CHAPTER – I

INTRODUCTION

1.1. Introduction

In recent years, thin film science has grown worldwide into a major research area. The major exploitation of thin film science is still in the field of microelectronics. However, there are growing applications in other areas like for optical and magnetic devices, electro chemistry, protective and decorative coatings and catalysis. Over the past few decades, there has been an intense level of research in the field of magnetic thin films, despite the fact that work with these intriguing materials began in the 1800s.

The preparation and magnetic properties of thin films of vacuum deposited permalloy were first reported by Blois in 1955 [1]. Due to their interesting magnetic properties, magnetic thin films have been extensively investigated in the recent years. Recently, demands for the ferromagnetic alloy have increased significantly in the field of high performance magnetic thin films such as in magnetic random access memory (MRAM), ultra high density perpendicular recording media and micro device applications such as micro electro mechanical systems (MEMS) for making actuators and valves with the dimensions in microns. Magnetic thin films with thicknesses of a few micrometers or less are used in the electronics industry. Magnetic films can be single-crystal, polycrystalline, amorphous, or multilayered in the
arrangement of their atoms. Applications include magneto-optic storage, inductive recording media, magneto-resistive sensors, and thin-film heads.

1.2. Classification of magnetic materials

Magnetic materials can be divided into three groups according to their bulk susceptibility ($\chi$). The materials with a small negative $\chi (\sim 10^{-5})$ are called diamagnetic materials. The magnetic response of these materials opposes the applied magnetic field. Examples of diamagnetic materials are copper, silver, gold, bismuth and beryllium. Superconductors are a special kind of diamagnetic materials with $\chi = -1$. The second group of materials includes aluminum, platinum and manganese. These are paramagnetic materials, which have a small positive $\chi (\sim 10^{-3} \text{ to } 10^{-5})$. Under the application of external field, the magnetization is weak but aligned parallel with the direction of the magnetic field.

The third and most useful group of magnetic materials is ferromagnetic materials, which has a large and positive susceptibility ($\sim 10^5$). Widely used ferromagnetic materials are iron, cobalt and nickel, as well as rare earth metals and their alloys [2]. They can be further classified into hard magnetic materials and soft magnetic materials.

(a) Hard magnetic material

Hard or permanent magnetic material in which the resistance to the movement of the domain wall is large, exhibit very high coercivity ($H_c$) and very large saturating field ($H_s$). The permeability is low and a large magnetization field is necessary to attain saturation magnetization of the
material. The hard magnetic materials are hard, permanent and brittle. The hard magnetic materials are used in MEMS, memory devices and in computer devices. Samarium-cobalt is a permanent magnetic material used widely in the 1960s. In the early 1980s, neodymium-iron-boron was developed as a low-cost high performance permanent magnet. The presence of Pr-Fe and Nd-Fe-based materials, a very hard magnetic phase with greater coercivity and energy product, leads to the superior magnetic properties [3-4]. The examples of recently emerging hard magnetic materials are Co-Ni-P, Co-Mn-P, Co-Ni-Mn-P, Co-W, Co-Mo, Co-Cr, Co-Pt, Co/Cu and Co-P etc. Thin films that are synthesized from above mentioned hard magnetic materials are known as hard magnetic thin films.

(b) Soft magnetic materials

The magnetic materials that exhibit low resistance to the movement of the domain walls and having low coercive force and small saturating field is called soft magnetic materials. These materials can be easily magnetized and de-magnetized. The main parameter is the relative permeability ($\mu_r$), which is a measure of how readily the material responds to the applied magnetic field.

The types of applications for soft magnetic materials fall into two main categories: AC and DC. In DC applications the material is magnetized in order to perform an operation and then demagnetized at the conclusion of the operation. In AC applications the material will be continuously cycled from being magnetized in one direction to the other, throughout the period of
operation. A high permeability will be desirable for each type of application but the significance of the other properties varies. Some examples of soft magnetic materials are Ni-Fe, Co-Ni-Fe and Co-Fe, etc. The soft magnetic materials are used in transformer cores, magnetic switching circuits, magnetic amplifiers, recording heads to write onto hard disks, and reading heads, etc.

Due to their high permeability and low coercivity, soft magnetic materials are used in electrical circuits to amplify the generated flux (e.g., power generation and transmission, receipt of radio signals, microwaves, inductors, relays and electromagnets). High saturation magnetization and low power loss are other desirable properties. Permalloy (81 % Ni and 19 % Fe alloy) is a versatile soft magnetic material used for many electromagnetic applications. Thin films that are synthesized from above mentioned hard magnetic materials are known as hard magnetic thin films.

