2005

Synthesis and characterization of Cobalt-Platinum thin films

Priya David
Louisiana State University and Agricultural and Mechanical College, pdavid3@lsu.edu

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_theses
Part of the Mechanical Engineering Commons

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_theses/2220

This Thesis is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Master's Theses by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
SYNTHESIS AND CHARACTERIZATION OF COBALT-PLATINUM THIN FILMS

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College In partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

By

Priya David
B.Tech, Jawaharlal Nehru Technological University, Hyderabad, India 2002
May 2005
ACKNOWLEDGEMENTS

It would take a book to author all the names that have been part of this challenging journey of completing my dissertation. But there are some people who deserve a special mention without whose love, support and encouragement, it would be impossible for me to accomplish this goal.

First and foremost, I would like to extend my deepest thanks and gratitude to my advisor, Dr. Efstathios I. Meletis for his academic guidance and support. Right from the time I started working on my thesis, he has been very helpful in organizing my ideas and putting together a very fine piece of work.

I would like to thank Dr. Dorel Moldovan and Dr. Muhammad A. Wahab and for being a very supportive and understanding committee. I also have to mention a very special “thank you” to Dr. Lawrence Henry and Dr. Monica Moldovan for their assistance in Magnetic Measurements, and Dr. Jiechao. Jiang and Dr. Xiaogang Xie for their assistance in TEM and SEM work.

I am extremely grateful to my dearest parents; Mary David and David Puthuparambil George for making me believe in myself and encourage me to pursue my Master’s degree. Their blessings, guidance and love have brought me a long way in my life. And hence, would like to dedicate this work to them.

Special thanks to all my colleagues, Dr. Nie, Qi, Varshni, Fengli, Pal, Krishna, David and Dr. K.Y. Wang in Surface and Nanostructure Engineering Laboratory at LSU for their regular sharing of ideas and support in my research.

Last, but not the least, I would like to express my heartfelt gratitude to my friends, Naveen, Rahul, Lavanya and Seema. Throughout my life as a graduate student, their
regular support, advice and friendship has been a vital factor in making it possible for me to see this day. God promised us that we are never alone in our journey of life. I give him all the credit for helping me reach my destination in this very important journey of my academic life.

This research is supported by the National Science Foundation (NSF) and the Board of Regents of the State of Louisiana under the contract No. NSF/LEQSF (2001-04) RII-03 and grants DMR-9871417 and DMR-0116757.
TABLE OF CONTENTS

ACKNOWLEDGEMENTS ................................................................. ii

LIST OF TABLES ........................................................................ vi

LIST OF FIGURES ....................................................................... vii

ABSTRACT .................................................................................. x

1 INTRODUCTION ...................................................................... 1

2 OBJECTIVE ............................................................................. 3

3 LITERATURE REVIEW ............................................................. 4
   3.1 Cobalt, Platinum and Their Properties ........................................ 4
   3.2 Deposition Techniques ........................................................... 4
      3.2.1 Electron Beam Co-evaporation .......................................... 4
      3.2.2 Magnetron Sputtering ....................................................... 5
         3.2.2.1 DC Magnetron Sputtering ............................................ 6
         3.2.2.2 RF Magnetron Sputtering ............................................ 6
      3.2.3 Molecular Beam Epitaxy .................................................. 6
   3.3 Structure of Thin Films ......................................................... 7
      3.3.1 Structure of Co Thin Films .............................................. 7
      3.3.2 Structure of Co-Pt Alloy Thin Films ................................. 8
         3.3.2.1 CoPt Alloy Thin Films .............................................. 9
         3.3.2.2 CoPt3 Alloy Thin Films ............................................ 11
         3.3.2.3 Co3Pt Alloy Thin Films ............................................ 11
   3.4 Magnetism and Anisotropy .................................................... 12
      3.4.1 Anisotropy .................................................................... 14
         3.4.1.1 Crystal Anisotropy ................................................... 15
         3.4.1.2 Shape Anisotropy .................................................... 15
         3.4.1.3 Exchange Anisotropy .............................................. 15
      3.4.2 Magnetic Properties of Co-Pt Alloy and Multilayered Thin Films .... 18
         3.4.2.1 CoPt Alloy Thin Films ............................................ 20
         3.4.2.2 CoPt3 Alloy Thin Films ........................................... 23
         3.4.2.3 Co3Pt Alloy Thin Films ........................................... 24
         3.4.2.4 Co/Pt Multilayered Films ....................................... 25

4 EXPERIMENTAL ................................................................. 27
   4.1 Film Synthesis by EBPVD ..................................................... 27
      4.1.1 Processing System ......................................................... 27
      4.1.2 Experimental Procedure for Thin Films and Multilayer Deposition .... 28
      4.1.3 Characterization of Thin Films ........................................ 28
         4.1.3.1 Thickness Measurements ......................................... 28
         4.1.3.2 Compositional and Microstructural Characterization .......... 29
### Results and Discussion

5.1 Microstructure of Synthesized Films

5.1.1 As-deposited Films

5.1.1.1 Pure Co Film

5.1.1.2 Pure Pt Film

5.1.1.3 Co-Pt Film

5.1.2 Annealed Films

5.1.2.1 Annealing at 300°C

5.1.2.2 Annealing at 400°C

5.1.3 Multilayered Pt/Co Films

5.2 Magnetic Property Measurements

5.2.1 In-Plane Measurements

5.2.1.1 Pure Co Film

5.2.1.2 Co-Pt As-deposited Film

5.2.1.3 Co-Pt Alloy Thin Film Annealed at 300°C

5.2.1.4 Co-Pt Alloy Thin Film Annealed at 400°C

5.2.1.5 Pt /Co Multilayered Film

5.2.2 Perpendicular Measurements

5.2.2.1 Pure Co Film

5.2.2.2 Co-Pt As-deposited Film

5.2.2.3 Co-Pt Alloy Thin Film Annealed at 300°C

5.2.2.4 Co-Pt Alloy Thin Film Annealed at 400°C

5.2.2.5 Pt /Co Multilayered Film

6 Conclusions

References

Vita
# LIST OF TABLES

<table>
<thead>
<tr>
<th></th>
<th>Table Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Processing parameters for synthesizing of Co-Pt alloy and Pt/Co multilayered films</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>Coercivity comparisons of various films at different temperatures, in parallel measurements</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>Coercivity comparisons of various films at different temperatures, in perpendicular measurements</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>Curie temperatures of FM materials</td>
<td>59</td>
</tr>
<tr>
<td>5</td>
<td>Neel temperatures of AFM materials</td>
<td>59</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

1  Phase diagram of Co-Pt alloy ................................................................. 9

2  TEM images and SAD patterns of CoPt/BN at different annealing stages. (a) as-made; (b) optimum annealed sample; and (c) over annealed sample [29]... 10

3  Micrographs and electron diffraction pattern of CoPt sample (a), (b) as-made; (c), (d) annealed at 700°C for 10 min; and (e), (f) annealed at 700°C for 60 min [30] ........................................................................................................ 10

4  XRD spectrum for a Co$_3$Pt film on Al$_2$O$_3$ (0001) deposited at 400°C [12] ........ 12

5  A gradual change in the magnetic dipole orientation across a domain wall [2].... 13

6  A typical hysteresis loop [2] ........................................................................ 14

7  Hysteresis loops measured at 77°K of oxide-coated Cobalt particles. Loop (1) results from cooling in a 10kOe field in the positive direction and loop; and (2) from cooling in zero field [1] .............................................................. 17

8  Hysteresis loops for CoPt/Ag films annealed for 2 hours at different temperatures [5] ........................................................................................................ 20

9  Evolution of microstructure with annealing time (a), (b), (c) CoPt (0.5 nm)/Ag (0.3 nm) films annealed at 600°C for 5, 10, 20 mins respectively; (d) CoPt (2 nm)/Ag (2 nm) films annealed at 550°C for 240 min [5] ................................. 21

10 Dependence of coercivity on annealing time CoPt/BN samples [7] ............... 22

11 Hysteresis loops for Co$_{50}$Pt$_{50}$-C and Co$_{57}$Pt$_{43}$-C composite films [6] ........ 23

12 Dependence of (a) coercivity; and (b) anisotropy constant on Pt content of the CoPt films deposited onto Borosilicate glass substrate at ambient temperatures [11] ........................................................................................................ 25

13 HRTEM showing diffraction pattern and grain structure of a pure Co thin film .. 34

14 EDS spectrum of a pure Co film ................................................................. 35

15 HRTEM showing diffraction pattern and grain structure of a pure Pt thin film ... 36

16 HRTEM showing the grain structure of as-deposited Co-Pt alloy thin film ....... 37

17 EDS spectrum of as-deposited Co-Pt alloy thin film ............................... 38
18 HRTEM showing diffraction pattern and grain structure of a Co-Pt alloy thin film annealed at 300°C ................................................................. 39
19 SE image of Co-Pt alloy thin film annealed at 300°C .......................... 40
20 BSE image of Co-Pt alloy thin film annealed at 300°C ......................... 40
21 EDS spectrum of a Co-Pt alloy thin film annealed at 300°C ................. 41
22 HRTEM showing the grain structure of a Co-Pt alloy thin film annealed at 400°C ................................................................. 42
23 SE image of a Co-Pt alloy thin film annealed at 400°C ....................... 43
24 EDS spectrum of a Co-Pt alloy thin film annealed at 400°C ................. 43
25 HRTEM cross-section micrograph of Pt/Co multilayered film .......... 44
26 EDS spectrum of a Pt/Co multilayered film of thickness 112 nm ......... 45
27 Hysteresis of pure Co film at 10°K ............................................. 46
28 Hysteresis of pure Co film at 300°K ........................................... 47
29 Hysteresis loop of a Co-Pt as-deposited film at 10°K ....................... 48
30 Hysteresis loop of a Co-Pt as-deposited film at 300°K ....................... 48
31 Hysteresis loop at 10°K for Co-Pt film annealed at 300°C................. 49
32 Hysteresis loop at 300°K for Co-Pt film annealed at 300°C................. 49
33 Hysteresis loop at 10°K for Co-Pt film annealed at 400°C ................. 50
34 Hysteresis loop at 300°K for Co-Pt film annealed at 400°C ................. 50
35 Hysteresis loop of Pt/Co multilayer at 10°K ................................ 51
36 Hysteresis loop of Pt/Co multilayer at 300°K ................................ 51
37 Hysteresis loop of Co film at 10°K ........................................... 52
38 Hysteresis loop of Co thin film at 300°K .................................... 53
39 Hysteresis loop of as–deposited Co-Pt film at 10°K ....................... 53
40  Hysterisis loop of as-deposited Co-Pt film at 300°K  
41  Hysterisis loop at 10°K for Co-Pt film annealed at 300°C  
42  Hysterisis loop at 300°K for Co-Pt film annealed at 300°C  
43  Hysterisis loop at 10°K for Co-Pt film annealed at 400°C  
44  Hysterisis loop at 300°K for Co-Pt film annealed at 400°C  
45  Hysterisis loop of Pt/Co multilayer at 10°K  
46  Hysterisis loop of Pt/Co multilayer at 300°K
ABSTRACT

Co-based alloy thin films have attracted a lot of interest, due to their excellent magnetic properties, that is essential in the field of magnetic recording media. Alloying Co with metals like Pt changes some of its intrinsic magnetic properties such as increasing the magnetocrystalline anisotropy constants of the alloy. Co-Pt thin films and multilayers are more suitable for ultra high-density magnetic recording media because they have high-magnetic anisotropy, chemical stability, excellent coercivity and resistance to corrosion.

