Chapter 1

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Since the discovery of the first magnetic material Loadstone, there has been intense development in magnetic materials. The invention of magnetic compass for navigation revolutionized the magnetism world. Today the new discoveries of magnetic materials have made it possible to develop various practical devices which work based on the principles of magnetism. One of the rapid technological advancements in the middle of the 20^{th} century is the application of magnetic property in the information storage device in computer technology. The density of storage devices has increased almost exponentially by successful fabrications of magnetic thin films. Almost all (nearly 90%) of the storage technologies use magnetic materials in either thin films or multilayer form [1,2]. Each bit of information is stored in a group of several magnetic grains (magnetic domains) in which the magnetic moment is directed in a particular direction or in the opposite direction that represents a binary code (0 or 1). The discovery of giant magnetoresistance (GMR) has boosted the technological development of storage technology, magnetic sensors, and magnetic actuator in which the resistance is manipulated by the spin orientation [3]. The GMR phenomenon is also made possible to fabricate a device called spin-valve sensor that can detect a bit stored in the storage media by measuring the change in resistance. The enhancement of the areal density of storage media can be achieved by reducing grain size to store one bit of information. However, superparamagnetic effect [4] has put a limitation on the reduction of bit size to increase storage density. The superparamagnetic effect occurs in sufficiently small ferromagnetic or ferromagnetic nanoparticles in which the magnetization randomly flips direction under the influence of temperature and their net magnetization appears to be zero if measurement time is greater than Neel relaxation time [5–7]. The superparamagnetic limit i.e., the thermal stability may be defined by the equation $K_U V/K_B T \approx 25$ [4,8]. Where, K_U is the anisotropy energy, V is volume, K_B is the Boltzmann constant and T is the temperature. Thus for an isolated single-domain particle with certain anisotropy energy K_U, the

volume V determines its thermal stability. Thus reduction in bit size must be accompanied by increasing anisotropy of the magnetic material to counter the superparamagnetic limit. Since then focus of the researchers was shifted to the read/write sensors based on in-plane magnetic anisotropy materials and magnetic materials with large anisotropy energy have been intensively investigated. Another way to increase areal density is to magnetize bits in a perpendicular direction for which large perpendicular magnetic anisotropy is required. Thus magnetic materials with perpendicular magnetic anisotropy have attracted the interest of researchers for perpendicular recording media. Therefore the research focus has moved from traditional materials like FePd, CoCrPt, etc. to materials with large magnetic anisotropic energy such as CoPt, SmCo, etc. [2,9]. The RE-TM and FePt-based alloys received interest because these materials exhibit large magnetic anisotropy and their magnetic properties can be easily manipulated by varying various parameters like deposition condition, film composition, film thickness, insertion of under layer and over layer, annealing condition, film surface roughness, etc. [10–16]. In this thesis work, the magnetic properties of Co-based RE-TM and Co-doped FePt ternary alloy thin films have been investigated.

1.1 Fundamentals of Magnetism

Magnetism occurs in magnetic materials due to the coupling of electronic spin and associated magnetic moment to one another and forms magnetically ordered states. The coupling, which is a quantum mechanical in nature, is known as the exchange interaction and is rooted in the overlap of electrons in conjunction with Pauli's exclusion principle [17,18]. Whether it is a ferromagnetic, antiferromagnetic, or ferrimagnetic, the exchange interaction between the neighboring magnetic ions will force the individual moments into parallel (ferromagnetic) or antiparallel (antiferromagnetic) alignment with their neighbours. The exchange energy can be written for many-electron atomic spin $\overrightarrow{S_1}$ and $\overrightarrow{S_2}$ in Heisenberg Hamiltonian [19,20] as-

$$H = -2J(\widehat{S_1}.\widehat{S_2})$$

Where S_1 and S_2 are dimensionless spin operators, and J is the exchange parameter. For positive J, the parallel configuration of spin has lower energy and for negative J, the anti-parallel configuration of spin has lower energy. The three types of exchange which are currently believed to exist are, (a) direct-exchange, (b) indirect-exchange, and (c) super-exchange.

1.1.1 Ferromagnetism

Ferromagnetism occurs in a special class of materials where the outermost shell electrons of the atom are free. These free electrons interact strongly through exchange forces and the spins are aligned in a particular direction within a region called magnetic domain even in the absence of external applied magnetic field. Thus, the most striking feature of ferromagnetism is the spontaneous magnetization. Another intrinsic feature of the ferromagnetic material is a hysteresis loop shown in Figure 1.1, which is the nonlinear response of magnetization (M) to an applied field (H). Magnetization is the magnetic moment per unit volume of the magnetic material.