1.3. Magnetic properties

The important properties of magnetic materials are remanence ($M_r$), coercivity ($H_c$), saturating field ($H_s$), saturation magnetization ($M_s$), curie temperature ($T_C$), magnetic susceptibility ($\chi$), domain, and magnetization energy and these are discussed briefly below.
(i) Remanence ($M_r$)

The magnetization remaining when the field applied is reduced from saturation to zero is called remanence. It is denoted as '$M_r$' and is measured in emu/cc.

(ii) Coercivity ($H_C$)

The size of the negative field required to reduce the magnetization to zero is known as coercivity or coercive force. It is denoted as '$H_C$' and is measured in units of Amp/m or Oersted (Oe).

(iii) Saturating field ($H_s$)

The applied magnetic field at which the magnetization gets completely saturated is known as saturating field, which is denoted as '$H_s$'. It is measured in Amp/m or Oersted (Oe).

(iv) Saturation magnetization ($M_s$)

The magnetization at which the magnetic polarization gets completely saturated is called magnetic saturation, which is denoted as '$M_s$'. It is measured in unit of emu/cc.

(v) Curie temperature ($T_C$)

Weak magnetic effects occur in all substances, but the greater proximity of the atoms in a solid can lead to stronger co-operative effects. If the interaction is such that the magnetism on the atom is aligned, this leads to the very strong magnetic field known as ferromagnetism below a certain temperature called Curie temperature.
(vi) Magnetic susceptibility ($\chi$)

The magnetic susceptibility is the measure, with which a material can be magnetized by a magnetic force per unit volume. $X$ is a dimensionless quantity.

$$X = M/H$$

(vii) Domain

The presence of domain requires the existence of transition region in which the magnetization goes smoothly from one direction to the other. The domain is a small region inside which the magnetic dipole moments are aligned in same direction.

(viii) Magnetization energy

The interaction energy, which makes the adjacent dipoles align themselves, is the exchange energy or the magnetic field energy.

The behavior of magnetic thin films may be different from that of bulk materials due to the following reasons.

(i) In contrast to the interior electron spins, the surface spins are usually in an environment of lower symmetry due to the fact that there are neighbors only on the film side.

(ii) The arrangement of the atoms of the first few layers on the substrate side of a film is influenced by the nature of the substrate and its temperature during deposition [5].
(iii) The surface inhomogeneities of a thin film may play an important role in its magnetic behavior and the study of the magnetic thin films can be expected to be more complicated than that of bulk matter.

(iv) The magnetization of the thin film state is also of considerable theoretical interest. Again, if the film is sufficiently thin, say less than 100 Å thick, its magnetization departs noticeably from the bulk value, according to the theories of Klein and Smith [6], and Valenta [7].

(v) The magnetic anisotropy, coercive force, and rectangularity of the easy-axis loop are parameters of both basic and applied significance. The magnetization reversal process in thin films of is special interest. It affords a unique opportunity for the study of various modes of magnetization reversal with minimum complications.

1.4. Applications of magnetic thin films

The ever increasing demands for faster and less expensive electronic systems, such as integrated circuits (ICs), micro electro mechanical systems (MEMS) and computer drives have resulted in the development of cost effective processes.

Hard and soft magnetic thin films are used in MEMS including micro actuators, sensors, micro motors, and frictionless micro gears because electromagnetically-actuated MEMS are more stable for high force and large gap applications, are more robust in harsh environments (dust, humidity), and can be actuated with low cost voltage controllers [8-11]. Soft magnetic thin films with high permeability and low coercivity are used in recording
heads to write into hard disks. These soft magnetic materials are incorporated in the induction recording heads for writing bit information into hard discs for several years [12].

Hard magnetic materials have low permeability and high coercivity such as ternary and quaternary alloys are used as data storage media [13]. The development of superior soft magnetic materials and films is the key to making high performance data storage devices with improved performance is considered to be of utmost importance in the field of information technology. Binary and ternary soft magnetic alloys such as Co-Ni, Ni-Fe, Co-B, Co-Fe-B, Co-Ni-P etc are being developed for potential applications in modern high density recording and data storage discs [14-18]. In recent years, nanostructured soft magnetic films have been effectively used to construct multilayer structures that exhibit giant magneto resistive (GMR) behavior [19]. There has been an increasing transport phenomenon, including the giant AC magneto resistance, giant magneto impedance, due to the possibility of using materials exhibiting this effect in a diversity of high sensitivity magnetic field detectors and magnetic recording heads [20]. The hard magnetic thin films possess the following properties for the fabrication of ICs and MEMS.