In the present study, Co-Pt alloy and Pt/Co multilayered films were deposited on Si substrate using dual electron beam co-evaporation. The Co-Pt alloy thin films are vacuum-sealed and annealed for 2 hours at 300°C and 400°C to study the annealing effects on structural and magnetic properties. All the films were characterized using scanning and transmission electron microscopy, electron microprobe, and profilometry. In Co-Pt alloy films, Co and Pt were present in the atomic ratio of 3:1. A mixture of hexagonal close packed and face centered cubic structure Co$_3$Pt was present in both as-deposited and annealed films. The magnetic measurements were conducted at 300°K and 10°K in both perpendicular and parallel orientations in physical property measurement system (PPMS) and magnetic property measurement system (MPMS).

The results from analytical and characterization techniques showed the addition of Pt to Co increased the coercivity of the films. Annealing enhanced the grain size and coercivity of the as-deposited Co$_3$Pt film. However, the presence of ε-Co decreased the coercivity of the Co-Pt film annealed at 400°C.

Asymmetry in the hysteresis loops was observed for all films at 10°K. The antiferromagnetic CoO and ferromagnetic Co and Co$_3$Pt undergo exchange coupling at the interface and give rise to exchange anisotropy leading to the shift in the hysteresis loop. This
property of the Co-Pt alloy thin film system may find its application in the magnetic sensor systems, like spin valve and magnetoresistance devices.
1 INTRODUCTION

In any magnetic recording system, one of the main components is the magnetic recording media. The hard disk drive, for example, which is one of the most widely used data storage devices, plays a very keen role in advanced information technology.

Magnetic recording media may be broadly classified into two kinds, longitudinal magnetic and perpendicular magnetic recording media. In hard disk drives they are in the form of thin magnetic layers where the binary data is stored. Co/Pt, Co/C, Co/Pd, Fe/Pt, Co/Ni, Co/Fe, Co/P, Fe, Ni, multilayers and thin films are some examples of materials used in perpendicular recording media.

The magnetic recording material can be of two types: soft and hard material. The hard magnetic materials are also referred to as permanent magnetic materials. These materials are difficult to demagnetize and hence are used in permanent recording media. The soft magnetic materials are easy to magnetize and demagnetize and are mostly used as shields and heads in recording media [1,2].

The key components of hard disk drives are the magnetic heads and magnetic recording media. A magnetic recording medium usually consists of layered thin films such as a polycrystalline Co based magnetic thin film on a substrate. The two most important factors for high density recording media are a small grain size to achieve small recording bits and excellent magnetic properties including high coercivity for thermal stability of small recording bits [3,4].

Interest in high density recording media has led to intensive research in the area of hard magnetic materials whose properties can be controlled at smaller size scales. Usually polycrystalline thin film materials are used for these applications. The desire to store information on an ever-decreasing smaller length scale requires a significant reduction in the
characteristic grain size. This has an effect on the grain microstructure, which is an important issue for designing magnetic recording media [5,6,7]. The factors influencing the magnetic properties of a nanocrystalline film are the grain size, grain orientation and grain distribution, grain shape, the thickness of the film and the grain boundary properties.

Co is widely used in magnetic recording because, it is the only one of the three room temperature ferromagnets that has uniaxial symmetry and therefore can be used in digital recording. Co mainly has a hexagonal close packed (hcp) structure and alloying with metals like Pt and Cr changes some of the intrinsic magnetic properties of Co. For example, alloying Co with Pt increases the magnetocrystalline anisotropy constants of the Co alloy. Co-Pt thin films and multilayers are more suitable for ultra high density magnetic recording media because they have excellent high-magnetic anisotropy, chemical stability, coercivity and resistance to corrosion [8,9].

However, up to date very little has been done in the area of developing Co$_3$Pt or Co/Pt multilayers as a means for inducing new or enhanced magnetic properties.
2 OBJECTIVE

The present work is concerned with Co-Pt alloy thin films synthesized using electron beam physical vapor deposition (EBPVD). The main objectives of this present work are:

1. Synthesis of Co$_3$Pt alloy and Pt/Co multilayered thin films;
2. Microstructural and structural characterization of Co$_3$Pt alloy and Pt/Co multilayered thin films; and
3. Study of the magnetic behavior of Co$_3$Pt alloy and Pt/Co multilayered thin films.
3 LITERATURE REVIEW

3.1 Cobalt, Platinum and Their Properties

Co is a transition metal with properties similar to those of Ni and Fe. Co is usually hard and brittle with an hcp crystal structure [10]. It is mostly used in corrosion resistant alloys, magnets, magnetic recording media, wear resistant alloys, etc. Co is ferromagnetic [FM] in nature. Also, upon heating at 425°C, Co exhibits an allotropic transformation and changes to face centered cubic (fcc) structure.

Pt is a scarcely available silvery gray metal that belongs to the eighth group of the periodic table of elements. Pt has a very high melting point and is usually nonreactive to other elements and ions. Pt has high hardness and good thermal and chemical stability. Pt finds several applications such as resistive films in the electronic circuits, jewelry, and catalyst and in thermocouples to measure elevated temperatures, etc [2]. Pt is not magnetic by nature. But Pt usually contains traces of iron in it, which gives rise to paramagnetism in Pt metal.

3.2 Deposition Techniques

Co-Pt alloy thin films can be produced using various techniques. Some of the most widely used techniques are electron beam co-evaporation, DC magnetron sputtering, molecular beam epitaxy, electron beam lithography, electro-deposition and other physical vapor deposition (PVD) or chemical vapor deposition (CVD) techniques.

3.2.1 Electron Beam Co-evaporation

Electron beam co-evaporation can be utilized to deposit Co-Pt alloys using two separate sources of Co and Pt. The source materials are held in two separate crucibles. The substrate can be held at various temperatures depending on the requirements of the film. This method is typically conducted under high vacuum and a base pressure of the chamber is maintained below
5x10^{-7} \text{Torr} [11,12]. Varying the e-beam current in this method, the deposition rate can be controlled and as a result the film composition. Film uniformity during electron beam co-evaporation is achieved by substrate rotation [13]. Typical substrates used in the synthesis of Co-Pt films and Co/Pt multilayers using e-beam co-evaporation are \text{Al}_2\text{O}_3, \text{Si}, \text{MgO} and glass [12,13,14].

### 3.2.2 Magnetron Sputtering

Sputtering is a method of depositing thin metal or ceramic films onto a substrate. Unlike evaporation, the material to be sputtered does not have to be heated. The sputtering process takes place in an evacuated chamber. Argon is introduced, and then ionized in the chamber, which contains the substrate and the target of the film material to be sputtered. The target is maintained at a negative potential relative to the positively charged Ar atoms. The positive ions accelerate towards the negative charge, striking the target with sufficient force to remove material. The Ar ions are not imbedded in the target. They slam into it and “tear” off some of the target material. Since the chamber is maintained at a vacuum, the liberated material settles on everything in the chamber, mainly the substrate. In magnetron sputtering, magnets are placed behind or at the sides of the targets. The escaping electrons are captured by these magnets and are confined to the vicinity of the target generating plasma. The plasma deposition method, which is also known as glow discharge deposition, utilizes the glow discharge to activate the gaseous species required for PVD and CVD. Charged and neutral particles that are electrically neutral on an average are known as plasma. The plasma enhanced (PE) CVD method uses two basic types of glow discharge types. They are direct current (dc) and radio frequency (rf). Magnetron sputtering deposition can be performed under both dc and rf plasma.
3.2.2.1 DC Magnetron Sputtering

In dc magnetron, a negative bias is applied to the substrate, which acts as an electrode. This bias voltage is responsible for ionizing the gas precursor to produce the plasma and the ions required for the deposition of the film. The substrate used should be an electrically conductive material for the deposition of films by dc glow discharge. Usually in dc magnetron sputtering, the Co and Pt targets are sputtered onto the substrates at a particular temperature [10,15]. The base pressure of $3 \times 10^{-8}$ Torr is mostly maintained before introducing Ar gas [10].

3.2.2.2 RF Magnetron Sputtering

In rf magnetron sputtering, the rf glow discharge is used to deposit films even on a nonconductive substrate. It uses capacitively coupled parallel plate rf discharge. The electron frequency is higher than the ion plasma frequency (ion mobility), which produces a negative dc self bias on the powered electrode. In the synthesis of equiatomic CoPt film by rf sputtering, the substrate is typically maintained at room temperature under Ar pressure of 3 to 10 mTorr [9,16,17,18].

3.2.3 Molecular Beam Epitaxy

Molecular beam epitaxy (MBE) was developed in the early 1970s. MBE has the ability to produce high-quality layers with very abrupt interfaces and good control of thickness, doping, and composition. A very high degree of control over the process is possible with MBE. In MBE, the target metals are deposited in the form of molecular beams onto a heated crystalline substrate to form thin epitaxial layers. The ‘molecular beams’ are usually from thermally evaporated elemental sources. It is very critical that the material sources are extremely pure and that the entire process is performed in an ultra-high vacuum in order to obtain high-purity layers. MBE has been used in the preparation of some of the highest quality Co-Pt alloy thin films [19,20,21].
3.3 Structure of Thin Films

3.3.1 Structure of Co Thin Films

Only two stable forms of bulk Co are known, hcp Co below 425°C and fcc at higher temperatures [22]. A third metastable phase of elemental Co called, ε-Co has been reported by Sun and Murray [23]. ε-Co has the complex cubic symmetry of the β phase of Mn and has been observed in particles produced by reduction of Co Chloride with Lithium Triethyl Borohydride [23].

In the recent times, Co-C nanocomposites have been synthesized using vacuum evaporation via co-deposition of two immiscible elements, Co and C at room temperature. The as-deposited metallic Co embedded in an amorphous C matrix had a granular amorphous like structure, depending on the deposition conditions and film composition. The as-deposited films showed ε-Co phase with a lattice parameter of 6.06 Å [22]. After annealing, it changed to hcp Co with a grain size of 5 nm and the films with grain size of 3 nm had fcc structure [22].

It has been reported earlier that, similar Co-C films synthesized at room temperature by ion beam and sputtering, were composed of Co carbides instead of metallic Co [23]. After a post annealing treatment at 350 – 450°C, they decompose into metallic Co and C or graphite. The lattice parameter of ε-Co phase was also reported as 6.12 Å and 6.09 Å [23,24].