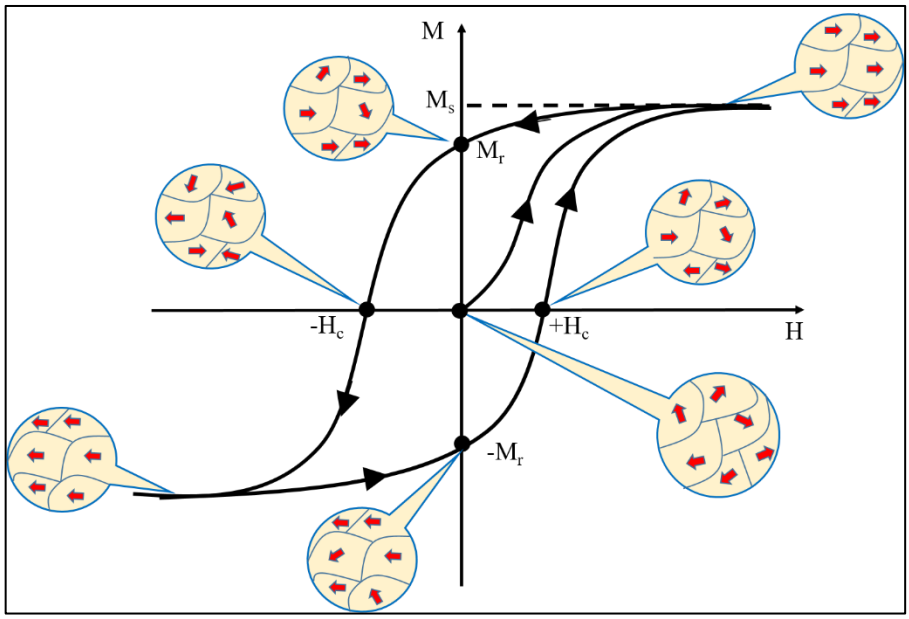

Figure 1.1. Schematic diagram of M-H hysteresis loop of a ferromagnetic material.

On application of an external magnetic field, the spontaneous magnetization at the microscopic level in magnetic domain starts aligning in the direction of applied field and the magnetization increases nonlinearly with the applied field, thereafter

saturating at a certain value of the applied field called saturation magnetization (M_S). At saturation magnetization, the spontaneous magnetizations in all magnetic domains of the material are aligned in the direction of applied magnetic field. On removal of the magnetic field, the spontaneous magnetization in magnetic domain starts aligning in a random direction due to thermal energy and the net magnetization starts decreasing. However, the few spontaneous magnetizations in the magnetic domain remain frozen in the direction of magnetic field and so the net magnetization does not decrease to zero at zero applied fields. The value of magnetization at zero field is called remanent magnetization (M_r). To reduce the magnetization to zero, a magnetic field must be applied in opposite direction called the coercive field (H_C). The schematic of domain structure at various applied magnetic fields is illustrated in Figure 1.1. Ferromagnetic materials can widely be classified as soft and hard ferromagnetic materials. Soft ferromagnetic materials have a narrow hysteresis loop and hence magnetization decreases as soon as the applied magnetic field is removed. While hard ferromagnetic materials have a broad hysteresis loop. When sufficiently large magnetic field is applied to saturate the magnetization, they remain in magnetized state on the removal of magnetic field and hence are suitable for application as permanent magnets [19]. Spontaneous magnetization also depends on temperature. At a certain temperature called Curie temperature (T_C), the spontaneous magnetization drops to zero [21]. Thus above T_C, ferromagnetic ordering collapses and changes to a disordered paramagnetic phase. In the paramagnetic regime, the magnetization (M) varies linearly at low applied fields (H). Below T_C, the magnetic susceptibility which is defined by $\chi = M(T)/H$ follow Curie-Wiess law [19–22] given by-

$$\chi = \frac{C}{T - T_C}$$

Where C is known as the Curie constant. Whereas above T_C in the paramagnetic regime, the susceptibility follows the Curie law given by [19,21]

$$\chi = \frac{C}{T_C}$$

Where C is a constant.

1.1.2 Antiferromagnetism

In antiferromagnetism, the atomic magnetic moments form two magnetic sublattices with equal magnetization but in opposite directions. So the net magnetization of antiferromagnetic material is zero [23,24]. The antiferromagnetic materials undergo a phase transition at Neel temperature (T_N) and the susceptibility exhibit a small peak at the T_N [19].

1.1.3 Ferrimagnetism

Ferrimagnetism originate from antiferromagnetic material due to a net non-zero magnetization. In ferrimagnetism, the atomic magnetic moments form two magnetic sub-lattices with unequal magnetizations in opposite direction [23]. The unequal magnetic moment of two sublattices may arise due to different numbers of a similar moment in two sub-lattices or equal numbers of dissimilar moments or due to the presence of two different moments in one sublattice and one of the two moments in the other sublattice [23,24]. Sometimes same atoms sit at two different lattices in the crystal making them behave differently. Both these atoms couple antiferromagnetically but with unequal moments. So there exist spontaneous magnetization which leads to ferrimagnetic ordering. One of the most famous ferrimagnetic materials is magnetite which has a spinel structure with the formula Fe_3O_4 [20].

1.2 Magnetic Anisotropy

1.2.1 Perpendicular Magnetic Anisotropy

Usually, the microscopic ferromagnetic domain is constrained to lie along easy axes, the direction along which the magnetization is saturated at the lower applied field. Hard magnetic material possesses a strong easy axis while soft magnetic materials possess near zero anisotropy. Generally, magnetic anisotropy is expressed by [19]

$$E_a = K_u sin^2\theta$$

Where, E_a anisotropy energy, K_u is anisotropy constant and θ is the angle between the easy axis and magnetization. In thin films, if the easy axis lies along the

