Chapter 7

Exchange bias in FeNiMoB-Zinc Ferrite bilayer films

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Lisha et al. (accepted for publication in Nuclear Instruments and Methods in Physics Research B)
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**7.1 INTRODUCTION**

The studies on single layer films of FeNiMoB and zinc ferrite and the modification of their properties by thermal annealing and ion irradiation was discussed in the previous chapters. The formation of bilayer system always gives rise to new properties and is highly influenced by the interface. Studies on bilayer of FeNiMoB and zinc ferrite are discussed in the present chapter. Exchange bias effect is an interface phenomenon and was observed earlier at ferromagnet (FM) and antiferromagnet (AFM) interface. Exchange bias effect is the phenomenon wherein the spins of ferromagnet (FM) and antiferromagnet (AFM) interact at the FM-AFM interface, and thereby forces the AFM spins to align parallel with FM spins at the interface on field cooling. The alignment of AFM spins exerts a torque which the FM spins has to overcome on reversal of applied magnetic field resulting in an apparent shift of hysteresis loop along the field axes when field cooled below the Neel temperature of AFM [1]. Along with hysteresis loop shift one may also observe vertical shift and enhancement of the hysteresis loop. Exchange bias effect is observed in FM-AFM layers, FM-AFM core shell systems and also in systems having ferromagnetic domain, spin glass (SG) or disordered surface spins [2]. In FM-SG systems the spin glass is modeled as a diluted AFM with long range interactions [3]. The exchange biased structures find application as spin valves, magnetic tunnel junctions and spintronic devices [1]. Applications involving exchange bias necessitate tailoring bias and coercive fields by appropriate techniques [4].

Many models have been proposed to explain the exchange bias effect [5, 6, 7]. Some models consider exchange bias solely as an interface phenomenon, [8] while some others assume exchange bias to be dependent on the whole of AFM [5, 6]. Many researchers have observed that the bias and coercive fields are
greatly influenced by both the FM and AFM thickness [9-12]. The most well studied exchange bias system is FeNi-FeMn. In this system it was reported that the bias field obeys a power law with AFM thickness as $1/t^\lambda$, where the exponent $\lambda$ ranges from 0 to 0.3 [12]. The inverse relation of exchange bias with AFM thickness was also observed in various other systems namely IrMn$_3$/Co, La$_{2/3}$Ca$_{1/3}$MnO$_3$/La$_{1/3}$Ca$_{2/3}$MnO$_3$, Ta/Py/IrMn/Pt [10, 11, 13]. In most of the studies carried out so far, the optimum thickness of the AFM layer is ~20 nm, the bias field disappears for thickness values greater than this optimum thickness [13-16]. In some other systems like CuMn-Co, it was observed that bias field increases with thickness and attains saturation [3, 17]. The effect of thickness on the exchange bias is not universal and found to vary from system to system. Thus the dependence of thickness on the exchange bias field is of great significance.

The exchange bias can be tailored by diluting the AFM with suitable non magnetic impurities or by creating defects by ion irradiation or other techniques [15, 18]. Ion irradiation offers unique possibilities in modifying exchange bias [1]. The changes in exchange bias with ion fluence have been modeled based on a competition between defect creation and interfacial mixing [19]. Most of the ion induced modification studies on exchange bias systems are found in the low energy regime [14, 15, 20, 21]. It must be noted here that low energy ions are suitable for modification of materials when the film thickness is small (~1-10nm). For larger film thickness (~ 100-1000 nm) the less energetic ions get embedded in the film; while, high energy ions can create amorphous tracks in films of much larger thickness. Contrary to low energy ions, where high fluences (~$10^{16}$) are required, high energy ions can produce the same effects at much lower fluences, three to four orders smaller than that of low energy ions. Mougin et al. studied the effect of 10keV He ions on 5nm-10 nm FeNi-FeMn thin films [15]. They observed
an enhancement of exchange bias at lower fluences and a decrease at higher fluence. Effect of high energy ions on the exchange bias properties would be an interesting research area since it offers an ideal template to investigate the effect of electronic energy loss on exchange bias properties. As mentioned earlier, the dominant mechanism of material modification at low energies is via nuclear energy loss, while in the case of high energy ions it is through electronic energy loss and hence effect of high energy ions on exchange bias properties is also interesting from a fundamental perspective.