Co-C thin films deposited previously by ion beam sputtering showed that structure of Co depended on the C concentration [25]. The Co-C thin film having 36%C, annealed at 350°C had an hcp and fcc Co phases. The annealed Co-C thin film having 46%C had a heavily faulted hcp Co phase and graphite like C boundaries .The annealed films having 57% C, mostly had crystalline Co grains and graphite-like C [25].
It has also been reported that, there is a close relation between the particle size of Co and its crystal structure [26]. For an average diameter < 200 Å, Co has a pure fcc β phase, and for an average diameter of 300 Å, a mixture of hcp α and β phases is found. For a diameter size of 400 Å, an α phase with inclusion of a very small amount of β phase is formed. The particle size and the crystal structure of Co are influenced by their growth conditions. An increase in the sputtering gas pressure has been found to increase the particle size as well as the preferential growth of α phase instead of β phase, substantiating the close relationship between the particle size and the crystal structure [26].

The fcc β phase nanocrystalline Co has been reported to be a high temperature phase in a bulk state and hcp α phase was stable in the size range of 100 nm in an ambient temperature. The nanocrystals fabricated by the sputtering were annealed in vacuum at temperature up to 680°C and the films consisted of both α and β crystals [27].

3.3.2 Structure of Co-Pt Alloy Thin Films

Co and Pt are mutually miscible and form homogeneous solid solutions over the entire range of composition [15]. Figure 1 shows the Co-Pt phase diagram. Very little work has been done on Co$_{1-x}$Pt$_x$ binary alloys on the Co rich side. At high temperature, a disordered fcc phase is stable for all x except when x < 0.25. At this composition range, the alloy transforms into a disordered hcp phase upon cooling to room temperature. For x > 0.25 the room temperature phase is normally disordered fcc phase [15].
3.3.2.1 CoPt Alloy Thin Films

The CoPt alloy having equal contents of metallic elements has been reported to experience a phase transformation from a disordered fcc structure to an ordered face centered tetragonal (fct) structure when cooled from high temperatures to below 835°C [5]. As-made CoPt/BN films deposited by dc magnetron sputtering from solid CoPt and C, consisted of fcc CoPt phase with small grain size of 3 nm. After annealing for four minutes at 700°C, ordered L1₀ phase is formed and particles start to grow having an average grain size of 5 nm [29]. Figure 2 shows the Microstructural changes at different stages of annealing. Prolonged annealing for about 1 hour led to a higher degree of ordering and a much larger particle size. These results indicate a rapid ordering process in the first few minutes of annealing, followed by both a particle size growth and a much slower ordering with further annealing [29].
CoPt/C films have been deposited in another study by rf magnetron sputtering from solid CoPt and C targets. The CoPt/C films deposited on Si consisted of Co-rich hexagonal Co-Pt particles in a C matrix with a granular structure. After annealing for 10 minutes at 700°C, an fct CoPt phase with larger particle size was formed. It is seen from Figure 3 that after prolonged annealing to 60 minutes more ordered fct CoPt is formed with much larger particle size [30].
3.3.2.2 CoPt₃ Alloy Thin Films

From the phase diagram of Co-Pt system, at high temperatures a chemically disordered fcc solid solution is known to exist over the whole composition range and at low temperatures CoPt₃ has a L1₂ fcc ordered phase. In the L1₂ phase, the majority atoms are located at the face centers of fcc unit cell and the minority atoms at the corners, while in the disordered fcc phase these sites are randomly occupied [31]. The bulk CoPt₃ alloy has an order-disorder transition temperature of 685°C with different Curie temperatures of ordered and disordered phases equal to 15 and 195°C, respectively. CoPt₃ (111) nanostructures prepared by self-assembling on WSe₂ (0001) substrates, presented a (111) oriented fcc structure [31]. In another study, a continuous CoPt₃ (111) film epitaxially grown on Pt (111) or Ru (0001) showed a L1₂ long-range ordering for deposition temperatures ranging between 550 and 700°C [4].

3.3.2.3 Co₃Pt Alloy Thin Films

From previous studies, it has been reported that, Co₃Pt thin films undergo a transformation from disordered fcc to disordered hcp structure [32]. Co₃Pt films, deposited on Si by RF sputtering had a mixture of fcc and hcp phases. The hcp phase had lattice constants of $a = 2.6$ Å and $c = 4.22$ Å. The fcc phase had a lattice constant $a = 3.66$ Å. Annealing these films above 600°C altered the amount of one phase in the other. Annealing followed by rapid cooling, resulted in fcc dominating over the hcp phase [32].

In recent times, it was reported that Co₃Pt films grown by e-beam evaporation had an hcp ordered structure and had lattice constants of $a = 2.64$ Å and $c = 4.26$ Å [15]. It has also been reported that, ion implantation followed by thermal processing has been used to synthesize Co₃Pt films having disordered fcc structure with a lattice constant $a = 3.67$ Å [33].

In a study conducted recently, Co₃Pt alloy thin films were deposited onto different substrates like Borosilicate glass, fused silica, MgO (111) and Al₂O₃ (0001), by e-beam co-
evaporation using Co and Pt sources to analyze the effect of substrate on the crystal structure of the film [11,12,13]. The substrates were held at temperatures between 25 and 500°C. The structure of Co3Pt films deposited on Borosilicate glass was a mixture of fcc and hcp in which, a (111) and (0001) texture in the film plane was developed. The structure of Co3Pt thin films deposited on the MgO (111) and Al2O3 (0001) substrate was hcp [11,12]. Co3Pt film deposited on Al2O3 showed a superlattice peak in the XRD spectrum in addition to the fundamental peaks (shown in Figure 4), confirming partial ordering of the Co3Pt films [12,13]. The ordering in these films have been reported to be produced by surface diffusion and the degree of ordering depended on the rate of deposition and $T_s$ [13].

![XRD spectrum](image)

**Figure 4.** XRD spectrum for a Co3Pt film on Al2O3 (0001) deposited at 400°C [12].

### 3.4 Magnetism and Anisotropy

Magnetism is a phenomenon by which a material asserts an attractive or repulsive force on other materials [2]. Magnetic forces are generated by moving, electrically charged particles. Each electron in an atom possesses a magnetic moment. Electron normally pair off in their orbital with as many spins “up” and “down”. An atom will appear magnetic, only when there is an unbalance in the spin of the electrons [34].
Magnetic materials contain domains. These are regions within the crystal in which all the unit cells have a common magnetic orientation. All the unit cells within a phase have the same arrangement of atoms. At higher temperatures, the magnetic dipoles of individual atoms are oriented randomly. During cooling past the Curie temperature, a coupling develops between magnetic dipoles of adjacent atoms. This coupling produces the same magnetic orientation across many unit cells to develop a domain [34]. Adjacent domains are separated by domain boundaries or walls, across which the direction of magnetization gradually changes. The magnetic dipole orientation across a domain wall is shown in Figure 5. For a polycrystalline material, there will be a large number of domains and all may have different magnetization orientations [2].

![Figure 5. A gradual change in the magnetic dipole orientation across a domain wall [2].](image)

When a field $H$ is applied to a material, then the domains change shape and size by the movement of domain boundaries. Initially, the moments of the constituent domains are randomly oriented such that there is no net $M$ field. As the external field is applied, the domains that are oriented in direction favorable to the applied field grow at the expense of the field strength until
the macroscopic specimen becomes a single domain, which is nearly aligned with the field. Saturation is achieved when this domain, by means of rotation, becomes oriented with the H field. From the saturation point, as the H field is reduced by the reversal of the field direction, the curve does not retrace its original path.

A hysteresis effect is produced in which the B field lags behind the applied field H, or decreases at a lower rate. At Zero H field, there exists a residual B field that is called remanence, or remanent flux density Br; the material remains magnetized in the absence of an external H field [1,2]. A typical hysteresis loop of a FM material is seen in Figure 6.

![Figure 6. A typical hysteresis loop][2]

### 3.4.1 Anisotropy

One factor, which can strongly affect the shape of M, H (or B, H) curve or shape of the hysteresis loop, is magnetic anisotropy. This term simply means that the magnetic properties depend on the direction in which they are measured. There are several kinds of anisotropy and some of them are crystal anisotropy, shape anisotropy, stress anisotropy, anisotropy induced by magnetic annealing, plastic deformation and irradiation and exchange anisotropy [1].
3.4.1.1 Crystal Anisotropy

Crystal anisotropy is the only type of anisotropy, which is intrinsic to the material while all the rest of them are extrinsic or induced. Crystal anisotropy is due to spin orbit coupling. Coupling means interaction. There is a coupling between the spin and orbital of each electron. When an external field tries to reorient the spin of an electron, the orbit of that electron also tends to reorient. As the orbit is strongly coupled with the lattice, it resists the attempt to rotate the spin axis. The energy required to rotate the spin system of the domain away from the easy direction is the energy required to overcome the spin orbit coupling and this is known as the anisotropy energy. This coupling is relatively weak, as a few hundred Oersteds (Oe) is enough to rotate the spin [1].

3.4.1.2 Shape Anisotropy

A polycrystalline specimen having no preferred orientation of its grains therefore, has no crystal anisotropy. If it is spherical in shape, the same applied field will magnetize it to the same extent in any direction. But if it is nonspherical, it will be easier to be magnetized along a long axis than along a short axis. The demagnetizing field along a short axis is stronger than along a long axis. The applied field along a short axis then has to be stronger to produce the same true field inside the specimen. Thus, shape alone can be a source of magnetic anisotropy [1]. This is known as shape anisotropy.

3.4.1.3 Exchange Anisotropy

Exchange bias or exchange anisotropy occurs when there is an exchange coupling of FM and antiferromagnetic [AFM] films across their common interface causing a shift in the hysteresis loop of the ferromagnet. This shift occurs after cooling the system with the magnetized FM layer below the Neel temperature of the AFM [35]. This shift finds its application in controlling the magnetization in devices, such as spin valves that sense the change in the
magnetic fields through the GMR effect. To measure the coercivity during this process, obtaining the hysteresis loop is a convenient method. Here, the magnetization is saturated in one direction and then the field is reversed linearly. As this is done, the hysteresis loop also shifts leading to an increase in the width of the loop, which means an increase in the coercivity. The characteristics of exchange bias depend on the constituent materials, thickness, temperature and the orientation of the applied fields. Both coercivity and exchange bias depend on the temperature. By increasing the temperature the exchange bias gets smaller while the coercivity increases and reaches a peak. Finally, the exchange bias reaches zero and the coercivity decreases again with increasing temperature and reaches a blocking temperature at which the exchange bias disappears [36].

