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Chapter 8
Magnetic alloys are an integral member belonging to the family of magnetic materials, which are of recent origin and increasingly being researched upon. They are amorphous in character and find extensive applications in many modern day devices. Metallic glasses belonging to the family of magnetic alloys is a new entrant and is promising and seen as a potential substitute to the existing conventional materials based on ferrites and permalloys. They are soft and the electrical conductivity is quite reasonable. Normally they are made in the form of ribbons. Though ribbons are amorphous in nature, nanocrystallinity can be induced and can be made crystalline. Newer applications like Magnetic Micro Electro Mechanical Systems (MEMS), Nano Electro Mechanical Systems (NEMS) and Tunnel Magneto Resistance (TMR) sensors necessitate that they are made in the thin film forms. The properties of ribbon and their thin film form need not be the same since ribbons are amorphous and on deposition they transform to crystalline.

Thin films of metallic glasses can be deposited on substrates from targets of appropriate compositions. Retention of the target composition in the film as well is an essential criterion. If one resorts to thermal evaporation, though good quality films can be obtained, the composition of the film are at variance with the parent target. This forces one to employ methods like RF sputtering and pulsed laser deposition. Though the target themselves are amorphous, the end film could be crystalline or vice versa. Hence post deposition thermal annealing is required to modify their magnetic properties. The employment of swift heavy ion (SHI) irradiation in the modification of magnetic properties is well known and thus SHI can be employed to modify the morphology and in turn the magnetic properties. This is part one of the present investigation, that is, fabricating thin films of metallic glass alloys based on Fe-Ni and the modification of their properties.
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Zinc ferrite in the bulk is a normal spinel and exhibits anomalous properties in the nanoregime. However, literature on their thin film forms are less abundant and an interesting area of research. Their modification by employing thermal annealing and SHI was another motive of the present study.

Exchange bias is a relatively newer phenomenon involving ferromagnetic-antiferromagnetic (FM-AFM) structures. A bilayer consisting of a zinc ferrite and metallic glass based on Fe-Ni was thought to be ideal where in zinc ferrite serve as an AFM/spin glass (SG) and Fe-Ni the FM component. This investigation was undertaken with a two pronged objective. Firstly, to see the feasibility of fabricating a bilayer exchange bias system, and secondly, to study the effect of SHI on the exchange bias and exchange field. This is phase two of the present investigation.

The salient findings of the present study is listed in this chapter. As it is natural for any human, we need to strive for perfection and in the search for perfection we often subject ourselves to criticism. All the demerits of this study is brought out as seen by the author and the scope for improvements and future studies is also discussed.

We started by depositing thin films from a target of Fe_{40}Ni_{38}Mo_{4}B_{18} by using RF sputtering method. From the compositional studies using X-ray Photoelectron Spectroscopy (XPS), it was found that we succeeded in incorporating Fe, Ni, Mo and B in the thin film; however the exact stoichiometry of the target composition could not be retained in the film due to the contamination of oxygen. Contrary to the target which was amorphous, thin films were crystalline and the phase was FeNiMoB which is predominantly non magnetic. However, the films were ferromagnetic at room temperature with
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diminished saturation magnetization. Post thermal annealing of these films did not improve their magnetic properties.

The next question that comes to our mind is can we improve the magnetic properties of FeNiMoB thin films? If the crystalline FeNiMoB phase is modified, there are chances that magnetic properties can be improved, as the amorphous counterparts exhibited superlative magnetic properties. To amorphise, SHI irradiation is a suitable technique. The high energy imparted to the material can cause localized high temperature zones and the sudden cooling when the ion transits results in amorphisation. SHI irradiation is a highly versatile technique used for nanostructuring and material modification. FeNiMoB films were irradiated using 100MeV Ag ions at different fluences. At an initial fluence of $1\times10^{12}$ and $1\times10^{13}$ ions/cm$^2$ an increase in grain size was observed from atomic force microscopy images, and at the highest fluence of $3\times10^{13}$ ions/cm$^2$, the grain size decreased rapidly. On irradiation, the crystalline FeNiMoB phase has been completely eliminated. The decrease in grain size along with amorphisation at the highest fluence of $3\times10^{13}$ ions/cm$^2$ substantially enhanced the magnetic properties of FeNiMoB thin films.

Zinc ferrite, an antiferromagnet with a Neel temperature of 10K is a normal spinel in the bulk. Thin films and nanostructures of zinc ferrite exhibit altogether different magnetic properties due to cation redistribution. Thus nanosized zinc ferrite is a subject of intense studies. Zinc ferrite thin films were prepared by RF sputtering and they exhibited room temperature ferrimagnetism with a saturation magnetization of 120emu/cc. The shift in the blocking temperature from 10K to higher temperatures is attributed to cation redistribution resulting in a possible $J_{AB}$ interaction. Zinc ferrite sample also exhibited spin glass behavior. Thermal annealing deteriorated the magnetic properties by lowering the
saturation magnetization and lowering the blocking temperature. On annealing, the cations have a tendency to reverse back to the normal spinel structure.