(a) Low deposit stress to prevent film cracking or structure deformation.
(b) Corrosion resistance to HF (hydrogen fluoride) and other strong acids with are frequently employed in MEMS to release and etch micromechanical structures and
(c) Good adhesion between the seed layer and the electrodeposited layers.

1.5. Preparation of thin films

Large varieties of deposition processes are available for thin film fabrication. Basically, thin film deposition technologies are either physical methods or chemical methods. Some of them are evaporation, sputtering, spray pyrolysis, chemical vapor deposition, solution growth, electroless deposition and electrodeposition. Of these techniques spray pyrolysis, chemical vapor deposition, solution growth and electrodeposition are some of the chemical deposition techniques which are particularly attractive for large area devices and also relatively cheap. Few of the cost effective techniques which are used for large area applications are discussed here.

1.5.1. Physical methods

(a) Evaporation

Vacuum evaporation has been employed to deposit thin films. The most common method is to support the material in a filament or direct heated or indirectly heated above the melting points of the materials to yield vapours in a vacuum chamber. The notable important control parameters are substrate temperature, evaporation rate and oxygen partial pressure.
Several metallic films, semiconductor oxide films and compound films have been prepared by several workers [21-22]. However, a careful control over the deposition parameters is necessary. Besides a vapor source, one requires numerous other accessories in the vacuum system. These include substrate heaters, source shutter, monitors, controllers of deposition rate and thickness.

(b) Sputtering

Sputtering technology was first discovered by Grove in 1852. When a solid or liquid is bombarded with atoms, ions or molecules, several phenomena may arise, depending on the kinetic energy of the bombarding particles. At very low kinetic energy (<5 eV), the interaction is confined to outer most layer of the target material. Vapour species may be created by kinetic ejection from the surface of the material by bombardment with energetic reactive or non-reactive ions. The momentum transfer between the impinging ions and the target surface sputters or ejects which are condensed on a substrate to form a thin film. Sputtering method provides a very simple and precise control on the rate of thin film deposition. The various sputtering methods are discussed below.

Diode sputtering

The material to be deposited is transported from the target to a substrate to form a film. This technique uses a plate of the material to be deposited as the RF powered electrode (target) in a slow discharge. Films of
pure metals or metal alloys are deposited using noble gas discharges with metal target.

**Magnetron sputtering**

Magnetron sputtering is a powerful and flexible technique which can be used to coat virtually any workpiece with a wide range of materials - any solid metal or alloy and a variety of compounds. Prior to the sputtering procedure a vacuum of less than one ten millionth of an atmosphere must be achieved. From this point a closely controlled flow of an inert gas such as argon is introduced. This raises the pressure to the minimum needed to operate the magnetrons, although it is still only a few ten thousandth of atmospheric pressure. When power is supplied to a magnetron a negative voltage of typically -300V or more is applied to the target. This negative voltage attracts positive ions to the target surface at speed. Generally when a positive ion collides with atoms at the surface of a solid an energy transfer occurs. If the energy transferred to a lattice site is greater than the binding energy, primary recoil atoms can be created which can collide with other atoms and distribute their energy via collision cascades. A surface atom becomes sputtered if the energy transferred to it normal to the surface is larger than about 3 times the surface binding energy.

**Bias sputtering**

In this technique, the source material need not originate from a sputtering target, but can be an evaporation source, a reactive gas with
condensable constituents and other gases that react with the condensed constituents to form films. The substrates are ion bombarded during deposition and prior to film deposition, the substrates should be thoroughly cleaned.

**Ion beam sputtering**

The target and substrates are situated in a high vacuum environment rather than high pressure glow discharge. From this method we can get the deposition of high purity films. In general, all these sputtering techniques necessitate either the use of high vacuum or low pressure and require an electrode to sustain a glow discharge.

**Reactive sputtering**

Using this technique, the compound is deposited directly from the film targets. Most of the reactive sputtering work is used to prepare oxide, nitride and sulphide films. The film to be deposited is either synthesized by sputtering elemental (or) alloy targets in reactive gases.

1.5.2. Chemical methods

**(a) Spray pyrolysis**

The spray pyrolysis technique involves spraying a solution containing soluble salts onto heated substrates. It lies some where between the thin film technology and thick film technology. Spray pyrolysis involves a thermally stimulated chemical reaction between the clusters of liquid/vapour atoms of different chemical species, with the help of the carrier gas. The chemical solution is atomized into a spray of fine droplets by a spray nozzle. Each and
every sprayed droplet reaching the surface of the hot substrate undergoes pyrolytic decomposition and forms a single crystallite or a cluster of crystallites of the product.