Exchange bias is more likely to be seen in FM/AFM bilayers when the Neel temperature is greater than the Curie temperature. Exchange bias or exchange anisotropy was first discovered when fine, single domain particles of Co were partially oxidized, such that each Co particle was covered with a layer of CoO. This system was then cooled in a strong field to 77°K and its hysteresis loop was measured at that temperature. The hysteresis loops were not symmetrical at the origin and shifted to left along the magnetic field. This can be seen in Figure 7. The Co-CoO particles showed a shift in the loop due to the exchange coupling between the spins of AFM CoO and FM Co at the interface between them [1]. The Neel temperature of CoO is 20°C. When a strong field is applied at 20°C the Co saturates and the oxide being paramagnetic is not really affected. The Co ions in the oxide are forced to be aligned parallel to the adjoining spins of Co metal, because of the positive exchange force between the spins of adjacent Co atoms. For the establishment of exchange coupling there are three requirements. Firstly, field cooling is done through the Neel temperature. Secondly, intimate contact between the AFM and FM is required,
such that the exchange coupling can occur across the interface. And lastly, there should be strong crystal anisotropy in the AFM.

![Hysterisis loops measured at 77°K of oxide-coated Co particles. Loop (1) results from cooling in a 10kOe field in the positive direction and loop; and (2) from cooling in zero field [1].](image)

Figure 7. Hysterisis loops measured at 77°K of oxide-coated Co particles. Loop (1) results from cooling in a 10kOe field in the positive direction and loop; and (2) from cooling in zero field [1].

Exchange anisotropy has also been found in disordered Ni$_3$Mn systems [1]. This system is paramagnetic at room temperature and showed exchange anisotropy when cooled at low temperatures. The loop is shifted so far that the retentivity is positive, after cooling in a field in the positive direction. The reason for the exchange bias is due to the composition fluctuations in the solid solution, which results in the formation of Mn rich clusters. The clusters are AFM; because of the exchange force between the Mn-Mn nearest neighbors is negative spin pure Mn. Outside the cluster the solid solution would be richer in Nickel than the average composition and the preponderance of Ni-Ni and Ni-Mn nearest neighbors would cause ferromagnetism. It may thus be concluded that for the exchange anisotropy to occur the system need not be a two phase alloy system, but can also be a single phase solid solution having the right kind of inhomogeneity [1].
3.4.2 Magnetic Properties of Co-Pt Alloy and Multilayered Thin Films

There has been a drastic growth in the field of magnetic information storage systems in the recent years. The most important parameters, which need to be taken into consideration in recording media, are grain size and magnetic coupling across the grain boundaries [4].

The increase in areal density on the recording media has brought a revolutionary change in the magnetic recording technology. The increase in the areal density implies the reduction in size of the actual magnetic bits. One of the many issues concerning the high density recording media is the media noise. Intergranular exchange coupling is one of the most important factors, which contributes to limiting the media noise that helps in controlling the areal density [6].

Magnetically isolated grains of size less than 10 nm are preferred for high magnetic recording density because of the need to reduce noise. In order to reduce thermal fluctuations and demagnetizing fields in such small grain sizes of less than 10 nm, they need to have high magnetocrystalline anisotropy. It is believed that for high-density magnetic recording media above 20 Gbits/in², the thermal stability is one of the main concerns. The reason is that thermal agitation is prominent for grain sizes less than 10 nm. To maintain good stability of written marks, the magnetic anisotropy of grains should be greater than $10^7$ ergs/cm³ and this is attainable by Co-Pt thin films [11]. High magnetocrystalline anisotropy is needed to destabilize the magnetization of the recorded bits. CoPt alloy thin films are of great interest due to their high anisotropy and coercivity [5].

Most widely used recording method is the longitudinal recording. Here the demagnetizing field gets stronger with the increase in the areal density and thus, influences the stability of the magnetic domain. Perpendicular recording has the ability to decrease the effect of demagnetizing field and can improve the stability of the magnetic domain. Large perpendicular
magnetic anisotropy (PMA) was seen in Co/Pt multilayers but the reason why they are not yet used in real recording is that the existence of strong intergranular magnetic coupling, which is the root, cause for transition media noise [3].

Co-Pt alloys are known for their high magnetic anisotropy and excellent coercivity [13]. The CoPt alloy thin films are used in magnetic devices like high density recording media and magnetic bias films of magneto resistive elements. An assembly of very fine noninteracting high anisotropy magnetic particles is magnetically hard which means it has large coercivity. This due to the fact that particles are single domains and that magnetic reversal takes place only by rotation of $M_s$ vectors against strong anisotropy forces. The magnetic hardness of permanent magnets depends on the size of the particles and the interaction between the particles. The particle growth on a substrate depends on the strength of interaction between atoms of growing film and the atoms of the substrate.

Magnetic properties of Co-Pt alloy thin films are a function of substrate, deposition temperature and the composition of the film [11,12,21]. CoPt alloys containing rich Co concentration are candidates for high magnetic anisotropy. CoPt films having equiatomic compositions have excellent magneto-crystalline anisotropy. The Co$_3$Pt alloy films show large PMA [13]. This PMA depends on the composition and the type of substrate used.

The sensitivity of the magnetic moments of Pt atoms in the CoPt alloy system depends on the concentration and local chemical environment. Therefore, the properties of the ordered/disordered state at the Curie temperature are diagnosed. In the Co-Pt system, for a temperature around 1400°K, the system orders ferromagnetically but stays atomically disordered in the systems where the concentration of Co is larger than Pt. At 840°K, an ordered Co$_3$Pt phase (L1$_2$) with maximum ordering temperature was formed [37].
3.4.2.1 CoPt Alloy Thin films

CoPt/Ag films consisting of fct CoPt have been subjected to annealing at different temperatures to study the magnetic properties and microstructural changes. Figure 8 represents the hysteresis loop of the film when annealed at different temperatures. This film was prepared by magnetron sputter deposition, using co-sputtering from two metallic targets. The substrate used was $p$-type Si (100) 60 $\mu$m thick [5]. It has been reported that CoPt alloy having equal compositions of metallic elements experience a phase transformation from a disordered fcc structure to an ordered fct structure when cooled from high temperature below 800°C [5]. When annealed, these films transform into fct structure and become magnetically hard. It was also seen that the coercivity increased drastically with the increase of temperature to 600°C. It was reported that another important factor influencing coercivity is the layer thickness [5]. CoPt films are known to have excellent magnetocrystalline anisotropy in the ordered face centered tetragonal (fct) phase and can have coercivities greater than 5 kOe [30].

Figure 8. Hysterisis loops for CoPt/Ag films annealed for 2 hours at different temperatures [5].
The microstructure of the films when annealed is seen in Figure 9. The size of the CoPt particles embedded in the Ag matrix varied from 7 to 100 nm depending on the annealing temperature and the composition of the film. The annealed samples showed single domain hard magnetic particles having weak interparticle interaction of dipolar nature, which is best suited for magnetic recording media [5].

![Figure 9. Evolution of microstructure with annealing time (a), (b), (c) CoPt (0.5 nm) /Ag (0.3 nm) films annealed at 600°C for 5, 10, 20 mins respectively; (d) CoPt (2 nm) /Ag (2 nm) films annealed at 550°C for 240 min [5].](image)

The CoPt/C films were reported to have lower coercivities due to low anisotropy of the hexagonal Co-rich particles in a C matrix. Therefore, CoPt/BN films having high anisotropic nanoparticles have been prepared [7]. These films are deposited on a Si substrate with 600 µm thickness. The as-deposited films had disordered fcc structure which were magnetically soft but hardened by the formation of fct phase when annealed in the temperature range of 600 to 800°C. The ordered fct phase had higher magnetocrystalline anisotropy, thereby resulting in very high coercivities [7]. These experiments concluded that the coercivity and magnetic grain isolation of the films can be varied by controlling the layer thickness and the aging heat treatment conditions [7,30]. Figure 10 shows the dependence of coercivity on the annealing time.
Figure 10. Dependence of coercivity on annealing time CoPt/BN samples [7].

CoPt alloy films of 10 nm thick have been prepared in another study, on fused quartz substrate by dc magnetron sputtering [10]. When annealed at 750°C, the film had the highest coercivity when it was measured perpendicular to the magnetic field at 300°C. But the coercivity decreased when annealed at 800°C. The growth of the crystals is partly responsible for the increases in coercivity due to annealing till 750°C. The smaller particles form almost a noninteracting system and have dimensions close to the single domain particle size, which leads to very high coercivity value [10]. But when annealed at 800°C, the reduction in coercivity may be attributed to the further crystallite growth, which results in the formation of multidomains. In short, the increase in coercivity at the beginning of the annealing stage is due to the growth of the crystallites, which reach the size of a magnetic single domain. After further annealing, the drop in coercivity of the films may be due to the increase in the crystallite size, which results in the multidomain formation [10].

Nanocomposite CoPt-C thin films consisting of nonmagnetic C matrix and high anisotropy fct CoPt nanocrystallites can be in demand in the high density recording media
because of its small grain size. The CoPt: C composite films can be prepared from a multilayered structure of Co/Pt/Co/C. Magnetic intergranular interactions can be calculated from the M curve measurements. Intergranular interactions in nanocomposite CoPt-C films are strongly dependent on the film composition and can be controlled by Co concentration [6]. Figure 11 shows the hysteresis loop of the composite thin films.

![Hysteresis Loop Diagram](image)

**Figure 11. Hysteresis loops for Co50Pt50-C and Co57Pt43-C composite films [6].**

### 3.4.2.2 CoPt3 Alloy Thin Films

Co-Pt binary alloys have strong PMA and are therefore, good candidates for high-density magneto-optical recording [19]. The ordered CoPt3 phase, which is a chemically ordered fcc structure having Pt at the face centers and Co atoms at the cube corners of the unit cell, has no PMA due to its symmetry. The same is true with the chemically disordered phase where Co and Pt on the fcc lattice are randomly distributed. Previously, the CoPt3 grown epitaxially on Pt and Ru in a temperature range of 200-400°C was found to have large coercivities and large PMA without chemical long range ordering [19]. These are explained by short range ordering effects. In a study conducted on CoPt3 films, the films were grown epitaxially by co-evaporation of Co
and Pt from two e-beam sources on surface crystals of WSe$_2$ (0001). A 3 nm thick CoPt$_3$ film had a coercivity of 200 Oe and a saturation magnetization of 520 emu/cm$^3$. Increase in the thickness of the film resulted in the decrease of domain size. A 6 nm thick CoPt$_3$ films showed strong PMA, and had very small grain size and hence can be used in data storage media [19].

3.4.2.3 Co$_3$Pt Alloy Thin films

For a long time no magnetic anisotropy was reported for Co$_3$Pt alloy films. Yamada et al [11,12,14] reported that large PMA exists in Co-Pt thin films rich in Co. Co$_3$Pt alloy films, where $x$ is ranging from 0 to 0.5 with a thickness 1000±100 Å have been deposited by e-beam co-evaporation on MgO, Al$_2$O$_3$, Borosilicate glass and fused silica substrates. The film has the maximum PMA constant $K_u$ at 25 at% Pt when compared to the other Co-Pt films of varying compositions deposited on Borosilicate glass substrate [11]. Figure 12 shows the effect of Pt concentration on the magnetic properties of the Co-Pt alloy system.