direction of the plane of the films the anisotropy is termed as in-plane anisotropy. If the easy axis i.e. the film is magnetized at a lower applied field along the direction perpendicular to the film plane such film is said to be exhibiting perpendicular magnetic anisotropy. There are different magnetic anisotropies. These are Magneto crystalline anisotropy, Shape anisotropy, Induced magnetic anisotropy, Stress anisotropy, and Surface and interface anisotropy. The magneto crystalline anisotropy is an intrinsic property of the material that originates from the crystal field interaction and spin-orbit interaction of electrons. Along different crystallographic axes, the orientation of spin-orbit interaction is different and hence the magnetization process. Along certain crystallographic axes, the material is easily magnetized while in other directions the magnetization saturates at a higher applied field leading to magnetic anisotropy [19,20,25,26]. The shape anisotropy is not an intrinsic property of magnetic materials but derives from the demagnetizing field which depends on the direction of magnetization and the shape of the sample. The shape anisotropy generally arises in non-spherical samples without the preferred orientation of grains [19,20]. Magnetic anisotropy can also be induced by the external application of stress or by depositing the sample and/or annealing the sample under an external magnetic field. Such anisotropy is called induced magnetic anisotropy. All these magnetic anisotropy arises in the constant lattice. When there exist lattice deformation, the anisotropy behaviour of material changes due to magneto-elastic interaction and reduced symmetry of the unit cell. This phenomenon is known as stress anisotropy. In low-dimensional materials surface and interfaces of the material also play a significant role in magnetic anisotropy. The broken symmetry at the surfaces and interfaces the magnetocrystalline anisotropy energy is modified by the surface and interface anisotropy energy which is forbidden for three dimensional material systems [20,27,28].

1.2.2 Estimation of Effective Magnetic Anisotropy Energy

To quantify the magnetic anisotropy, it is worth calculating the effective magnetic anisotropy energies (K_{eff}). The field range at which the magnetization of both in-

plane and out-plane M-H curves are saturated is called an anisotropy field. One of the easiest methods for estimating the K_{eff} for thin films is from the area enclosed by the M-H loop. Both in-plane (longitudinal) and out-of-plane (perpendicular) M-H curves are plotted together by retaining only initial magnetization curves. The area enclosed by longitudinal and perpendicular initial magnetization curves and the y-axis (field) is then calculated by integrating. The difference in the area enclosed by perpendicular and longitudinal magnetization curves is the indicative value of effective anisotropy energy [11,29–33]. The other method to estimate the effective anisotropy energy from the M-H loop for a perfectly square M-H loop is by using the equation $K_{eff}=H_kM_S/2$, where M_S is saturation magnetization and H_K is anisotropy field [34–36]. The anisotropy field H_k is measured at which saturation magnetization of the easy axis M-H curve and extrapolation of unsaturated magnetization of the hard axis M-H curve intersect [37].

1.3 Magnetic Anisotropy of RE-TM and FePt-Based Alloys Thin Films: Literature Review

1.3.1 Perpendicular Magnetic Anisotropy of RE-TM Alloys and Review on Various Materials

Magnetic anisotropy in amorphous rare-earth-transition metal (RE-TM) alloys has been one of the major subjects of a number of investigations in magnetism in recent years. The materials with perpendicular magnetic anisotropy have attracted researchers for academic research and their potential applications in various practical devices such as spintronics, perpendicular magnetic recording media, random access memory STT RAM, etc. The magnetism of 14 rare earth (RE) elements arises primarily due to the partially filled *4f* orbital. On the other hand, the magnetism of transition metal (TM) occurs due to *3d* orbital electrons. In RE-TM alloys two sublattices, one RE-sublattice and the other TM sublattice are formed and result in net magnetization from the two sublattices. In RE-TM alloys with light RE elements (number of *4f* electrons<7), the two sublattices are exchange-coupled ferromagnetically. On the other hand, in RE-TM alloy with heavy RE elements

(number of *4f* electrons ≥7), the two sublattices are exchange-coupled antiferromagnetically, forming a ferrimagnet [38]. The net magnetization of RE-TM alloys is dependent on concentration and temperature and is either along the RE sublattice or TM sublattice [39,40]. Since TM elements have high Curie temperatures, the magnetization of RE sublattice has a strong dependence on temperature, and also Curie temperature decreases with an increase in RE content of the alloy. At particular temperatures called compensation temperature T_{com} the magnetization of the two sublattices becomes equal and opposite resulting in zero net magnetization. Below T_{com}, the net magnetization of RE-TM alloys is parallel to the RE moment and above T_{com} it is parallel to the TM moment [38]. RE-TM alloys, such as RE=Gd, Tb, Dy, Ho, etc., and TM=Fe, Co, Fe-Co alloys, etc. all form amorphous ferromagnetic alloys. Despite their amorphous nature, these compounds exhibit a wide range of magnetic parameters such as spin-orbit coupling, exchange coupling, perpendicular magnetic anisotropy, magnetic compensation temperatures, etc. [38]. The magnetism of Co-based RE-TM alloys is less sensitive to structural disorder and so the transition from crystalline to amorphous is associated with less dramatic changes in magnetic properties [40]. The Curie temperature for Co-based amorphous RE-TM alloys is however higher than the corresponding crystalline counterparts due to structural disorders such as fluctuations in the nearest-neighbor distance and coordination number [41].