The system under investigation is zinc ferrite-metallic glass. Zinc ferrite is an antiferromagnet with a Neel temperature of 10K, while metallic glass, an alloy of Fe, Ni, Mo, B is an excellent soft ferromagnetic material with a Curie temperature of 600K. Zinc ferrite in the nano regime is purported to be exhibiting anomalous magnetic behavior namely, ferrimagnetic, superparamagnetic, antiferromagnetic or even glassy behavior depending on cation distribution in the A and B sites of the spinel structure [22-27]. Hysen et al. and Senoy et al. reported soft magnetic properties in thin films of Fe-Ni alloys and the properties could be tailored by thermal annealing and swift heavy ion irradiation [28-30]. Substantial amount of work has been carried out in the past on these materials namely, zinc ferrite and Fe-Ni alloys in our laboratory, [26-30] and it was thought fit to look at the possibilities of inducing exchange bias on a bilayer consisting of zinc ferrite and FeNiMoB alloys fabricated using RF sputtering. The effect of swift heavy ion irradiation, layer thicknesses and thermal annealing on the exchange bias field and coercivity is of interest to the scientific community and are the motives of the present investigation.

The present chapter is divided into two sections; the first part deals with the dependence of film thickness and thermal annealing on exchange bias effect;
the role of swift heavy ions in tailoring the exchange bias properties is probed in the second part.

7.2 EXPERIMENTAL METHODS

![Schematic of the bilayer structure](image)

The bilayer film of FeNiMoB-zinc ferrite was prepared by RF sputtering using targets of Fe$_{30}$Ni$_{48}$Mo$_4$B$_{18}$ ribbon and zinc ferrite (prepared by sol gel auto combustion technique). The films were deposited on naturally oxidized Si substrate. The schematic is shown in figure 1. FeNiMoB was deposited initially on natively oxidized Si substrate for 30 minutes at an RF power of 100 Watts. Subsequent to that zinc ferrite was deposited at an RF power of 150 watts for 90 minutes. The thickness was controlled by varying the Ar gas flow. For both depositions the pre deposition pressure in the chamber was 6x10$^{-6}$ Torr which reduced to 5x10$^{-2}$ Torr during deposition. The films of higher thickness were annealed at 873K for 1 hour. Rutherford Backscattering Spectrometry (RBS) was carried out to determine the film thickness and composition. The obtained experimental results were simulated using the XRUMP software. The magnetisation measurements at room temperature and at 10 K were carried out employing SQUID VSM. The low temperature magnetic measurements were performed by field cooling at 5000 Oe.
The films of higher thicknesses annealed at 873K were subjected to swift heavy ion irradiation employing 100 MeV Ag$^{8+}$ ions at fluences of $1 \times 10^{11}$, $1 \times 10^{12}$, $1 \times 10^{13}$ and $3 \times 10^{13}$ ions /cm$^2$. The range and energy loss of ions was calculated using Stopping Range of Ions in Matter (SRIM) code [31]. The structural characterization was done using Glancing X-Ray Diffractometer (GXRD). Magnetic measurements were carried out as described earlier.

7.3 RESULTS AND DISCUSSION

7.3.1 Dependence of film thickness and thermal annealing on Exchange Bias

From RBS (figure 2), zinc ferrite layer was found to be 120 nm thick with a composition of Zn 11.1%, Fe 22.2% and O 66.7% and FeNiMoB was 60 nm thick with a composition of Fe 19.1%, Ni 19.1%, Mo 1.5% and O 58.8%. This set of film is coded as FNMB-ZF1.

The film of higher thickness is coded as FNMB-ZF2. The zinc ferrite layer has a thickness of ~350 nm and a composition corresponding to Zn 12.5 %, Fe 25 %, O 62.5 %. The Fe-Ni-Mo-B layer was ~270 nm thick and has a composition of Fe 17 %, Ni 17 %, Mo 3% and O 63%.
Hysteresis curve at room temperature and at 10K with field cooling of films of different thickness and film annealed at 873K is shown in figure 3. It is evident that MH at 10K with field cooling exhibits an enhancement of the hysteresis loop along with field shift. The exchange field $H_E$ value for FNMB-ZF1 was 75 Oe. FNMB-ZF2 exhibited an exchange field of 50 Oe and on annealing the exchange field increased to 63 Oe. No major changes in exchange field was observed with film thickness and annealing.
The observed exchange bias effect in FeNiMoB-Zinc ferrite bilayer film is not due to FM-AFM interaction, because thin film forms of zinc ferrite are not antiferromagnetic at 10K. They exhibit ferrimagnetic ordering along with glassy behavior [22, 32]. Studies on zinc ferrite thin films presented in previous chapters also suggest the existence of glassy behavior. Many groups have reported exchange bias in spin glass ferromagnetic system [3, 17, 33]. In such cases the spin glass is considered to be diluted AFM system with long range interaction [3].
All related effects of exchange bias in FM-AFM systems are observed in FM-SG systems also. Thus the exchange bias observed in the present system could also be attributed to FM-SG interaction. The wide discrepancy between FC and ZFC in the MT curve (figure 4) also indicates glassy state of the system. The blocking temperature $T_B$ for pristine film is 100K and is found to be independent of thickness.