The $K_u$ values of films deposited on MgO (111), Al$_2$O$_3$ (0001) and fused silica are maximum in the substrate temperature range of 180 to 400°C. Therefore, it is said that the Co$_3$Pt film deposited on Al$_2$O$_3$, MgO and fused silica substrates using e-beam co-evaporation have a PMA greater than 10$^7$ ergs/cm$^3$ in the temperature range 180 to 400°C. The reasons for the high PMA have been attributed to the anisotropic distribution of Co-Co bonds in the hcp ordered structure [11].
A correlation between the origin of magnetic anisotropy and the ordered phase of Co$_3$Pt was made. The experiments suggested that the $K_u$ is dependent on composition, nature of the substrate and the substrate temperature [12,14]. $K_u$ varies linearly with order parameter $S$ for substrate temperature $T_s$ ranging from 380 to 450°C. No correlation was found in the temperature range of 230 to 380°C. Hence, it has been concluded that $S$ and $K_u$ were dependent on $T_s$ [12,13,14].

### 3.4.2.4 Co/Pt Multilayered Films

The multilayers of Co/Pt exhibit structure sensitive magnetic anisotropy and giant magneto resistance (GMR). Co/Pt multilayer thin films have large ratio of coercive field to saturation magnetization ratio. Pt/Co multilayers are found to exhibit large coercivities in both sputtered and evaporated film [38]. The coercivities of sputtered Co/Pt films depend on the
annealing temperature in controlled atmospheres. Annealing has been performed in different atmospheres like air and 10% H$_2$ in N$_2$ in the range of 100 to 400°C. The coercivity was found to increase in atmospheres having large amount of O$_2$. The coercivity also increased after annealing in vacuum or in air. In the multilayer films, it was observed that as the coercivity increased, the saturation magnetization decreased and hence it was concluded that an increase in coercivity is due to the presence of CoO. It was also seen that annealing in 10% H$_2$ in N$_2$ reverses the increase in coercivity. Initially, the reason for the increase of coercivity was thought to be the presence of oxygen in the multilayered films but the further increase in coercivity was attributed to the presence of domain wall pinning [38].

The multilayers of Co/Pt and Co/Cu are believed to exhibit structure sensitive magnetic anisotropy and GMR [39]. Co, Pt layers have been deposited in the past on glass substrate using ion-assisted deposition. The effects on the ion-treated Co/Pt multilayers can be compared to the Co/Pt multilayers that are sputtered deposited in thermalizing conditions. These films had rougher interfaces, coarser microstructures, stronger perpendicular anisotropy and larger coercivities. There was a progressive loss of GMR and AFM coupling in the ion assisted Co/Cu multilayers. This has been attributed to modifications of the microstructure and texture of the layers or interface regions [39].

The above literature review shows that a lot of interest and investigative effort exists in the area of Co-Pt alloy thin films and Co/Pt multilayers and their properties. An issue where very little information exists is the synthesis of Co$_3$Pt and Pt/Co multilayers with alternative technique such as e-beam evaporation. Such an effort would help in better understanding the structural and magnetic behavior of these thin films.
4 EXPERIMENTAL

4.1 Film Synthesis by EBPVD

Thin films of Co, Pt, Co-Pt alloy and Pt/Co multilayers were synthesized using the EBPVD technique. All the films were deposited on the Si (100) substrate.

4.1.1 Processing System

An Edwards AUTO 306 Vacuum Coater with a cryo pump and a dual electron gun was used to synthesize the thin films and multilayers. The system is designed for PVD under high vacuum. This PVD system has two electron beam guns allowing flexibility for depositing multilayered or alloy films. The EBPVD is a low temperature method, through which deposition of alloy, composites and multilayers with sharp interfaces can be achieved.

The important components of the system are: two e-beam guns, a pumping system consisting of a rotary mechanical pump and cryodrive pump, base plate, and an electrical system with a controller. The system has a vacuum chamber attached to the base plate. Thickness monitors are placed above the substrate holder to monitor the deposition rates. The work piece holder and heater accessories are used to support and heat the substrate materials to be coated in the vacuum chamber. The work piece holder ring can be adjusted horizontally or vertically according to the experimental need. A radiant heater and a quartz heater are used to heat the substrate before and during deposition process to prevent the adsorption of moisture and contaminants by the substrate material. A quartz heater is used with the rotary work piece holder and a radiant heater with the spherical work holder dome.
4.1.2 Experimental Procedure for Thin Film and Multilayer Deposition

Co, Pt, Co-Pt alloy and Pt/Co multilayer thin films were processed using the aforementioned system. Individual pure Co and Pt thin films were prepared for the purpose of calibration. Powder of Co (99.95%) and Pt pellets (99.99%) were used as source materials for the preparation of Co-Pt and multilayer thin films. The source materials were placed separately in the two graphite crucible liners. The base pressure in the chamber prior to deposition was $5 \times 10^{-6}$ Torr. During deposition the electron gun voltage was kept at 4.5 kV. The beam current 30 mA and 115 mA were used for Co and Pt, respectively. Two thickness monitors positioned higher than the substrate holder were used to monitor and control the deposition rates and thickness of the films. The rate of deposition was 0.002-0.003 nm/min and 0.004-0.006 nm/min, for Co and Pt, respectively.

Table 1. Processing parameters for synthesizing of Co-Pt alloy and Pt/Co multilayered films.

<table>
<thead>
<tr>
<th>Thin films / Multilayers</th>
<th>Source Material</th>
<th>Beam Current (mA)</th>
<th>Deposition Rate (nm/ min)</th>
<th>Pressure (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Powder</td>
<td>30-35</td>
<td>0.005-0.006</td>
<td>$4.0 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>Co (99.95%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>Pellets</td>
<td>115-125</td>
<td>0.002-0.003</td>
<td>$4.0 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>Pt (99.99%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.1.3 Characterization of Thin Films

4.1.3.1 Thickness Measurements

A small area of the sample was masked to allow thickness measurement after deposition. The thickness of the films was measured by a WYKO NT 1000 surface optical profilometer.
This instrument functions on the principle of interference of light. The deposition rate of Co-Pt thin films was estimated by the ratio of the observed thickness to the total deposition. Film thickness was measured by using the surface optical profilometer at a magnification of 10X. The phase shift interference (PSI) mode of the profilometer used for the measurement has a vertical resolution of about 3 Å. Thickness values represent the average of at least three measurements.

4.1.3.2 Compositional and Microstructural Characterization

4.1.3.2.1 TEM

High-resolution (HR) TEM analysis of Co-Pt as deposited films, Co-Pt annealed films and Pt/Co multilayers was performed on a JEOL JEM 2010 electron microscope operated at 200 keV with a point-to-point resolution of 2.3 Å. Plan view and cross sectional TEM samples were prepared for analysis. Cross sectional slices were obtained by cutting the samples along a direction normal to the coating surface and then gluing, face-to-face the two coating surfaces. Cross-sectional specimens for TEM observation were prepared by mechanical grinding, polishing, and dimpling followed by Ar-ion milling using a Gatan Precision Ion Polishing System (PIPS™, Model 691) at 4.5 keV, at an angle of 5°.

4.1.3.2.2 SEM

A Hitachi S-3600N scanning electron microscope (SEM), equipped with an Energy Dispersive Spectroscopy (EDS) detector, was used in this study to investigate the surface morphology and composition of all films. Images in the SEM can be obtained using a secondary electron detector or a back scattered electron detector. Some preliminary compositional analysis of the Co-Pt and Pt/Co multilayer film was carried out with EDS. However, this technique has a large excitation depth larger than the film thickness and thus may not be the most appropriate technique for compositional analysis.
4.1.3.2.3 Microprobe

A JAX-733 electron microprobe was used for compositional analysis of thin films. Microprobe is using an electro beam accelerated at a voltage of 15 kV and a beam current of 10 nA. The microprobe has a wavelength dispersive spectrometer (WDS) allowing accurate compositional analysis based on the characteristic wavelength of X-rays emitted by each element.

4.1.3.3 Characterization of Magnetic Properties of Thin Films

4.1.3.3.1 MPMS

The Quantum Design’s Magnetic Property Measurement system (MPMS) is a highly integrated instrument, designed to be a primary research tool for magnetic properties. A MPMS–5 model was used for analysis. It has a field range of –5.5 to +5.5 Tesla i.e., 55000 Gauss and a field stability of 1 ppm. The temperature range at the sample space is 1.9°K to 400°K and it has a He capacity of 56 l. The principle components of this measurement comprise of a temperature control system, magnet control system, superconducting SQUID amplifier system, sample handling system and a computer operating system.

In the magnet control system, the current from a power supply is set to provide magnetic fields from zero to positive and negative seven teslas. The magnet can be operated in either persistent or non-persistent modes, and the user can select several charging options. In the superconducting SQUID amplifier system, the rf SQUID detector is the heat of the magnetic
moment detection system. It provides reset circuitry, auto ranging capability, a highly balanced second derivative sample coil array and EMI protection.

The ability to step and rotate the sample smoothly through the detection coils without transmitting undue mechanical vibration to the SQUID is of primary importance. The sample handling system allows for varied scan lengths and options as to how data are acquired for a given measurement. All operating features of the MPMS are under automated, computer control. The user interface at the PC console provides the option of working under standard sequence controls, or diagnostic controls, which will invoke individual functions. For the MPMS, superconductivity is the critical enabling technology that provides for both the production of large, very stable magnetic field, and the ability to measure changes in those fields, which are 14 orders of magnitude smaller.

4.1.3.3.2 PPMS

The Quantum Design’s Physical Property Measurement System (PPMS) is a versatile DC magnetometer and AC susceptometer. A MODEL 6000 was used for analysis in the present study. It has a field range of –9.0 to +9.0 Tesla i.e., 90000 Gauss. The AC Measurement System (ACMS) insert houses the drive and detection coils, thermometer and electrical connections for the ACMS system. The insert fits directly into the PPMS sample chamber and contains a sample space that lies within a uniform magnetic field region of host PPMS, so the DC field and the temperature control can be performed with conventional PPMS methods. The sample is held within the insert coil set on the end of a thin rigid sample rod. A DC servomotor located in the ACMS sample transport assembly translates the sample holder longitudinally. The DC servomotor provides rapid and very smooth longitudinal sample motion. The ACMS sample transport assembly mounts on the top of the PPMS probe.
During DC measurements, a constant field is applied to the measurement region and the sample is moved quickly through both sets of coils inducing a signal in them according to the Faraday's law. During DC measurement, the amplitude of the detection coil signal is dependent upon both the extraction speed and the sample's magnetic moment.
5 RESULTS AND DISCUSSION

Thin films of pure Co, pure Pt, as-deposited Co-Pt alloy, annealed Co-Pt alloy and Pt/Co multilayers were characterized by profilometry, SEM, TEM, MPMS and PPMS. The Co-Pt alloy film composition was obtained using the electron microprobe analysis, and was found to have Co and Pt in the atomic ratio of 3:1. Thickness of the films was measured using profilometry. Surface morphology was characterized using SEM and microstructure was studied using TEM. MPMS and PPMS were used for measuring magnetic properties of the films. Results obtained from the above experiments are presented in the following sections.