Since the last 60 years, magnetic properties, in particular, the anisotropic behaviour of alloy thin films as well as multilayers have been studied extensively. Rare earth-transition metal (RE-TM) amorphous alloy thin films are found to show relatively large uniaxial magnetic anisotropy. Typically the value of anisotropic constant is of the order of 10^5 to 10^7 erg/cc with its axis perpendicular to the film plane [42]. The anisotropic constant K_u is an important property for the application in various practical devices like magneto-optical memory, spintronics, magnetic RAM, etc. However, the origin of K_u in the RE-TM amorphous system is still hardly known. Magnetic anisotropy in RE-TM amorphous materials is closely related to the preparation conditions and deviation from isotropy in arrangements of atoms in these amorphous alloys [43–45]. Magnetic anisotropy generally occurs from three mechanisms [45], (1) anisotropy arising due to spin-orbit coupling, which is either

single-ion anisotropy or anisotropic exchange, (2) Anisotropy involving magnetic dipolar interactions, which originate from microscopic atomic moment pairs and anisotropic microstructural heterogeneity, and (3) Anisotropy involving magnetostriction and anisotropic stress distributions. Gambino and Cuomo [46] showed that the magnetic anisotropy of the GdCo amorphous system increases with sputtering bias voltage upto a certain critical bias voltage and thereafter decreases with further increase in bias voltage. They proposed a model to explain this phenomenon in which they treated the selective re-sputtering responsible for the formation of anisotropic pair ordering with respect to the growth direction. Mizoguchi and Cargill [45] suggested that magnetic dipolar interactions make large contributions to magnetic anisotropy in amorphous GdCo-based ferromagnetic alloy systems where the alloys contain structural anisotropies at either atomic or microstructural scales. They also pointed out that the shape anisotropy from a columnar structure would be much smaller required to be accounted for the observed K_u [45,46]. On the other hand, inverse magnetostriction may be regraded responsible for a part of K_u [46]. Another observation has also been reported that the major part of K_u, remains even after films are removed from substrates [47–49]. This indicates that other mechanisms are involved in the formation of magnetic anisotropies in these amorphous RE-TM alloy systems. The single ion anisotropy of RE-atoms on the other hand is supposed to play important role in the formation of K_u. Yoshino *et al.* [48] also reported that the annealing of the amorphous TbCo films also influences perpendicular anisotropy considerably along with bias voltage. Manli Ding and S. Joseph Poon [50] have shown that the magnetic anisotropy of amorphous RE-TM ferromagnetic GdFeCo films is very sensitive to the composition as well as the temperature. TbCo ferromagnetic amorphous alloy films exhibit strong bulk PMA as a function of film thickness. The nonmagnetic Ta underlayer plays a significant role in enhancing the PMA which also serves as a source of spin-orbit torques essential property for application in spintronic devices [12]. These amorphous films offer tunable magnetic properties for application in various nano-magnetic devices. Ching-Ming Lee *et al.* [51] reported the annealing effect of coercivity and perpendicular anisotropy constant of GdFeCo and TbFeCo amorphous films. They have shown that the coercivity and

anisotropy constant are reduced upon annealing treatment of the film combined with the insertion of an underlayer and overlayer. There has been a number of reports which established that the nucleation and domain wall propagation of TbCo and TbFe based RE-TM alloy films at a field lower than the coercive field are thermally activated [52–56].

The magnetic properties of RE-TM alloy films are also found to be sensitive to the film surface roughness. The key factor from which coercivity arises in amorphous RE-TM films is the interaction between the domain wall and features of the film such as impurities, density fluctuation, surface roughness, etc. on the scale of domain wall width which act as pinning centers [57–61]. The roughness of the underlayer can also introduce pinning sites which then impede the domain wall movement thereby affecting the coercivity of RE-TM films [62,63]. Katayama *et al*. studied the influence of Al-underlayer on the coercivity of laser-assisted TbFeCo magnetic recording media [64]. Their results showed that the coercivity of TbFeCo increases for Al-underlayered film due to interface roughness of the Al-underlayer. A shifting of magnetization reversal process from wall motion mode to a rotational mode along with the change in magnetic anisotropy was also observed for underlayered films [65,66]. Such magnetization reversal shifting process arises due to the pinning of domain wall motion due to underlayer surface roughness. On the other hand, it is usually observed that a flatter interface deteriorates the perpendicular anisotropy of thin magnetic layer [60,62].

The important parameter of magnetic material for application in practical devices is magnetization reversal and in these films is mainly due to domain wall motion [54]. One of the most famous effects of the interaction of light with magnetic materials known as the magneto-optical Faraday effect has successfully been utilized in switching the magnetization using light. Due to Faraday effect the polarization of incident light changes upon transmission through the magnetic material. The inverse effect of the change of magnetic state of the magnetic material by polarized light is also observed [67,68]. Thus the magnetization in RE-TM alloys can also be switched by laser heating above the magnetic compensation point or above Curie temperature and subsequent cooling under an external magnetic

field [69–72]. It has also been reported that it is possible to switch the magnetization by using circularly polarized laser pulses in absence of external magnetic fields [67,73,74]. Such optical switching is also observed in several RE/TM multilayer films.