![Fig. 4 FC-ZFC of a) FNMB-ZF1 b) FNMB-ZF2](image)

**7.3.2 Dependence of swift heavy ion irradiation on Exchange Bias**

The electronic energy loss of 100 MeV ions in zinc ferrite is 0.015 MeV/nm as simulated using SRIM code (figure 5) [31]. The range of ions is about 12μm, which is much greater than the film thickness. The ions on traversing through the zinc ferrite layer of thickness 400 nm lose energy of 6 MeV and the remaining 94 MeV is transferred to the next layer. The energy loss in FeNiMoB layer is 0.016 MeV/nm. The range of ions in this layer is about 11μm, and the ions get deposited in the substrate terminally.
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Fig. 5 Energy loss of 100 MeV ions in a) zinc ferrite and b) FeNiMoB

In the GXRD studies, (figure 6) the (311) plane corresponding to spinel zinc ferrite is observed. It is difficult to obtain the Fe-Ni phase for the second layer by GXRD due to the nominal concentration of Fe-Ni crystallites. The crystallite size is calculated using Scherrer formula and is ~ 7 nm. The (311) plane narrows out on annealing at 873K and consequently the crystallite size increases to 12 nm. The crystallite size increases for films irradiated at \(1 \times 10^{11}\) ions/cm\(^2\) and is ~15 nm and reduces to ~10 nm at \(1 \times 10^{12}\) ions/cm\(^2\). At higher fluences, complete amorphisation of films takes place.
Fig. 6 GXRD pattern of a) pristine film b) film annealed at 873K, film annealed at 873K and irradiated at fluences of c) $1 \times 10^{11}$ d) $1 \times 10^{12}$ e) $1 \times 10^{13}$ and f) $3 \times 10^{13}$ ions/cm$^2$

FC-ZFC measurements (figure 7) were conducted to study the magnetic ordering and the influence of ion fluence on $T_B$. The $T_B$ for the sample irradiated at fluence of $1 \times 10^{12}$ ions/cm$^2$ is around 100K same as that of pristine film. On irradiation not much changes in blocking temperature was observed. However $T_{irr}$, the temperature at which FC-ZFC curve bifurcate shifts to room temperature at higher fluences. The large irreversability between FC and ZFC indicates glassy behaviour of the system. The saturation of FC below $T_B$ is also indicative of a glassy behaviour.
Fig. 7 FC-ZFC curves of FeNiMoB-Zinc ferrite film annealed at 873K and irradiated at fluences of a) $1\times10^{12}$ b) $1\times10^{13}$ and c) $3\times10^{13}$ ions/cm$^2$

Hysteresis (MH) loops at room temperature and at 10K of the irradiated films with field cooling of 5000 Oe are shown in figure 8. An exchange field of around 50 Oe is observed in the pristine film and on annealing at 873K, the exchange field increased to ~63 Oe (figure 3b-3c). On irradiation, it is observed that at low fluences, in particular $1\times10^{11}$ and $1\times10^{12}$ ions/cm$^2$, exchange field shows an enhancement and then decreases on further increase of ion fluence. A maximum exchange field of 210 Oe is observed for the film irradiated at $1\times10^{12}$ ions/cm$^2$. The $H_E$ value decreases to ~25 Oe for film irradiated at $1\times10^{13}$ and
3×10^{13} \text{ ions/cm}^2. The variation of exchange field with ion fluence is shown in figure 9. Apart from variation in exchange bias field and coercivity, other phenomena related to exchange bias like loop widening and shift in positive magnetization is also observed.