The formation of latent tracks in ferrites by swift heavy ion irradiation offers possibilities to study the stress induced magnetic properties. Zinc ferrite thin films were irradiated with 100 MeV Ag ions. The crystalline percentage of the spinel structure reduced on ion irradiation. At initial fluences, the grain size decreased and at the highest fluence of $3 \times 10^{13}$ ions/cm$^2$ the grain size enhanced. This increase in grain size was visible from atomic force microscopy images and is due to agglomeration. The magnetic properties were dependent on grain size and highest saturation magnetization was for the pristine sample. With ion irradiation, the magnetization shows an initial decrease and at highest fluence a nominal increase was observed. This has been correlated with grain size. Another interesting observation was that at 5K of temperature, the pristine samples did not saturate even at the highest applied field of 60 kOe. But as irradiation progressed, films attained saturation at very low fields. Irradiation reduced the antiferromagnetic contribution.

It is well known that an FM-AFM or a FM-SG can exhibit exchange bias effect and these kinds of exchange coupled systems are highly desirable in various spintronic devices. The ferromagnetic property of FeNiMoB films can be coupled with the antiferromagnetic or spin glass property of zinc ferrite. To realize an exchange bias system we have adopted a bilayer structure of FeNiMoB and zinc ferrite. The role of thickness, thermal annealing and ion irradiation on the exchange bias was examined. The bilayer film of FeNiMoB and zinc ferrite exhibited exchange bias at 10K with an exchange field of 75 Oe. The observed exchange bias was attributed to FM-SG interaction. On increasing the layer thickness exchange field reduced to 50 Oe and on annealing a small increase of
13 Oe in exchange bias was observed. Appreciable changes in exchange bias properties could not be obtained by altering the thickness and annealing temperatures.

As the exchange bias is influenced by the interface, modification of interface can substantially cause changes in exchange field. The bilayer films were irradiated using 100 MeV Ag ions. The exchange field increased at initial fluence, reached a peak value of 210 Oe at a fluence of $1 \times 10^{12}$ ions/cm$^2$, and then decreased on further increase of ion fluence. The variation of exchange field with ion fluence is modeled as a competition between ion induced defect formation and interfacial mixing. At lower fluences, ions create defects in the AFM and these defects can act as pinning centers for domain wall formation thereby enhancing the exchange bias. At higher fluences, due to interfacial mixing the exchange field gets suppressed. Thus the role of ion irradiation as an efficient tool to modify the exchange bias was examined.

Further systematic studies on preparation of FeNiMoB by RF sputtering by changing the deposition parameters like RF power may result in the formation of magnetic Fe-Ni phase. The oxidation of these films is a major cause for worry and a reason for the decrease in magnetization. The target composition could not be retained due to oxidation. Passivation is an alternative, and can be passivated by coating a thin film of gold or a polymer.

Even though zinc ferrite films exhibited room temperature ferrimagnetic behavior; the actual reason for this change is still elusive. Extensive studies on deducing the structure and the cation distributions have to be performed by high end analytical tools such as Extended X-ray Absorption Fine spectroscopy (EXAFS) and neutron scattering. The track formation in spinels as a result of ion irradiation also has to be visualized by cross sectional TEM. Once the tracks and
its diameter are evaluated by appropriate tuning of ion energy and fluence, the track diameter can be tailored and nanostructures can be obtained.

The main application of exchange coupled systems is in magnetic tunnel junctions. The pinning of ferromagnetic layer can be achieved by exchange coupling with an AFM. But most of the AFM materials have Neel temperature below room temperature which are not of much use from an application point of view. Fabricating an exchange coupled system, under an applied magnetic field will ensure proper alignment of the top AFM layer. The modification of exchange bias properties by SHI is a highly efficient method. But visualization of interface by cross sectional TEM is rather difficult. The exact cause of the change can be ascertained only after observing the interface. Also, micromagnetic simulation on ion induced modifications can be looked after as a theoretical study.

When a thesis is being submitted a barrage of questions crop up in one’s mind, very often the questions transcend from science to philosophy and society. A few of the pertinent questions are, whether I could deliver what I intended? Whether my thesis has the required quality, whether this piece of investigation going to benefit the society at large or not! Most often the answers to these questions are found in the very philosophy of research itself. That is, if this work is not earth shattering, has it added value to the existing? In this case, the answer is yes, it has contributed incrementally. This is often referred to as incremental science! Every thesis contributes incrementally to the knowledge base. This thesis is no exception to this! Pondering over the question of reproduction of results or repeatability, one often, repeats the experiment twice or thrice, the idea is to ‘kill’ the new result, if it remerges like the phoenix it is accepted and a new result. The observance of exchange bias in a bilayer film of FeNiMoB-zinc ferrite was repeated and verified as a new result.
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Another obvious criticism is the employment of SHI for material modification, which is exorbitantly expensive and not suitable for large area application. However one take solace in the fact that if one can thoroughly understand the Physics behind the modification of material properties by SHI, a suitable inexpensive ‘down to earth’ technique can be devised to achieve the same effects. This is positive thinking and is earmarked for future.

In this investigation we have only looked at the possibility of an exchange coupled system using a bilayer of FeNiMoB and zinc ferrite. Fe-Ni based alloy thin films can also be used to fabricate TMR sensors and or even a cantilever consisting of a Fe-Ni phase for sensing gases or magnetic fields. These are some devices which can be fabricated by simple fabrication technique. However these propositions are futuristic. With the emergence of internet of things sensors are going to play a significant role. So metallic glasses can be a component of a energy harvester along with a magneto electric component for self driven sensors.

Any researcher who does not think differently and do not intend to innovate is not delivering his duty. Finally let me conclude with the words of JRD Tata, “More than ever before we must be ready to think every problem afresh, to change and innovate”.

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