1.3.2 Magnetic Anisotropy of FePt and FePt-based Alloy Films and Review on Various Materials

Along with RE-TM metal alloys, the TM-TM metal alloys have also drawn considerable interest to the research community for various potential applications, particularly in magnetic storage technology. [11,31,33,75–81]. Since the superparamagnetic limit has been discovered with the reduction in bit size in thin film recording media one of the key challenges in the development of recording media is thermal stability [4,82,83]. In recent years, $L1_0$ ordered FePt-based alloy thin films have attracted the attention of researchers considerably because of their potential applications in high density perpendicular magnetic recording and heat assisted magnetic recording (HAMR) media [84–88], and magnetic random access memory [89,90] due to their large magnetic anisotropy energy density, magnetocrystalline anisotropy (MCA), and thermal stability.

Under normal preparation (as-deposition) conditions, FePt films are usually crystallized in chemically disordered FCC structure which tends to show (111) texture [91–95]. The Fe and Pt atom may occupy any lattice sites, either face center or corner or both due to disorder structure. This disordered FCC structure exhibit in-plane magnetic anisotropy with an easy axis along the film plane. They are found to possess low magnetic anisotropy energy and soft magnetic properties [85]. However, for the application of FePt and FePt-based thin films as magnetic recording media, they must be fully transformed from a disordered face center cubic (FCC) structure to $L1_0$ ordered face-centered tetragonal (FCT) structure. The chemically ordered $L1_0$ ordered FCT structure consists of an alternate stacking of Fe and Pt atoms along the *c* axis. $L1_0$ ordered structure can be obtained by two methods in epitaxial growth and non-epitaxial growth FePt-based films. In epitaxially growth films, heated single-crystal, textured substrates, and seed layers,

such as MgO, etc. can be used to grow the FePt-based films in the *c*-axis perpendicular to the film plane [96–98]. On the other hand, in non-epitaxially growth films FePt-based films can be first as-deposited on the substrate (Si/glass, etc.) directly in the form of continuous film or multi-layered structure and then anneal the as-deposited films at a temperature sufficient to transform into $L1_0$ structure [22,98,99]. The annealing temperature controls the growth and ordering of the FePt grains, on the other hand, annealing time controls the growth of FePt grains in a particular orientation.

For the application of FePt alloy in recording system, the ferromagnetic ordering temperature and structural ordering temperature have to be reduced and the easy axis must be tuned either parallel or perpendicular to the film plane according to the recording mode [93]. It was observed that the annealing of FePt films at elevated temperatures above 400 ℃ [82,83,88,89] transforms the disordered FCC structure to $L1_0$ ordered with an easy axis tilted 35° away from the plane of the film, which has to be further tuned in a direction parallel or perpendicular to the film plane [91,92]. The ordered FePt films fabricated by annealing of the films exhibit superior magnetic properties as compared to the disordered structure which is as-deposited [102–104]. As annealing and deposition of films at high temperatures can lead to a large grain size which becomes unsuitable for magnetic recording application, an effort has to be put to reduce the grain size either by third element doping to lower the annealing and deposition temperatures [105–107] or forming nanocomposite films [108]. So intensive investigations have been carried out on FePt alloy films, FePt-based bilayer films, and third element doped FePt-based ternary alloy thin films due to their potential application to replace the present conventional CoCrPt-based storage media [108–112] as well as application in high energy permanent magnets [113]. For application in high areal density (~ Tb/in^2) recording media, FePt-based films must have high magnetocrystalline anisotropy energy, beyond room temperature Curie temperature (T_C) and a high saturation magnetization (M_S) [114]. It has been reported by Wang *et al.* that annealing of FePt films under magnetic field can lower the structural ordering temperature [115]. They also observed larger coercivity for magnetic field annealed films than annealed films without magnetic field. The magnetic field

annealing at Curie temperature can be used to induce chemical order of (001) texture and induce perpendicular anisotropy [84]. The sputtering chamber base pressure of sputter-deposited FePt-based alloy films is also reported to play a significant role in the reduction of structural ordering temperature [116]. The magnetic properties like magnetic anisotropy, Curie temperature, structural ordering temperature, and crystallographic orientation of FePt alloy films can also be tuned by adding third elements such as Ag, Au, Cr, Zr, Mn, Cu, Ni, Nb, etc. [30, 32, 74, 95, 97, 103–107,108, 109] substrate temperature [124] as well as by varying thickness of films [125]. Substitutional doping of third elements such as *3d* transition metal (TM) or *5f* rare earth (RE) metal to replace Fe sites may help to reduce structural ordering temperature and T_C of $L1_0$ FePt-based alloy films maintaining the desired K_u and M_S. For instance, partial substitution of Cu to replace Fe sites has proven to reduce the ordering temperature and T_C of FePt films but results reduction in K_u and M_S due to tetragonal distortion [32,118,120,126–128]. The transformation to $L1_0$ ordered structure of Fe substituted FePtCu films were obtained by post annealing of film at 400℃ for a relatively short time of 10 seconds as reported by Gilbert *et al.* [120]. However, the M_S and K_u of the films are reduced due to the tetragonal distortion in the c-axis. On the other hand, $L1_0$ structure of $(Fe_{49}Pt_{51})_{1-x}Cu_x$ was obtained by annealing at 600℃ for 5 minutes as reported by Yan *et al.* in which they observed a steady reduction of saturation magnetization and coercivity with the increase in Cu content [129]. Takahashi *et al.* also reported the reduction of ordering temperature by the addition of Cu to 4 at. % from 600℃ to 400℃ which resulted in increased grain size and large coercivity [127]. The annealing temperature can further be decreased down to 350℃ by increasing Cu addition for films with the ratio of (FeCu) to Pt in the range of 1.1–1.2 which is accompanied by increased coercivity [128]. So tuning of Cu doping concentration is necessary to obtain high K_u and M_S along with reduced T_C and ordering temperature for application in future heat assisted magnetic memory [114,130]. In the study of nonstoichiometric sputtered deposited $(FePt)_{100-x}Cr_x$ films on naturally oxidized Si (111) substrate by Kuo *et al.*, the addition of Cr resulted in a reduction in magnetization and coercivity, and could inhibit the grain growth during annealing of the films [131]. They annealed the