5.1 Microstructure of Synthesized Films

5.1.1 As-deposited Films

5.1.1.1 Pure Co Film

Figure 13 shows a typical TEM micrograph of a 21 nm thick pure Co film deposited on TEM Cu grit. Inset is a selected-area electron diffraction pattern (SAED) from the film. Microstructure of the film shows a nodular structure with an average grain size in the range of 6 to 7 nm. The Co film may have nanocrystalline grains of CoO along with Co grains. From the electron diffraction pattern, the Co seems to have a mixture of hcp and ε structure, whereas the CoO has a structure similar to NaCl. The diffraction rings of the SAED pattern in Figure 13 have a $d$-spacing of 2.51, 2.22, 1.99, 1.52, 1.29, 1.2, 1.09, 0.98, 0.89, 0.83, 0.71 and 0.63 Å.

i. The $d$-spacing of 2.51, 1.52, 1.29, 1.2, 1.09, 0.98, 0.89, 0.83, 0.71 and 0.63 Å corresponds to the (111), (220), (311), (222), (400), (331), (422), (333), (600) and (622) reflection of NaCl type CoO.
Figure 13. HRTEM showing diffraction pattern and grain structure of a pure Co thin film.

ii. The $d$-spacing of 2.22, 1.99, 1.52, 1.29, 1.2, 1.09, 0.98, 0.89, 0.83, 0.71 and 0.63 Å corresponds to the (100), (101), (102), (110), (111), (200), (202), (203), (210), (301) and (220) reflection of hcp Co.

iii. The $d$-spacing of 2.51, 2.22, 1.99, 1.52, 1.29, 1.2, 1.09, 0.98, 0.89, 0.83, 0.71 and 0.63 Å corresponds to the (211), (220), (310), (400), (332), (431), (440), (661), (444), (721), (743) and (755) reflection of ε-Co.

Figure 14 shows a typical EDS spectrum of Co film. The results indicate the presence of Oxygen (O) in the film. Some of the Co in the film seems to have reacted with O to form CoO, which is AFM in nature. Therefore, it can be concluded that the $d$-spacing of 2.51, 1.52, 1.29, 1.2, 1.09, 0.98, 0.89, 0.83, 0.71 and 0.63 Å indeed corresponds to (111), (220), (311), (222), (400), (331), (422), (333), (600) and (622) reflection of NaCl type CoO.
5.1.1.2 Pure Pt Film

Figure 15 shows a typical TEM micrograph of a Pt film deposited on TEM Cu grit. The microstructure of the film shows a nodular structure with an average grain size in the range of 3 to 4 nm. The diffraction rings in the SAED pattern in Figure 15 have a $d$-spacing of 2.63, 2.22, 1.38, 1.16, 0.99, 0.88, 0.80, 0.76 and 0.66 Å.

i. The $d$-spacing 2.63, 2.22, 1.38, 1.16, 0.99, 0.88, 0.80, 0.76 and 0.66 Å corresponds to (111), (200), (220), (311), (400), (420), (422), (333) and (531) reflection of fcc Pt.

Therefore, it can be concluded that the pure Pt film has an fcc structure.
Figure 15. HRTEM showing diffraction pattern and grain structure of a pure Pt thin film.

5.1.1.3 Co-Pt Film

Figure 16 shows a plan view TEM micrograph of a typical Co-Pt thin film with an original thickness of 145 nm. The microstructure shows an average grain size in the range of 5 to 6 nm. A mixture of fcc and hcp Co$_3$Pt seem to exist along with the presence of $\varepsilon$-Co and NaCl type CoO. The lattice constants of hcp Co$_3$Pt are $a = 2.64$ Å and $c = 4.21$ Å. The lattice constant of fcc Co$_3$Pt $a = 3.69$ Å. The lattice constant of simple cubic $\varepsilon$-Co, $a = 6.12$ Å. The diffraction rings in Figure 16 show a $d$-spacing of 2.51, 2.22, 1.87, 1.52, 1.31, 1.11, 0.93, 0.84, 0.76, 0.72 and 0.63 Å.

i. The $d$-spacing 2.51, 1.52, 1.31, 1.11, 0.93, 0.84, 0.76, 0.72 and 0.63 Å corresponds to (111), (220), (311), (400), (420), (333), (440), (531) and (622) reflection of NaCl type CoO.

ii. The $d$-spacing 2.22, 1.52, 1.31, 1.11, 0.93, 0.84, 0.76, 0.72 and 0.63 Å corresponds to (100), (101), (110), (201), (202), (211), (300), (302) and (222) reflection of hcp Co$_3$Pt.
iii. The $d$-spacing 1.87, 1.31, 1.11, 0.93, 0.84, 0.76, 0.72 and 0.63 Å corresponds to (200), (220), (311), (400), (331), (422), (511) and (531) reflection of fcc Co$_3$Pt.

![HRTEM Image](image)

**Figure 16. HRTEM showing the grain structure of as-deposited Co-Pt alloy thin film.**

iv. The $d$-spacing 2.51, 2.22, 1.87, 1.52, 1.31, 1.11, 0.93, 0.84, 0.76, 0.72 and 0.63 Å corresponds to the (211), (220), (311), (400), (332), (521), (533), (720), (740), (743) and (763) reflection of $\varepsilon$-Co.

Figure 17 shows a typical EDS spectrum of an as-deposited Co-Pt alloy thin film. Again, the presence of O is observed, which supports the conclusion that CoO is present in this film and that the $d$-spacing of 2.51, 1.52, 1.31, 1.11, 0.93, 0.84, 0.76, 0.72 and 0.63 Å indeed corresponds to (111), (220), (311), (400), (420), (333), (440), (531) and (622) reflection of NaCl type CoO.
5.1.2 Annealed Films

5.1.2.1 Annealing at 300°C

Figure 18 shows a plan view TEM micrograph of a vacuum-sealed Co-Pt film, annealed at 300°C in a high temperature furnace for 2 hours. The microstructure of the film shows an average grain size of about 6 to 7 nm. Grains of the annealed film show a slight growth when compared to the grains of the as-deposited Co-Pt film. The diffraction rings in Figure 18 have a \(d\)-spacing of 2.51, 2.22, 1.81, 1.47, 1.31, 1.11, 1.05, 0.95, 0.83, 0.75, 0.71 and 0.64 Å.

i. The \(d\)-spacing 2.51, 1.47, 1.31, 1.05, 0.95, 0.83, 0.75, 0.71 and 0.64 Å corresponds to (111), (220), (311), (400) (420), (333), (440), (600) and (622) reflection of NaCl type CoO.

ii. The \(d\)-spacing 2.22, 1.31, 1.11, 1.05, 0.95, 0.83, 0.75, 0.71 and 0.64 Å corresponds to (100), (110), (112), (202), (113), (211), (301), (302) and (310) reflection of hcp Co₃Pt.
iii. The $d$-spacing of 1.81, 1.31, 1.11, 1.05, 0.95, 0.83, 0.75, 0.71 and 0.64 Å corresponds to (200), (220), (311), (222), (400), (420), (422), (511) and (440) reflection of fcc Co$_3$Pt.

iv. The $d$-spacing of 2.51, 2.22, 1.81, 1.47, 1.31, 1.11, 1.05, 0.95, 0.83, 0.75, 0.71 and 0.64 Å corresponds to (211), (220), (311), (410), (332), (521), (433), (621), (721), (741), (743) and (754) reflection of $\varepsilon$-Co.

Again, a mixture of fcc and hcp Co$_3$Pt seems to exist along with of $\varepsilon$-Co and NaCl type CoO as seen in the case of the as-deposited film.

Figures 19 and 20 show the SE and BSE image of a Co-Pt alloy film annealed at 300°C. SE image usually shows the topography of the phases in a film. Regions appearing dark in the image are higher in topography than the regions appearing bright. The different phases in a film can be analyzed using BSE. The constituent phase appearing bright in a BSE image is denser (high atomic number, Z) than the phase appearing dark. Since Co$_3$Pt has a higher density and is
heavier than CoO and Co, it appears as the bright region in the image, whereas CoO and Co appears as the dark region.

Figure 19. SE image of Co-Pt alloy thin film annealed at 300°C.

Figure 20. BSE image of Co-Pt alloy thin film annealed at 300°C.
Figure 21 shows a typical EDS spectrum of a Co-Pt alloy film annealed at 300°C. The presence of O, Co and Pt is observed along with Si. It is more likely that O is present in the form of CoO, as the formation of Pt oxide is very difficult to occur.

### 5.1.2.2 Annealing at 400°C

Figure 22 shows the plan view TEM micrograph of a Co-Pt film, which is vacuum-sealed in glass and annealed at 400°C in a high temperature furnace for 2 hours. Microstructure of the film indicates an average grain size of 10 nm. A significant grain growth is observed when the specimen is annealed at 400°C. The diffraction rings in Figure 23 have a $d$-spacing of 4.53, 2.86, 2.41, 2.12, 2.03, 1.84, 1.64, 1.54, 1.47, 1.42, 1.35, 1.26, 1.22, 1.13 and 1.04 Å.

- The $d$-spacing of 2.41, 2.12, 1.54, 1.26, 1.22 and 1.04 Å corresponds to (111), (200), (220), (311), (222) and (400) reflection of NaCl type CoO.
Figure 22. HRTEM showing the grain structure of a Co-Pt alloy thin film annealed at 400°C.

ii. The \(d\)-spacing of 2.03, 1.54, 1.35, 1.26, 1.22, 1.13 and 1.04 Å corresponds to (101), (102), (110), (111), (103), (112) and (202) reflection of hcp Co\textsubscript{3}Pt.

iii. The \(d\)-spacing of 2.12, 1.84, 1.35, 1.13 and 1.04 Å corresponds to (111), (200), (220), (311), (222) and (400) reflection of fcc Co\textsubscript{3}Pt.

iv. The \(d\)-spacing of 4.53, 2.86, 2.41, 2.12, 2.03, 1.84, 1.64, 1.54, 1.47, 1.42, 1.35, 1.26, 1.22, 1.13 and 1.04 Å corresponds to (110), (210), (211), (220), (300), (311), (321), (400), (410), (330), (421), (422), (430), (432) and (531) reflection of \(\varepsilon\)-Co.