(b) Solution growth process

The solution growth technique was pioneered by the work of Bode [23] and co-workers. Thin films are prepared without any external power supply. The substrates are immersed vertically in a reaction bath stirred continuously by using a magnetic stirrer. One feed back circuit is used to maintain the bath temperature. When the ionic product (IP) of metal and alloys, exceeds the solubility product (SP) of the corresponding meal, a metallic alloy film is formed on the substrate by ion-by-ion reaction. Initially, the film growth rate is negligible because an incubation period is required for the formation of critical nuclei from a homogeneous system on to a clean surface. Once the nucleation occurs, the deposition rate rises rapidly until the rate of deposition equals the rate of dissolution (i.e. ionic product = solubility product). When the nucleation centers already exist on the surface of the substrate, incubation time is not required.

(c) Chemical vapour deposition

Thin films are deposited by a chemical reaction or decomposition of a mixture of gas at elevated temperature at the wafer surface. This process is similar to sputtering or evaporation techniques. The principle of chemical vapor deposition is based on the chemical reactions of the type such as oxidation, thermal decomposition, and hydrolysis, reduction, carbide, nitrite
formation, chemical transport, disproportionation and synthesis reaction etc. Currently, chemical vapour deposition technique has been extended to a vast variety of films, including insulators, conductors, resistors and ferrites. But this kind of technique requires some special kind of reactors and atmospheres such as carrier gases, temperature controllers for the deposition of different material at different temperatures.

(d) Electroless deposition

Electroless technique involves the reduction of metal ions to form deposits, but no external power supply is required to provide electrons. They are provided by a chemical reducing agent in the solution. Further, a catalytic surface is used to initiate the deposition and then the metal itself must be catalytic for the deposition process. These enable one to grow metal and alloy films on non-conducting substrates. The principle is the reacting anions and cations combine slowly throughout the solution leading to the preparation of hydrated oxides. Hard and well adherent films can be obtained by the post-heat treatment. This is one of the leading techniques to deposit magnetic alloy thin films.

(e) Electrodeposition

Electrodeposition is a process of depositing a film upon an electrode by electrolysis. The first application of the principle of electrolysis to the deposition of metal films is the subject of controversy but probably took place in 1838 [24]. The experimental arrangement requires a suitable electrolyte
through which current is passed between two electrodes. The phenomenon of electrolysis is governed by Faraday’s law.

When an electrode is dipped in a solution containing ions of that metal, a dynamic equilibrium is set up.

\[ M \rightarrow M^{x+} + xe^- \]

Where ‘M’ is the metal atom. The electrode gains a certain charge on itself which attracts oppositely charged ions and water molecules holding them at the electrode/electrolyte interface by the electrostatic force. A double layer consisting of an inner layer interposed by preferentially absorbed ions immediately on the electrode. It is followed by a second layer of charge opposite to that of the electrode surface and it is moved to stable position on it, release their ligands (water molecules) if solvated, release their charges and the process undergo stimulating electrochemical reaction. The rapid depletion of the deposited ions from the double layer region is compensated by a continuous supply of fresh ions from the bulk of electrolyte. Magnetic materials belonging to ferromagnetic group are mainly prepared by co-deposition. In the present work, preparations of Ni-P and Co-Ni-P are carried out by galvanostatic electrodeposition method.

1.6. Review on Ni-P alloy thin films

Nickel-Phosphorous (Ni-P) alloy deposits have been widely studied because this alloy system represented a good model material for amorphous metallic alloys [25]. Ni-P alloys have many industrial applications owing to their bright appearance, good mechanical properties, high hardness,
excellent wear resistance, solderability, polishability as well as catalytic properties [26-30].

At sufficiently high P contents, Ni-P alloys are amorphous and non magnetic. Due to this property combination, Ni-P deposits have long been successfully applied as an underlayer for the magnetic storage media in hard drives of present day computers [31-32]. More recently, these alloys are also receiving considerable interest as catalysts and as potential materials for making ohmic contact to III – V devices. Shao Guangjie et al [33] have reported that the initial electrodeposition behavior of Ni-P alloys on carbon steel was found to be greatly influenced by the morphology of the substrate.

