealed samples has been observed repeatedly, in multiple samples. This is consistent with atomic force microscopy results, in which the films annealed at 200 °C have higher roughness values and also higher coercivities than either the as-deposited films or those annealed at 400 °C.

The presence of disordered regions in these samples also means that as-deposited MZFO film magnetizations are reduced from bulk values (~ 700 emu/cm³ at 10 K), as seen in Figure 3a[26]. In these disordered regions, the magnetic moments may not be able to align with the applied field due to frustrated, spin-glass-like behavior. After annealing, the crystalline regions grow at the expense of the more disordered regions, in turn contributing to higher magnetizations. Another possible contribution to the difference in magnetization between the as-deposited and annealed samples could be a change in the cation distribution among the octahedral and tetrahedral sites of the mixed spinel structure MZFO characterized by a so-called inversion parameter. Spinel has the general stoichiometry $(M_{\delta^{2+}}M_{1-\delta^{3+}})[M_{1-\delta^{2+}}M_{\delta^{3+}}]$ where () encloses tetrahedrally coordinated cations, [] encloses octahedrally coordinated cations, and for MZFO, M can be cations of Mn, Fe, or Zn. If

$\delta = 1$, the spinel is said to be “normal”, whereas if $\delta = 0$, the spinel is “inverse”. Mixed spinels have $0 < \delta < 1$ [29]. Cation redistribution in these ferrimagnets alters the magnetization of the material, and could influence the change in magnetism of our MZFO thin films [21,30,31]. To probe whether there was a significant cation redistribution in these samples, we used x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) to probe the cation absorption edges of MZFO.

The most likely cations of MZFO are Mn^{2+} , Mn^{3+} , Fe^{2+} , Fe^{3+} and Zn^{2+} . Zn^{2+} is known to have a strong preference for the tetrahedral site in mixed-valent spinels due to its comparatively large ionic radius, though some studies have shown that Zn^{2+} can still occupy the octahedral site in zinc-based ferrites [31–35]. The other Mn and Fe cations are nominally free to redistribute on the tetrahedral (Td) and octahedral (Oh) sites. Figure 6 shows the XAS and XMCD spectra for Mn $L_{3,2}$. While there are few noticeable changes in the XAS, the XMCD spectra for the as-deposited and 200 °C annealed cases do show differences in their lineshapes compared to samples annealed at higher temperatures. Below the dashed line in Figure 6b are calculations for individual Mn^{2+} and Mn^{3+} spectra from Kang *et al.* for comparison with the experimental data [36]. The features at (i) and (ii) marked by arrows are distinct indications of Mn^{3+} . Thus, we can deduce that after annealing, the Mn^{2+} concentration of the films increases. However, this change is not enough to noticeably affect the Mn XAS (Figure 6a).

FIG. 6. (a) X-ray absorption spectroscopy on the Mn $L_{3,2}$ edges for as-deposited and annealed MZFO samples. The spectra have been normalized for comparison such that the pre-edge is set to 0 and the main L_3 absorption peak is set to 1. As shown, there is very little change in the spectral lineshape with annealing. (b) The x-ray magnetic circular dichroism (XMCD) spectra of the as-deposited and annealed MZFO films, as indicated. Below the dashed black line, calculated XMCD spectra for Mn^{2+} and Mn^{3+} from Kang *et al.* are given for comparison[36]. All spectra have been normalized such that the pre-edge is 0 and the first main absorption peak is at -1. The peaks of interest marked by (i) and (ii) are indicators of Mn^{3+} .

The results for Fe XAS and XMCD are given in Figure 7. In the XAS (Figure 7a), all films have similar lineshapes, with each exhibiting a peak on the low-energy shoulder of Fe. This peak has been shown to result from the presence of Fe^{3+} [37,38]. In our samples, there is not a significant correlation between the intensity of this peak, (i.e., the concentration of Fe^{3+}), and the annealing temperature. The Fe $L_{3,2}$ XMCD spectra in spinel ferrites is unique in that it is straightforward to extract both valence and site-specific information. The Fe $L_{3,2}$ edges are shown in Figure 7b. Each peak in the XMCD corresponds to a distinct valence of Fe in a particular bonding configuration. As indicated in Figure 7b, the first peak corresponds to Fe^{2+}_{Oh} in an octahedral environment, the second peak represents Fe^{3+}_{Td} in a tetrahedral coordination, and the third peak indicates Fe^{3+}_{Oh} on octahedral sites[38]. These well-resolved features demonstrate that the MZFO films are mixed-valent spinels. In Figure 7b, the XMCD spectra are normalized by the first peak, corresponding to Fe^{2+}_{Oh} , so that the differences between the concentration of Fe^{3+} on tetrahedral sites can be compared to that on octahedral sites. As shown, there is little to no change to the spectra after annealing. It is also apparent that octahedral iron is aligned with the applied magnetic field, and that tetrahedral iron is aligned antiparallel to the applied field. The Mn^{2+} signal is similarly antiparallel to the field, suggesting tetrahedral occupation of the interstitial sites.

FIG. 7. (a) X-ray absorption spectroscopy on the Fe $L_{3,2}$ edge, comparing the as-deposited and annealed samples. The spectra have been normalized for comparison such that the pre-edge is set to 0 and the main L_3 absorption peak is set to 1. (b) XMCD of the same absorption edge, normalized by the first peak corresponding to Fe^{2+} on octahedral sites.

The XAS and XMCD results have no clear trend or predictable evolution of the lineshape with annealing temperature. This suggests that even if there is a redistribution of cations after annealing, the extent is not sufficient for explaining the drastic change in saturation magnetization after annealing via changes in the inversion parameter. We conclude that the large change in the magnetization after annealing is due largely to a reduction in defects through thermal activation.

Despite the large lattice mismatch between MZFO and MAO, we demonstrate the ability to grow ordered films of MZFO on MAO at room temperature while still maintaining an epitaxial relationship between the film and the substrate. We have found that disorder is directly correlated with increased exchange bias, increased coercivities, and decreased magnetizations. We can tune the degree of order, and therefore the magnetic properties, through annealing. This is an effective and reliable way to control exchange bias in a “self-biased” system consisting of compositionally homogeneous but microstructurally distinct regions.

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