The surface morphology of the Co-Pt thin film annealed at 400°C is shown in Figure 23. A significant change in morphology of the film is seen when compared to film annealed at 300°C. This indicates that heat treatments at different temperatures have a significant effect on surface morphology of the films. A rather uniform distribution of the particles is shown in Figure 23, suggesting some rearrangement under the high temperature exposure.
Figure 23. SE image of a Co-Pt alloy thin film annealed at 400 °C.

Figure 24 presents the EDS spectrum of a film annealed at 400°C. The EDS spectra of all the films showed presence of O. Though, the exact source of O is not clearly known, Co has a tendency of easily reacting with O to form CoO. Therefore, either Co may have reacted with O
immediately after the film deposition, or oxidation may have occurred in the film during vacuum sealing of the sample.

5.1.3 Multilayered Pt/Co Films

Figure 25 shows a typical cross section TEM micrograph of a Pt/Co multilayered film with a thickness of 112 nm. The first layer on the Si is Pt followed by Co. A total of 8 layers were deposited (4 layers each of Pt and Co). The deposition rates were altered such that a desired thickness of 21 nm of Co and a thickness of 7 nm of Pt were obtained.

![Figure 25. HRTEM cross-section micrograph of Pt/Co multilayered film.](image)

Figure 25 also shows an electron diffraction pattern of the Pt/Co multilayered film. The diffraction rings have a $d$-spacing of 2.51, 2.28, 2.07, 1.87, 1.52, 1.38, 1.26, 1.2, 1.13 and 1.06 Å.

i. The $d$-spacing of 2.28, 1.96, 1.38, 1.2 and 1.13 Å corresponds to (111), (200), (220), (311) and (222) reflection of fcc Pt.
ii. The $d$-spacing of 2.51, 2.07, 1.87, 1.52, 1.38, 1.26, 1.2, 1.13 and 1.06 Å corresponds to $(211), (221), (300), (400), (422), (431), (432)$ and $(441)$ reflection of ε-Co.

iii. The $d$-spacing of 1.87, 1.52, 1.26, 1.2, 1.13 and 1.06 Å corresponds to $(101), (102), (110), (111), (103)$ and $(112)$ reflection of hcp Co.

iv. The $d$-spacing 2.51, 1.52, 1.26, 1.2 and 1.06 Å corresponds to $(111), (220), (311), (222)$ and $(400)$ reflection of NaCl type CoO.

Figure 26 presents a typical EDS spectrum of a Pt/Co multilayered film and shows the presence of Co and Pt. There may be some O, present in the film. However, there is no corresponding peak visible. The presence of O can be explained by the $d$-spacing of 2.51, 1.52, 1.26, 1.2 and 1.06 Å corresponding to $(111), (220), (311), (222)$ and $(400)$ reflection of NaCl type CoO.
5.2 Magnetic Property Measurements

Magnetic properties can be mainly performed in two different ways using the in-plane (field parallel to the film) and perpendicular (field normal to the film) measurement methods. The pure Co film, as-deposited Co-Pt alloy film, and Co-Pt alloy films annealed at 300°C and 400°C were measured for hysteresis using the MPMS at 10°C and 300°C. The magnetic measurements were conducted at two different orientations namely, parallel and perpendicular.

5.2.1 In-Plane Measurements

5.2.1.1 Pure Co Film

Figures 27 and 28 present the magnetization-magnetic field (M-H) hysteresis loops measured in MPMS at 10°C and 300°C for the pure Co film. Coercivities of 1400 emu/cm³ and 75 emu/cm³ were obtained at 10°C and 300°C, respectively. Magnetic saturation ($M_s$), of a FM material represents the magnetization that results when all the magnetic dipoles in the film are mutually aligned with the external field. In other words, $M_s$ is the maximum possible magnetization in a specimen.

![Figure 27. Hysteresis of pure Co film at 10°C.](image)
Figure 28. Hysteresis of a pure Co film at 300°K.

Ms of 300 emu/cm³ is obtained at 300°K. At 10°K the film does not saturate, even after applying a field of 50 kOe. From this, it can be concluded that, pure Co film saturates easily at room temperature and has a higher saturation value at lower temperatures.

5.2.1.2 Co-Pt As-deposited Film

Figures 29 and 30 present hysteresis loops measured at 10°K and 300°K, respectively for the as-deposited Co-Pt alloy thin film. Coercivities of 2490 emu/cm³ and 98 emu/cm³ were obtained at 10°K and 300°K, respectively. Mₘ for the as-deposited Co-Pt alloy at 300°K is around 370 emu/cm³. But, Mₘ at 10°K does not occur, even after applying a field of 50 kOe. The Ms of pure Co is lower than that of as-deposited Co-Pt alloy film. Therefore, it can be concluded that, addition of Pt to Co, has increased the Mₘ of Co.
5.2.1.3 Co-Pt Alloy Thin Film Annealed at 300°C

Figures 31 and 32 show the hysteresis loops for a Co-Pt alloy film annealed at 300°C, measured at 10°C and 300°C, respectively. Coercivities of 1960 emu/cm³ and 91 emu/cm³ were obtained at 10°C and 300°C, respectively. $M_s$ values could not be obtained at 10°C and 300°C,
as the film does not saturate, even after applying a field of 50 kOe. It is clearly seen that, annealing the film at 300°C, has increased the saturation of Co-Pt alloy film to a large extent.

![Graph showing hysteresis loop](image)

**Figure 31.** Hysteresis loop at 10°K for Co-Pt film annealed at 300°C.

![Graph showing hysteresis loop](image)

**Figure 32.** Hysteresis loop at 300°K for Co-Pt film annealed at 300°C.

### 5.2.1.4 Co-Pt Alloy Thin Film Annealed at 400°C

Figures 33 and 34 present hysteresis loops of Co-Pt alloy film annealed at 400°C, which was measured at 10°K and 300°K, respectively. Coercivities of 1280 emu/cm³ and 100 emu/cm³ were obtained at 10°K and 300°K, respectively. \( M_s \) values were not obtained at 10°K and 300°K,
as the film did not saturate, even after applying a field of 50 kOe. A similar trend in the hysteresis loop is seen in Co-Pt film annealed at 300°C. So it may be concluded, that annealing has an effect on the magnetic properties of the film.

Figure 33. Hysteresis loop at 10°K for Co-Pt film annealed at 400°C.

Figure 34. Hysteresis loop at 300°K for Co-Pt film annealed at 400°C.
5.2.1.5 Pt/Co Multilayered Film

The hysteresis loops obtained in a PPMS machine at 10°K and 300°K for the Pt/Co multilayered film is shown in Figures 35 and 36, respectively. A field up to 9 Tesla was applied for measurements.

Figure 35. Hysteresis loop of Pt/Co multilayer at 10°K.

Figure 36. Hysteresis loop of Pt/Co multilayer at 300°K.
Coercivities of 1100 emu/cm$^3$ and 45 emu/cm$^3$ were obtained at 10$^\circ$K and 300$^\circ$K emu/cm$^3$, respectively. This film has $M_s$ of 1000 emu/cm$^3$ at 10$^\circ$K and 1060 emu/cm$^3$ at 300$^\circ$K. The saturation point is almost the same at both the temperatures.

5.2.2 Perpendicular Measurements

5.2.2.1 Pure Co Film

Figures 37 and 38 present the hysteresis loops of pure Co film measured at 10$^\circ$K and 300$^\circ$K, respectively. Coercivities of 900 emu/cm$^3$ and 260 emu/cm$^3$ were obtained at 10$^\circ$K and 300$^\circ$K, respectively. $M_s$ of 120 emu/cm$^3$ was obtained at 300$^\circ$K. At 10$^\circ$K the film does not saturate, even after applying a field of 50 kOe.

Figure 37. Hysterisis loop of Co film at 10$^\circ$K.
5.2.2.2 Co-Pt As-deposited Film

Figures 39 and 40 present the hysteresis loops of an as-deposited Co-Pt alloy film measured at 10°K and 300°K, respectively. Coercivities of 2200 emu/cm$^3$ and 262 emu/cm$^3$ were obtained at 10°K and 300°K, respectively.
Figure 40. Hysteresis loop of as-deposited Co-Pt film at 300°K.

Mₘ for the as-deposited Co-Pt alloy at 300°K and 10°K does not occur, even after applying a field of 50 kOe. The Mₘ of pure Co is lower than that of as-deposited Co-Pt alloy film and it reconfirms the fact that the addition of Pt to Co indeed increases the Mₘ value of Co.

5.2.2.3 Co-Pt Alloy Thin Film Annealed at 300°C

Figures 41 and 42 present the hysteresis loops of the Co-Pt alloy thin film annealed at 300°C measured at 10°K and 300°K, respectively. Coercivities of 3150 emu/cm³ and 241 emu/cm³ were obtained at temperatures 10°K and 300°K, respectively. Mₘ values could not be obtained at 10°K and 300°K, as the film does not saturate, even after applying a field of 50 kOe.
5.2.2.4 Co-Pt Alloy Thin Film Annealed at 400°C

Figures 43 and 44 present the hysterisis loops of the Co-Pt alloy thin film annealed at 400°C measured at 10°K and 300°K, respectively. Coercivities of 1420 emu/cm³ and 282 emu/cm³ were obtained at 10°K and 300°K, respectively. $M_s$ values were not obtained at 10°K, as the film did not saturate, even after applying a field of 50 kOe. A similar trend in the hysterisis loop is seen in Co-Pt film annealed at 300°C. At 300°K it seems to be around 200 emu/cm³.
5.2.2.5 Pt/Co Multilayered Film

Figures 45 and 46 present the hysteresis loops of the Pt/Co multilayered film measured at 10°K and 300°K, respectively. Coercivities of 1200 emu/cm³ and 100 emu/cm³ were obtained at 10°K and 300°K, respectively. This film has $M_s$ of 1285 emu/cm³ at 10°K and 1142 emu/cm³ at 300°K. The saturation point is almost the same at both the temperatures.
Figure 45. Hysterisis loop of Pt/Co multilayer at 10°K.

Figure 46. Hysterisis loop of Pt/Co multilayer at 300°K.