Li et al [34] have studied electrodeposited Ni-P alloy containing about 6-8 at% phosphorous and high catalytic activity for hydrogen evolution reaction (HER), not capable of growing a thick coating with good physical stability. This result showed that the catalyst Ni-P alloy could be prepared using a low concentration of the phosphorous-offering reagent and a high concentration of ammonium, instead of using a conventional bath containing a relatively high phosphorous-offering reagent. Preferred nucleation of Ni-P alloy coatings takes place at the crystal boundaries. Electrochemical methods such as electroless deposition and electrodeposition are identified as the most practical and inexpensive techniques to synthesize Ni-P alloy films.
Carbajal et al [35] have reported that electrodeposited Ni-P alloys are found to be mirror-bright and corrosion resistant when the phosphorus content of the deposits is above 18 at%. The mechanism of Ni-P deposition with plating variables such as H$_2$PO$_3$ concentration, current density, bath pH and temperature in a Ni-citrate bath was discussed by Morikawa et al [36]. Li et al [37] studied the Ni-P amorphous alloy onto a p-type silicon substrate and underwent a cyclic oxidation-reduction or crystallization treatments. Lu and Zangari [38] studied the corrosion behavior of Ni-P based alloy films synthesized using an autocatalytic deposition. Seo and co-workers [39] reported the characteristics of a Ni-P alloy electrodeposited from a sulfamate bath. Kurowski et al [40] have studied the evolution of growth morphology and composition of deposits during the initial stages of Ni-P electrodeposition using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Kroliskowski et al [41] have reported the hydrogen evolution reaction (HER) on electrodeposited Ni-P alloys containing 7, 20 and 28 at% P. Potentiodynamic, potentiostatic and impedance spectroscopy measurements were performed in 0.10 M H$_2$SO$_4$ solution.

Ordine et al [42] have reported the kinetics of P incorporation during Ni-P electrodeposition by means of interfacial pH measurements, cathodic polarization curves and electrochemical impedance spectroscopy. Zeng and Zhou [43] have reported the co-deposition of P with Ni on a Ni-Ag alloy electrode by means of in-situ surface enhanced Raman spectroscopy.
(SERS) to obtain information about the P- incorporation mechanism during electrodeposition of Ni-P alloys.

The Ni-P amorphous alloy/ceramics composite membrane reactor was recently reported by Li et al [44]. Li et al [45] have reported Ni-P amorphous alloy deposited on the p-type silicon slice by electroless plating, which was then crystallized by heating it at high temperature from 550K to 610K in nitrogen flow for 2 hour and its crystallization process was investigated by using ICP, XRD, XPS, TEM, SEM, and STM. Shimizu et al [46] have reported the oxidation behavior of an amorphous Ni\textsubscript{77}P\textsubscript{23} alloy, prepared by electrodeposition, in air and in dry oxygen at 300°C. The morphology, structure and composition of the oxide developed on the alloy were examined by XPS, SIMS, and HRTEM of ultra micromed sections.

Elesener et al [47] examined the amorphous electrodeposited Ni-P alloys with 22 at% of phosphorous in the amorphous and re-crystallized state by EDXD and XPS. The re-crystallization kinetics has been determined following in situ structural changes by EDXD. Distinct diffraction patterns indicating the presence of Ni\textsubscript{3}P confirm alloy re-crystallization at 645°C. The XPS studies showed that all the core level binding energies of nickel such as Ni2P\textsubscript{3/2} and Ni2P\textsubscript{1/2} and phosphorous (P2p, P2s) remained constant after the change from amorphous to crystalline structure.

Haseeb et al [48] have found electrodeposited Ni-P alloy coatings with structural and chemical investigations by XRD, XPS and SIMS. XRD has
shown a broad peak indicating an amorphous structure. XPS has shown the presence of Ni₃P compound and also revealed the amount of phosphorous in both coatings to be around 10.20 wt%. Ashassi-Sorkhabi et al [49] have reported Ni-P initial deposition rates from a glycine bath by means of the quartz crystal microbalance method. SEM and EDAX studies were also used to study the morphology and elemental analysis of deposits. The effect of pH, temperature and the type of activation process on the initial deposition rate, surface morphology and surface elemental analysis of deposits were evaluated. The surface morphology depends on P-content of deposits. By increasing the P-content of deposits, the grain size increases.

Winowlin Jappes et al [50] have studied the effect of process parameters such as stabilizer concentrations and plating bath temperature of the Ni-P coatings on efficiency and crystallinity. Both the nickel recovery and coating efficiencies are defined, quantified and analyzed by varying the above stated basic input parameters. The integral breadth, crystallite size, microstrain and the relative proportions of amorphous and crystalline phases present in the coating are obtained using XRD and analyzed.

1.7. Review on Co-Ni-P alloy thin films

The development of superior hard and soft ferromagnetic materials is the key to making high performance less expensive electronic systems, such as integrated circuits (ICs), micro electro mechanical systems (MEMS) and computer drives. Recently, binary and ternary soft magnetic alloys are being
developed for potential applications in modern high density recording and data storage discs [13, 16, 51-53].