Mougin et al. explained the change in exchange field with low energy ion irradiation with the help of a diluted AFM model [15]. He proposed that ion irradiation creates defects in the AFM and these defects act as pinning centres and thereby enhances the exchange field. The ion beam mixing at the interface presumably destroys magnetic order and suppresses exchange field. The net effect of ion dose on exchange field is given by the following expression

$$\frac{H_{EB}}{H_{EB,ini}} = (1 \pm aptN) \times e^{-b_1 N}$$  \hspace{1cm} (7.1)

where $H_{EB}/H_{EB,ini}$ is the normalised exchange bias field with respect to exchange field before irradiation, ‘N’ is the ion dose, ‘t’ thickness of AFM layer, ‘p’ the probability of the atom to be displaced per incoming ion per unit length, ‘a’ the parameter that describes the efficiency of the ion to create a defect in AFM and ‘b_1’ is the parameter that indicates the efficiency of the defect at the interface to decrease exchange field. Most of the experiments carried out on irradiation induced exchange bias follow this equation; according to which, an increase in exchange bias is observed at low fluences and at higher fluences exchange bias is decreased [19, 34].
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Fig. 8. MH loops of FeNiMoB-Zinc ferrite film annealed at 873K and irradiated at fluences a) $1 \times 10^{12}$ b) $1 \times 10^{13}$ and c) $3 \times 10^{13}$ ions/cm$^2$ (inset shows enlarged graphs)

Our experimental result is fitted by using equation 7.1 and the fitting is found good at lower fluences, while at higher fluences, an exact fitting with experimental data is not possible (figure 9). The value of a and b was observed to be 0.6 and 18. Thus, the observed increase in exchange bias at low fluences can be explained as a result of defect creation in the zinc ferrite layer. These defects act as pinning centres for domain wall formation which can reduce the domain wall energy leading to stabilisation of the system. The formation of domain walls
results in enhanced loop shift. Further increase of ion fluence leads to excessive ion beam mixing at the interface, which affects the magnetic order in AFM layer. This decreases exchange coupling and thereby the exchange bias.

![Graph](image)

**Fig. 9 Variation of exchange field with ion fluence**

The variation of coercivity with ion fluence is shown in figure 10. $H_c$ initially increases, exhibits a maximum value of 610 Oe at $1 \times 10^{12}$ ions/cm$^2$ and then decreases. The correlation between coercivity and exchange field can provide information regarding the microscopic origin of exchange anisotropy and was studied by different groups [35, 36, 37, 38]. Leighton et al. observed that the enhancement of coercivity is proportional to the exchange coupling and the increase in coercivity is attributed to enhanced pinning of domain walls [35]. Morales et al. observed no direct correlation between coercivity and exchange field in Ni and Py layers [38]. In our study we have observed direct relation between variation of coercivity and exchange field with ion fluence and is fitted using equation 7.1. The fitting parameters a and b are 2 and 21. According to the
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theoretical fit, the variation of coercivity can be explained as follows; at low fluences, the defect enhances the coercivity, while at higher fluences mixing of ions lowers the coercivity. The mechanism responsible for variation of exchange field with ion fluence is also responsible for the variation of coercivity.

Fig. 10 Variation of coercivity with ion fluence

The sample irradiated at $1 \times 10^{12}$ ions/cm$^2$ which exhibits the maximum exchange field was subjected to field cooled MH measurements at different temperatures of 40K, 50K, 80K, 100K and 120K (figure 11). No field shift is observed which establishes the fact that exchange field is observed far below the transition temperature which is 100K in the present case.
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![MH loops of film irradiated at fluence of $1 \times 10^{12}$ ions/cm$^2$ at different temperatures](image)

7.4 CONCLUSION

In summary, FeNiMoB-Zinc ferrite bilayer films exhibiting exchange bias was fabricated by RF sputtering at different FM and AFM thicknesses. Exchange bias was observed in FeNiMoB-Zinc ferrite films of both thicknesses and is attributed to FM-SG coupling. The exchange bias decreased on increasing the FM-AFM thickness and on annealing, significant changes in exchange bias was not observed.

The films annealed at 873K were irradiated with 100 MeV Ag ions at different fluences. Ion irradiation enhanced exchange bias at lower fluences and decreased at higher fluences. Highest exchange field of 2100e was obtained on irradiation at a fluence of $1 \times 10^{12}$ ions/cm$^2$. The variation in exchange bias with ion fluence is modeled based on the competition between defect creation in AFM layer and interfacial mixing. The defect created by ions act as pinning centers in the AFM and this causes an enhancement in exchange bias at lower fluences. At higher fluences, the defects destroy the order at the FM-AFM interface, and hence
exchange bias decreases. The behavior of coercivity with ion fluence follows the variation of exchange field which implies that both the exchange field and coercivity are correlated. Thus both exchange field and coercivity can be tailored by swift heavy ion irradiation.

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Conclusions and Future Scope