Tables 2 and 3 present the coercivities of pure Co, as-deposited, annealed Co-Pt alloy and Pt/Co multilayered thin films measured in both parallel and perpendicular directions to the applied fields.
Table 2. Coercivity comparison of various films at different temperatures, in parallel measurements.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Coercivity (emu/cm³)</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10°K</td>
</tr>
<tr>
<td>Pure Co Film</td>
<td></td>
<td>1400</td>
</tr>
<tr>
<td>Co-Pt Thin Film</td>
<td>As-deposited</td>
<td>2490</td>
</tr>
<tr>
<td></td>
<td>300 Annealed</td>
<td>1960</td>
</tr>
<tr>
<td></td>
<td>400 Annealed</td>
<td>1280</td>
</tr>
<tr>
<td>Pt/Co Multilayered Film</td>
<td></td>
<td>1100</td>
</tr>
</tbody>
</table>

Table 3. Coercivity comparisons of various films at different temperatures, in perpendicular measurements.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Coercivity (emu/cm³)</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10°K</td>
</tr>
<tr>
<td>Pure Co Film</td>
<td></td>
<td>900</td>
</tr>
<tr>
<td>Co-Pt Thin Film</td>
<td>As-deposited</td>
<td>2200</td>
</tr>
<tr>
<td></td>
<td>300 Annealed</td>
<td>3150</td>
</tr>
<tr>
<td></td>
<td>400 Annealed</td>
<td>1420</td>
</tr>
<tr>
<td>Pt/Co Multilayered Film</td>
<td></td>
<td>1200</td>
</tr>
</tbody>
</table>

For AFM materials, the Neel temperature is used for analyzing the magnetic properties, whereas for FM materials, the Curie temperature is used for analyzing the magnetic properties. Above the Neel temperature, an AFM material changes into a paramagnetic material, whereas above the Curie temperature, an FM material turns into a paramagnetic material. Tables 4 and 5 show the Curie and Neel temperatures of some magnetic materials.
Table 4. Curie temperatures of FM materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Curie Temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>1382-1400</td>
</tr>
<tr>
<td>CoPt</td>
<td>830</td>
</tr>
</tbody>
</table>

Table 5. Neel temperatures of AFM materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Neel Temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO</td>
<td>260-280</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>40</td>
</tr>
</tbody>
</table>

A shift is observed in the hysteresis loops of all films, along the magnetic field axis at 10°K. This may be due to the exchange anisotropy or exchange bias phenomenon. Exchange bias occurs due to the exchange coupling of FM / AFM layers, leading to a shift in the hysteresis loop along the magnetic field axis. This shift usually occurs after field cooling the system containing the magnetized FM layer below the Neel temperature of AFM layer. During cooling these AFM domains lead to a small net magnetization at the FM /AFM interface. This magnetization is stabilized towards lower temperatures resulting in a shift in the hysteresis loop. All the hysteresis measurements in the present experiments have been conducted under zero-field cooling, where cooling takes place without the presence of any external fields. The shift in hysteresis loop is not possible at zero-field cooling. Hence, there is a possibility of the existence of some residual field in the MPMS, during the magnetic measurements, which results in a shift in the hysteresis loops at 10°K.

EDS spectra indicates the presence of O along with Co and Pt in the films. Co and Co₃Pt are FM whereas CoO is AFM in nature. The Neel temperature of CoO exists somewhere between 260 and 280°K. At 10°K, which is below the Neel temperature of AFM CoO, exchange
interactions may have taken place at the FM/AFM interface resulting in the exchange anisotropy. This may be a reason for the shift in hysteresis loops at 10°K, subsequently leading to an increase in coercivity of the films. At 300°K, symmetric hysteresis loops are observed at which indicate no exchange bias has occurred.

Temperature is one of the most important factors taken into consideration while measuring magnetic properties. It is well known that raising the temperature causes an increase in the magnitude of thermal vibrations of atoms in the material. Since the magnetic moments are free to rotate, an increase in the temperature causes an increase in the thermal vibrations of the atoms and tends to randomize the direction of any moments that may be aligned. In a FM and AFM material, atomic thermal motions counteract the coupling forces between adjacent atomic dipole moments, causing some dipole misalignment, regardless of whether an external field is present or not. This results in a decrease in the Ms in the FM materials. At 0°K the maximum value for Ms is obtained, since thermal vibrations are minimum at this temperature. As the temperature increases, Ms decreases and becomes zero at the Curie temperature [1]. In this study, the magnetic measurements were conducted at 10°K and 300°K. As a general trend it has been observed that the Ms is maximum for measurements conducted at 10°K.

Tables 3 and 4 present the coercivities of various films measured in two different orientations namely, parallel and perpendicular. In parallel measurement, the field is applied along the easy axis of the film and the hysteresis loop is expected to be a square in shape. The Ms and coercivity can be measured directly from the loop. In perpendicular measurement, the field is applied along a hard axis that produces the linear M, H relation [2]. A typical hysteresis loop of this kind is shown in Figures 37 and 39. If the field is large enough to produce saturation, the film breaks up into domains upon reduction of the field. The easy axis coercivity is usually less
than hard axis coercivity. This can be seen in as-deposited and annealed of Co-Pt and Pt/Co multilayered films.

Coercivities of the Co-Pt as-deposited and Co-Pt annealed films are much lower when compared to corresponding values of Co$_3$Pt films reported earlier. One of the reasons for this behavior may be the presence of O in the films. From the SAED patterns, it can be concluded that, O may be present in the films in the form of CoO. The SAED patterns of Co-Pt alloy films also show that, some of the Co is either present in the form of CoO or ε-Co. Also, the facts that ε phase is a softer phase of Co, and that CoO is an AFM material possessing very low FM properties, may have played a key role in deteriorating the magnetic properties of Co-Pt alloy thin films. At 300°C, very low coercivities were observed for pure Co, as-deposited alloy, annealed Co-Pt alloy and Pt/Co multilayered thin films. The Néel temperature of CoO is in the range of 260 to 280°C. Above this temperature the AFM CoO turns paramagnetic. Therefore, when measured at 300°C, CoO present in these films turned paramagnetic, resulting in further deterioration of coercivity of the films.

Coercivity of the annealed films, especially the film annealed at 400°C decreases to a large extent, when compared to as-deposited and 300°C annealed Co-Pt alloy films. There are three possibilities for this behavior.

i. It is known that the as-deposited and annealed films have a mixture of hcp and fcc Co$_3$Pt phase. It is a known fact at the hcp structures Co$_3$Pt has high magnetic anisotropy and the phase becomes unstable above 400°C as the uniaxial anisotropy collapses above this temperature [32]. So, in the films annealed at 400°C, the hcp phase must have just begun to become unstable and thus resulted in the decrease in coercivity. Annealing to higher temperatures may have altered the composition of phases resulting in a decrease in
coercivity [31]. The hcp to fcc phase transition in bulk Co-Pt is martensitic which means that the transition occurs by collective motion of large groups of atoms. This occurs at higher temperatures and the inverse transition from fcc to hcp occurs at decreasing temperatures [21]. The hcp structure is not as ductile as the fcc structure. Therefore, fcc phase is softer than hcp and thus must have resulted in a sudden decrease in coercivity of the films.

ii. Increase in coercivity at the beginning stage of annealing may be due to the growth of crystallites, which reach the size of magnetic single domain, which means a uniformly magnetized large single crystal. When the grain size decreases, a critical size is reached below which a grain can no longer accommodate a wall. Within the wall, the magnetization must change direction from that in one domain to that in the other. Below this critical size, the grains contain a single domain. The maximum coercivity in a material is known to occur within its single domain range [1]. The average grain size of as-deposited Co-Pt film was 5 nm, which increased upto 6 nm upon annealing at 300°C, which is not a very significant increase. Upon further annealing at 400°C for 2 hours, the average grain size increased upto 10 nm. The reason for decrease in coercivity of Co-Pt film annealed at 400°C may be the formation of multidomains. The multidomains are magnetically soft with low values of coercivities. As the grain size increases, the coercivity decreases when the grain subdivides into domains. The magnetization of the multidomain wall can however be changed by translating the domain wall. The drop in coercivity may be due to an increase in the size of crystallites, resulting in multidomain formation.
iii. From the SAED pattern of Co-Pt film annealed at 400°C, it is observed that the presence of ε-Co is more prominent along with fcc and hcp Co₃Pt phases. ε-Co, which is a metastable phase having simple cubic structure, is much softer when compared to the fcc and hcp Co₃Pt [22,23]. As ε-Co phase dominates over hcp and fcc Co₃Pt, an overall decrease in the coercivity of the Co-Pt film annealed at 400°C is observed.

For use in applications such as high-density storage media, magnetic properties of these films must be improved. In order to prevent the formation of CoO, it is imperative that O should not be present in the films at any stage during analysis. Optimum annealing temperatures should be used in order to avoid the formation of ε-Co, which results in the softening of films. Grain size of less than 10nm has been formed and this is a desirable feature in high density recording media, as they play a very important role in reducing the noise [11].

However, the exchange anisotropy caused by the presence of exchange coupling between AFM CoO, FM Co₃Pt, and FM Co in the Co₃Pt alloy and Pt/Co multilayered films, may make it desirable in applications such as magnetic sensor systems, spin valve and magnetoresistance devices. The magnitude of exchange bias needs to be taken into consideration before using the films for the above-mentioned applications.
6 CONCLUSIONS

The following are the conclusions which can be drawn from the present work:

1. Co-Pt alloy and Pt/Co multilayered thin films of 145 nm and 112 nm in thickness respectively were synthesized using a dual electron beam co-evaporation by altering the deposition rates. The films were deposited on the Si substrate. Pure Co and pure Pt films of 21 and 7 nm thick respectively were also deposited for calibration purposes.

2. The compositional analysis of the Co-Pt alloy thin film showed that Co and Pt were in the atomic weight ratio of 3:1.

3. TEM analysis revealed that pure Co film had both hcp and ε phases present along with the presence of NaCl type CoO. The as-deposited and annealed Co-Pt alloy films showed a mixture of hcp and fcc Co₃Pt, ε-Co. Pt/Co multilayered films had fcc Pt, hcp and ε-Co. Presence of NaCl type CoO was also detected in both Co-Pt alloy and Pt/Co multilayered films.

4. Annealing increased the grain size of the particles in Co-Pt alloy thin films. Annealing at 300°C increased the grain size to 6 nm, though not a very significant increase when compared to the as-deposited film of 5 nm. Annealing at 400°C increased the grain size to 10 nm.

5. Magnetic measurements were conducted on the alloy and multilayered films showed that the addition of Pt to Co increased the coercivity of the films.

6. The coercivity of the films decreases all of a sudden for the film annealed at 400°C. This may be due to the formation of multidomain. And it may also be due to the presence of ε-Co, which is a soft phase.
7. Symmetric magnetic hysteresis loop is observed for the films at 300°K. But a shift in the hysteresis loop to the left of the applied field is observed when measured at 10°K. This shift may be attributed to exchange coupling taking place at the interface of the AFM CoO and FM Co$_3$Pt and Co. This phenomenon is known as exchange anisotropy.
REFERENCES


VITA

Priya David was born in Andhra Pradesh on 12th November 1980, India. She earned her primary and secondary education from Carmel Convent High School in Mancherial, Andhra Pradesh. After finishing her high school in Mancherial, she took a very competitive entrance examination for engineering known as EAMCET. After qualifying this examination she got admission to, department of Metallurgical Engineering, Jawaharlal Nehru Technological University. She received her Bachelor of Technology in Metallurgical Engineering from Jawaharlal Nehru Technological University, Hyderabad, India, in 2002. After her graduation, she came to United States of America for her higher studies. She then joined the graduate program at Louisiana State University, Baton Rouge, in January 2003. She is a candidate for the degree of Master of Science in Mechanical Engineering to be awarded at the commencement of spring, 2005.