deposited thin films at temperatures 300℃ to 750℃ to transform the soft γ-FePt phase to the hard γ_1-FePt phase. However, their study did not account for K_u of FePt films. The Cr addition to FePtCu ternary alloy film could also limit the grain growth even if the films were annealed at temperatures as high as 600℃ and enhanced the activation energy of ordering [132]. These Cr-doped FePtCu films also displayed a very large coercive force of 12.8 kOe and a small magnetization of 658 emu/cc. Different results were observed by Chu *et al.* in post annealed Cr-doped FePt films [133]. The post annealing was carried out at 600℃ under vacuum and their results showed a reduction in coercivity and increased saturation magnetization with the refinement of grain size. The vacuum annealing also retained the disordered FePt phase. In $(Fe\text{-}Cr)_{50}Pt_{50}$ films deposited at substrate temperatures of 100−500℃, an increase in K_u was observed with increase in Fe content, thus antiferromagnetic interaction may be expected due to Cr addition [134]. In Cr-substitution epitaxially growth FeCrPt film, sputter deposited at elevated temperature of 770℃, a strong reduction of perpendicular anisotropy and coercive field in easy axis direction has been reported by Schmidt *et al.* [135]. Their results also showed that Cr substitution above 20 at. % substantially reduces the Curie temperature to below room temperature.

Several researchers have also performed theoretical studies based on first principle calculations on substitutional doping of third elements such as Mn to FePt by replacing Fe with Mn [136,137]. Their calculations showed the reduction in anisotropy constant and coercivity with an increase in Mn-doping by increasing antiferromagnetic interaction. Another relativistic first principle calculation on the influence of Fe substitution by TM (=Cr, Mn, Co, Ni, Cu) of bulk $L1_0$ FePt alloy with fixed Pt was reported in [119]. Their calculations showed the changes in effective number of valence electrons which induced different tetragonal geometry and changes in magnetic anisotropy and net magnetic moment thus allowing the tuning of magnetic anisotropy and net magnetic moment. On the contrary, the experimental study by Manoharan *et al.* on a high temperature annealed/deposited Mn substitution doped FeMnPt ternary alloy film found a significant increase of coercivity due to tetragonal distortion resulting from the Fe site replaced by Mn [138]. But K_u and M_S were found to be maximum for undoped FePt than

epitaxially growth sputter deposited FeMnPt films as reported by Meyer and Thiele [139]. In their study, the films were deposited at the substrate temperature of 550℃ to achieve $L1_0$ ordered phase. In their study Mn addition to FePt resulted in a steady reduction of magnetocrystalline anisotropy and M_S of the films due to the antiparallel alignment of magnetic moments of Fe and Mn. Similar results were reported by C. A. Huang *et al.* on small percentage Mn doped molecular beam epitaxial grown $(FePt)_{1-x}Mn_x$ films [82]. In their study, the FePtMn were made by multilayer growth of Fe/Pt/Mn at 100℃ and post annealing at 600℃ to obtain $L1_0$ ordered structure. Their results showed that, a small percentage of Mn (=1%) exhibits better perpendicular magnetic anisotropy than undoped FePt film. Whereas reduction in perpendicular anisotropy was observed with the increase in Mn doping above 1 at. %. The effect of TM element Ni and Cu addition to FePt film on the structural property, ordering temperatures and magnetic properties such as Curie temperatures, perpendicular anisotropy and coercivity has also been intensively studied in the recent years [140–142]. For instance, in magnetron sputter deposited epitaxially grown $Fe_{55-x}Ni_xPt_{45}$ films at substrate temperature 550℃, a steady reduction in magnetic ordering temperature with increase in Ni content was reported by Thiele *et al.* [143]. Along with the ordering temperature, reduction in magnetization, perpendicular anisotropy, and perpendicular coercivity were also observed with Ni addition. R.f. sputter-deposited FePtNi films on glass substrates were reported by Dong *et al.* in which similar results of a steady reduction in perpendicular coercivity, magnetization, and Curie temperature were observed with Ni addition from 0 to 30 at. % [144]. In their study, the structure of as-deposited FePtNi films was transformed to $L1_0$ order by vacuum annealing at 550 ℃. Similar results were observed by Yan *et al.* in sputter-deposited FePtNi thin films made by multilayer growth of [Fe/Pt/Ni] [145]. They also observed a steady reduction in magnetization and coercivity with Ni-addition to the FePtNi films. They carried out rapid thermal annealing of as-deposited films at 600℃ for 5−10 minutes to transform to (001) oriented FCT structure. Though TM element addition to FePt film results in lowering of ordering temperature, the reduction in perpendicular anisotropy and magnetization can also be seen. The small percentage co-doping of B and Ag to FePt film in $(Fe_{0.48}Pt_{0.52})_{90}(B_{0.7}Ag_{0.3})_{10}$ film can effectively improve