Electrodeposition of Co-Ni-P magnetic thin films is the recent interest to the researchers. In recent years, the possibility to use magnetic Co-Ni-P alloy thin films for various functional applications such as perpendicular magnetic recording media [54-56], micro electro mechanical systems, electronic and automotive industries [57], attracts the attention of many investigators, because of their unique and highly attractive magnetic, mechanical, physical and chemical properties. Few of the earlier studies focused on the hard magnetic properties of Co-Ni-P films for perpendicular magnetic recording media [58-59]. Electrochemical deposition of Co-Ni-P alloys is widespread due to their unique properties which are manifold and highly dependent upon the electrodeposition parameters, making fine-tuning various applications such as memory and mechanical devices. Few of the earlier reported studies focused on the soft magnetic properties of Co-Ni-P films for data storage devices [60-61].

Homma et al [59] gradient control of magnetic properties in the electroless deposited Co-Ni-P films and microstructural origin of the gradient properties. Control of the single and dual gradient in magnetic properties, such as coercivity in the direction of the film thickness was achieved by controlling the rotational speed of substrates during the deposition. The results of cross-sectional SEM and TEM investigations clarified that the size of the crystallites changed according to the speed of the rotation, forming the
'graded' microstructure in the film thickness direction, which resulted in the graded properties. Co-Ni-P films exhibiting low coercivity and square-loop hysteresis was reported by Herzer et al [56]. Itakura et al [57] have investigated the effect of deposition site condition on the growth process of electroless Co-Ni-P films by employing the intermediate treatment step during the deposition and the effect of chemical species in the bath on the deposition sites, i.e., the film growth process using SEM and AFM.

Murthy et al [61] have studied ternary Co-Ni-P soft magnetic thin films deposited on silicon substrates by the autocatalytic electroless process. The deposition of these magnetic thin films were carried out by using different concentrations of cobalt ($\text{Co}^{2+}$), nickel ($\text{Ni}^{2+}$) and hypophosphite ($\text{H}_2\text{PO}_2^-$) ions in the bath, and by maintaining the bath at different pH levels. The composition and the magnetic characteristics of the deposited films were studied. The effects of varying the concentration of both metal ions and non-metal ions on the magnetic properties of the films were explored by increasing the concentration of precursor salts.

Park et al [62] studied magnetic Co-Ni-P thin films electrodeposited from solutions at pH < 2.25, exhibited soft magnetic properties, while the films deposited at pH > 2.25 showed hard magnetic behavior. The effect of solution composition, solution pH and film thickness on the magnetic properties, microstructure and phases of electrodeposited Co-Ni-P films were investigated. They also found that solution pH and NaH$_2$PO$_2$ concentration significantly influenced the magnetic properties of Co-Ni-P deposits. Alben et
al [63] deposited Co-Ni-P films at room temperature conditions by the electroless method. They found that Co-Ni-P films exhibited an \( H_C \) value of 1000 Oe. Herzer et al [64] studied Co-Ni-P films with coercivity as low as 1 Oe deposited using a bath operated at 90\(^{\circ}\) C with few complexing agents.

Nicholson and Khan [65] examined the dependence of nucleation, microstructure and magnetic properties of electroless Co-Ni-P deposits on solution pH. Matsuda et al [66] varied the pH, metal ion ratio and operating temperature of sulfate plating baths and obtained a maximum deposit coercivity of 1500 Oe for electroless Co-Ni-P deposits (0.1 \( \mu \)m film thickness). They attributed the maximum coercivity to segregation of fine Ni-P particles in Co grain boundaries. Homma et al [67] correlated the magnetic properties to the microstructure of electroless Co-Ni-P deposits obtained from sulfate baths. They obtained a maximum \( H_C \) of \( \sim 2600 \) Oe in Co-Ni-P deposits with average grain size of \( \sim 35 \) nm from pH < 8 solutions and substantially lower perpendicular coercivity with smaller grains of \( \sim 20 \) nm from solutions of pH > 8.5. Byun et al [68] reported that the coercivity of Co-Ni-P deposits is dependent on sodium hypophosphite concentration and surface conditions.

Homma et al [69] have investigated the correlation between magnetic and structural properties of electroless-deposited Co-Ni-P films for the use of perpendicular magnetic recording media. The media with various perpendicular Coercivity were examined and higher medium showed a clear phase-separated condition which was confirmed by selective chemical-etching technique. It was strongly indicated that such a structure plays an
important role in attaining a high coercivity and in forming an hcp structure in a film with a Ni-rich average composition.