the grain separation and formation of (001) texture due to high mobility of Ag [146]. With the increase in Ag content grain-refinement and c-axis orientation are further improved as reported by Tsai *et al*. Zhang *et al*. had successfully fabricated $L1_0$ ordered FePt and FePtC alloy films using electric treatment which is believed to be an alternative method that does not cause excessive growth of grain as thermal annealing [147]. The magnetic property measurement of these films showed enhanced coercivity, perpendicular anisotropy, and chemical ordering parameters with increase in applied voltage. The addition of RE elements such as Nd, Tb, Pr, etc. as third elements has shown significant reduction in ordering temperature and enhance coercivity of FePtX (X=Nd, Tb, Pr) films [30,148,149]. The RE elements can also be used to act as grain refiners by inhibiting grain growth [149]. Recently, Schmidt *et al*. have reported the influence of RE third element Gd addition to $L1_0$ FePt films sputtered deposited at elevated temperature of 800℃ [150]. Their results showed deterioration of $L1_0$ chemical ordering and reduction in perpendicular magnetic anisotropy, and saturation magnetization with the increase in Gd addition due to the antiferromagnetic interaction of Gd and Fe magnetic moment. They also observed the change of magnetization easy axis from perpendicular to in-plane for Gd addition at high atomic percentage. Recently, interstitial doped $L1_0$ FePt film by oxygen and nitrogen has been studied, and found that magnetocrystalline anisotropy significantly increased due to strong hybridization of d-orbitals with 2p-orbitals of O or N [151].

Along with third element doping, the insertion of underlayers has also proven an alternate method to reduce the ordering temperature and enhance the magnetic properties of FePt and FePt-based alloy thin films [152]. In particular, the insertion of an Ag layer of thickness 175 nm as an underlayer for $Fe_{55}Pt_{45}$ film of thickness 2.5 to 30 nm showed a contraction of FCC FePt unit cell constants in normal direction and expansion in film plane [91]. This induced a tendency for epitaxial growth FePt films to form $L1_0$ ordered phase in presence of Ag underlayer at low temperature due to crystal lattice mismatch between Ag (001) and FePt (001) [153]. Depending on the position (top, intermediate or bottom) of the Ag layer, the structural and magnetic properties of $L1_0$ ordered $Fe_{50}Pt_{50}$ films are found to be different [154]. The addition of Ag layer at different positions induces

mechanical stresses during deposition and annealing of the film due to the difference in coefficient of thermal expansion and lattice mismatch of FePt film, Ag layer, and substrate. This stress affects the ordering temperature which can reduce to a comparatively low temperature of 370℃ [154]. Similar results were reported in $Cr_{100-x}Ru_x$, CrMo, CrTi, CrW, etc. underlayered magnetron sputter deposited $Fe_{50}Pt_{50}$ thin films [155–157]. The $L1_0$ ordering temperature of $Fe_{50}Pt_{50}$ film was effectively reduced to 350℃ retaining good magnetic anisotropy and high coercivity. The insertion of Pt buffer layer between CrRu underlayer and FePt film was also found to influence the long-range order parameter and vary with the thickness of the buffer layer. A linear increase in out-of-plane coercivity of the films was reported with the increase in thickness of the Pt buffer layer [156]. The introduction of equiatomic AuCu underlayer of thickness 0-50 nm has also proven to reduce the $L1_0$ ordering temperature of FePt films from 600℃ to 350℃ retaining relatively high coercivity [158]. Thus lattice mismatch between films and underlayer plays a significant role in reducing the disorder-order transformation temperature and the thickness of underlayer has a significant influence on the coercivity of FePt films.

1.4 Applications of RE-TM Ternary Alloys

Starting from permanent magnet applications RE-TM, magnetic materials have been extensively studied for many other applications like recording technology, Spintronic applications, etc. Amorphous RE-TM alloy films such as α-GdCo and α-GdFe are intensively studied for application for magnetic-bubble-device and magneto-optic recording devices due to their uniaxial magnetic anisotropy property and remarkably good signal-to-noise ratio in thermomagnetically written thin films [44,159]. Ternary alloy films such as GdTbFe and GdTbCo are also extensively studied for their potential application in magneto-optical devices [54]. One of the industrial applications of these materials is magnetic random access memory (MRAM) and spin transfer torque (STT) MRAM. The iron-based RE-TM alloy films also exhibit large magnetostriction for which these materials become suitable for application for microactuators, microsensors, and tunable surface-

acoustic wave devices, and spin valve sensors [160–162]. The industrial applications of spin valve sensors include the magnetic read/write head, angular and linear sensors, integrated magnetic compass, etc. [163], and biomedical applications such as microelectrode for magnetic field probing, integrated cell cytometers, etc. [164]. Many different RE-TM ferromagnetic alloys and multilayers have been used in spin valves. In 1997 Bellouard *et al.* formed trilayer CoFe/Ag/CoFePd spin valve by inserting Ag in between CoFe and CoFeGd [165]. Other fabrications of spin valve devices with RE-TM alloys are FeCoGd/Cu/FeCoGd [166], Pt/Ta/CoGd/Cu/CoFe/Cu [167], Gd-Co/Co/Cu/Co [168], Ta/Gd/CoFe/Cu/ CoFe/FeMn/Ta [169] which are temperature dependent spin valves have been reported. These spin valve structures can also be used in magnetic recording with the advantage of current providing both magnetic field and switching heat. Other fabrications of RE-TM based spin valves include FeGd/Ta/DyCo5 [170], Ta/Tb/$Ni_{80}Fe_{20}$/ Cu/$Fe_{50}Co_{50}$/Gd/Ta [171], etc. which are potentially useful for ultrafast magnetic recording and high-frequency spintronic applications. The ferromagnetic RE-TM alloys have also proven as a potential candidate for application in spin-orbit-torque (SOT) devices as their magnetic property can easily be varied by varying composition and also as they exhibit PMA in the thin film as well as in bulk form. GdCo was the first reported RE-TM alloy fabricated as a magnetic layer for SOT device which had proven successfully to increase the efficiency of SOT effect near the magnetic compensation point [172]. GdCoFe is another potential candidate for use as a magnetic layer in the fabrication of SOT devices that exhibit interfacial torque with high thermal stability [173,174]. The ferromagnetic RE-TM alloys are also potential candidates for application for high speed domain wall devices as antiparallel coupling show faster spin dynamics than parallel coupling in ferromagnetic system [175]. The controlled domain wall manipulation has future application in 3D memory called racetrack memories in which information may be stored in a 3D array [176,177]. In recent years the switching phenomena of the magnetic moment about the hard axis called all optical switching has been observed in RE-TM alloy thin films such as GdFeCo [73], TbFe [178], TbCo [179–181], etc. This optical switching which is 1000 times faster than processional

switching [73,182,183] by the external magnetic field can lead to a new paradigm of recording technology to develop ultra-high density and ultra-fast access time storage media with less power consumption.

1.5 Applications of FePt-based Alloy Thin Films

FePt and FePt-based alloy thin films have been intensively investigated for applications in future high-density magnetic recording technology due to high magnetocrystalline anisotropy. Various methods such as epitaxial growth at certain substrate temperatures, third element doping, strain-stress induced $L1_0$ ordering, etc. have been employed to reduce the ordering temperatures and T_C of these films to make them suitable for application in recording media. Third element doping such as TM=Cr, Mn, Ni, Cu, etc.; RE=Nd, Gd, Tb, etc. have been studied for ultra-high density magnetic recording, HAMR, and magnetic random access memory applications [84,85,130,86–90,105,106,126]. Strain-induced phase transformation method resulting from lattice mismatch, sputtering pressure, etc. was used to lower the structural ordering temperature of FePt films for application in high density recording [91,155,157,184,185]. $L1_0$-FePt film has also been studied by Seki *et al.* for application in GMR device by integrating FePt in CPP-GMR pillars and achieved a huge K_u value of 5.1×10^7 erg/cc [186]. They also demonstrated the STT effect in FePt/Au/FePt GMR structure. FeCo is an alloy having a high magnetic moment which may be a possible alternative candidate to rare-earth based alloy permanent magnet. The $L1_0$ ordered $FePt/Fe_{45}Co_{55}$ films constructing a hard/soft exchange spring system have been investigated for application in rare-earth free permanent magnet due to the large energy product of 50 MGOe [187].

1.6 Motivation and Objectives of the Present Thesis Work

The Co-based RE-TM alloy thin films have a bright technological future for their exciting magnetic properties. Though amorphous RE-TM alloy films lack structural ordering, they exhibit high magnetic anisotropy. The interest in amorphous Ferrimagnetic RE-TM alloys is due to that they exhibit large but smaller perpendicular magnetic anisotropy than ferromagnetic metals because of partial

compensation of magnetic moment in two sublattices that RE-TM material is composed of. Though several studies have already been done on Co-Tb binary alloy films and multilayers, very few reports are available on the magnetic property of ternary alloy films. The magnetic properties of various RE-TM ternary alloy films such as GdTbFe, GdTbCo, TbCoFe, etc., have already been studied and magnetic anisotropic behavior is well established. However, no reports have been found on RE-TM ternary alloy films with TM=Ni metal. The Ni metal shows ferromagnetic ordering at room temperature because of partially filled two *3d* subshells.

Along with RE-TM alloy films, FePt-based alloy thin films also exhibit excellent magnetic properties such as high magnetocrystalline anisotropy, huge magnetization, and large coercivity, large thermal stability. The structural and magnetic properties of FePt-based thin films are found sensitive to the deposition conditions, annealing temperature, elemental doping, insertion of underlayer/overlayer, etc. Thus FePt-based thin films can be fabricated with desired structural and magnetic properties which may be an alternative candidate for application in practical devices such as high-density magnetic recording devices, HAMR, magnetic RAM as well as permanent magnetic. Several studies have been carried out on various third elements (TM, RE, C, N, etc.) doped FePt-based thin films to enhance the structural and magnetic properties. However, limited studies were done on Co-doped FePt thin films due to which the influence of Co doping on structural and magnetic properties is not well understood.

The main objectives of the present thesis work are as follows

- To investigate the magnetic property of CoTbNi and FePtCo ternary alloy thin films prepared by co-sputtering using DC magnetron sputtering system.
- To study the compositional dependence of magnetic property
- To explore the influence of surface roughness on the magnetic property
- To explore the influence of depositions condition on crystal structure and magnetic property
- To quantify magnetic anisotropy.