Guan and Nelson [70] have reported low residual stress hard magnetic Co-Ni-P alloy coatings prepared by electrodeposition technique. Besides electrolyte chemicals, various electrodeposition parameters including applied current density, film thickness, electrolyte agitation, electrolyte pH and temperature are optimized to yield thick films with low residual stress. The resulting hard magnetic Co-Ni-P alloy exhibits a relatively high perpendicular coercivity of around 700-1200 Oe. They have succeeded in realizing thick films up to 52 μm with a low residual stress. Tarozite et al [71] deposited Co-Ni-P and Co-Ni-P-Cu films electrolessly and with simultaneous electrolysis applied. They found films coercivity passed through the maximum by such a potential which enabled to get 5.5 at% of phosphorous in the film and, thus, to form a specific microstructure.

1.8. Aim of the present work

Systematic investigation on the deposition and characterization of Ni-P and Co-Ni-P alloy thin films are the main subject of this thesis. Ni-P alloy deposits represent a good model material for amorphous metallic alloys. Ni-P alloy films are used as an underlayer for magnetic storage media in hard drives of present day computers owing to their physical and chemical properties.
Co-Ni-P alloy thin films are widespread due to their unique, physical, chemical, mechanical and magnetic properties of these materials which are widely used in mechanical and memory devices. The electrodeposition technique has been chosen to deposit Ni-P and Co-Ni-P alloy films. It is a simple, non-vacuum, low temperature process, and cheap method for processing large area surfaces with an easy control of the film thickness, morphology, structure, composition and magnetic properties.

The aims of the present works are to:

(i) Deposit good quality Ni-P and Co-Ni-P alloy thin films by electrodeposition technique by optimizing the deposition conditions through cyclic voltammetric studies.

(ii) Study the electrochemical properties and reaction mechanism of the films by cyclic voltammetric and linear sweep voltammetric studies using cyclic voltammogram (CV) and linear sweep voltammogram (LSV).

(iii) Study the composition of the films using energy dispersive x-ray analysis (EDAX).

(iv) Study the structure of the films by structural properties of the films using x-ray diffraction (XRD).

(v) Study the morphology of the films using scanning electron microscope (SEM) and atomic force microscope (AFM).

(vi) Study the hard and soft magnetic behavior of the films by the magnetic properties using vibrating sample magneto meter (VSM).
(vii) Analyze the feasibility of using Ni-P and Co-Ni-P alloy films for recording applications. The results of the present work are described in the following chapters as follows.

(i) The theoretical background relevant to electrodeposition and theory of magnetic properties are described. Linear sweep and cyclic voltammetric fundamentals for the film deposition are briefly described. Relevant theoretical aspects for the structural, compositional, morphological and magnetic characterization of thin films are also given in chapter II.

(ii) In chapter III, the experimental techniques used to prepare the sample with necessary in the course of the present work. The various experimental techniques performed for structural, compositional, morphological and magnetic property analysis are also briefly discussed.

(iii) In chapter IV, electrochemical and compositional properties of electrodeposited Ni-P alloy thin films are analyzed under various electrodeposition parameters. These studies are carried out using cyclic voltammetry (CV), linear sweep voltammetry (LSV) and energy dispersive analysis of x-rays (EDAX). Thickness of the films under various electrodeposition parameters are analyzed using stylus profilometer.

(iv) In chapter V, deals with the structural and morphological properties of Ni-P alloy thin films. These studies are carried out using XRD, SEM and AFM under various electrodeposition parameters such as, solution
pH, current density, concentration of NaH$_2$PO$_2$, concentration of Ni$^{2+}$ and concentration of NaCl.

(v) In chapter VI, electrochemical and compositional properties of electrodeposited Co-Ni-P alloy thin films are analyzed under various electrodeposition parameters. These studies are carried out using cyclic voltammetry (CV), linear sweep voltammetry (LSV) and energy dispersive analysis of x-rays (EDAX). Thickness of the films under various electrodeposition parameters are analyzed using stylus profilometer.

(vi) In chapter VII, deals with the structural and morphological properties of Co-Ni-P alloy thin films. These studies are carried out using XRD, SEM and AFM under various electrodeposition parameters such as, solution pH, current density, concentration of Co$^{2+}$, concentration of NaH$_2$PO$_2$, concentration of NH$_4$Cl and of NaCl as supporting electrolytes.

(vii) The highlights of important conclusion have drawn on the basis of the present work and scope of the future work in the field of Ni-P and Co-Ni-P alloy thin films are presented in chapter VIII.

1.9. Conclusions

The Ni-P and Co-Ni-P alloy thin films and their properties are emphasized. The importance of Ni-P and Co-Ni-P alloy thin films are also given with an extensive bibliography. Besides, a brief outline of the various cost effective techniques have been added. The advantage of electrodeposition method over other method which motivated to choose this technique for the present study has also been specified.
REFERENCES

1. M.S. Blois


2. J.P. Jakubovics


3. J. I. Betancourt and H. A. Davies


5. Ronald F. Soohoo


6. M.J. Klein and R.S. Smith

   Physical Review. 81 (1951) 378.

7. L. Valenta

   Czechoslovak Journal of Physics. 7 (1957) 127.

8. T.S. Chin


9. J.W. Judy and R.S. Muller


10. J.W. Judy, R.S. Muller, and H.H. Zappe
11. C.H. Ahn and M.G. Allen

Institute of Electrical and Electronics Engineers, Transactions on Industrial Electronics. 45 (1998) 866.

12. P.C. Andricacos and N. Robertson


13. L.L. Lee, D.E. Laughlin and D.N. Lambeth

Institute of Electrical and Electronics Engineers, Transactions on Magnetics. 34 (1998) 1561.

14. B. Lochel and A. Maciossek


15. A. Brenner


16. E. Gomez and E. Valles


17. O. Takano and S. Ishibashi
18. D. Kim, K. Aoki and O. Takano


19. V. Hartman


21. E. Shanthi, A. Banerjee, V. Dutta, and K.L. Chopra


22. P. Nath, R.F. Bunshah, B.M. Masol and O.M. Stuffs


23. D.E. Bode


24. B. Gore

25. G.S. Cargill III


26. H.G. Kyoukai


27. S. Grimsley


29. A. Krolikowski, P. Marcus, B. Baroux, and M. Keddam


30. H. Li, H. Li, W.L. Dai, W. Wang, Z. Fang, and J.F. Deng


32. Y. Suganuma, H. Tanaka, M. Yanagisawa, F. Goto and S. Hatano
Institute of Electrical and Electronics Engineers, Transactions on Magnetics. 18 (1982) 1215.

33. Shao Guangjie, Chen Ling, Wang Fengyan, Chen Junming and Qin Xiujuan


34. L. Li, Yi. Zhang, S. Deng, and Y. Chen


35. J.L. Carbajal, and R.E. White


36. T. Morikawa, T. Nakade, M. Yokoi, Y. Fukumoto, and C. Iwakura


37. H. Li, L. Wang, H.Chen, and J.F.Deng


38. G. Lu, and G. Zangari


40. A. Kurowski, J.W. Schultze, and G. Staikov


41. A. Krolikowski, and A. Wiecko


42. A.P. Ordine, S.L. Diaz, I.C.P. Margarit, O.E. Barcia and O.R. Mattos


43. Yue. Zeng, and Shaomin. Zhou


44. B. Liu and H. Li


45. H. Li, H. Chen, S. Dong, J. Yang, and J. Deng


47. B. Elsener, D. Atzei, A. Krolikowski, V. Rossi Albertini, C. Sadun, R.
Caminiti and A. Rossi


49. H. Ashassi-Sorkhabi, A. Mirmohseni, and H. Harrafi


50. J. T. Winowlin Jappes, B. Ramamoorthy, and P. Kesavan Nair


51. E. Gomez, J. Ramirez and E. Valles


52. T. Osaka, T. Homma, K. Kageyama, Y. Matsunae, and O. Shinoura


53. G. Herzer

Institute of Electrical and Electronics Engineers Transactions on Magnetics. 26 (1990) 1397.

54. K. Itakura, T. Homma, and T. Osaka
55. T. Homma, M. Suzuki, and T. Osaka


56. T. Homma, Y. Sezai and T. Osaka


57. S. Djokić


58. T. Homma, Y. Kita and T. Osaka


59. T. Homma, Y. Sezai, T. Osaka, Y. Maeda and D.M. Bonner


60. D. Kim, K. Aoki and O. Takano


63. R. Alben, J.J. Becker and M.C. Chi


64. G. Herzer


65. E.L. Nicholson, and M.R. Khan


66. H. Matsuda, G.A. Jones, O. Takano, and P.J. Grundy


67. T. Homma, J. Shiokawa, Y. Sezai, and T. Osaka


68. C. Byun, G.C. Rauch, D.J. Young, and C.A. Klepper


69. T. Homma, T. Osaka, Y. Yamazaki and T. Namikava


70. Shan Guan and Bradley Nelson
71. R. Tarozaite, G. Stalnionis, A. Sudavicius, and M. Kurtinaitiene