UPPSALA UNIVERSITY
MASTER THESIS

Structure and Magnetic Properties of Co$_{25}$Pd$_{75}$ alloy thin films

Daohai Hou

Supervisors: Anna Ravensburg

Materials Physics
Department of Physics and Astronomy

June 2022
Abstrakt

Magnetiska metalliska tunnfilmer har väckt intresse för både grundforskning och industriell tillämpningar, på grund av deras unika magnetiska egenskaper som beror på deras dimensionalitet och bruten symmetri vid gränssytor. Utvecklingen av nanofabrikationsmetoder ökar möjligheterna att växa tunna filmer med hög kristall kvalitet, vilket främjar undersökningen av mekanismerna och dynamiken i deras magnetism.

I detta arbete undersöks kristallstrukturen och de magnetiska egenskaperna hos tunnfilmer av legeringen Co25 Pd75. Filmerna har deponerats vid rumstemperatur genom de magnetronsputtering. Tunnna filmerna av Fe25 Pd75 -legering tillverkades också för att jämföra CoPd och FePd. Tjockleken på de tunna filmerna varierades för att undersöka tjockleksberoendet av de magnetiska egenskaperna.

Den faktiska kemiska sammansättningen bestämdes med hjälp av Rutherforddspektrometri. Tjockleken och grovheten hos skikt, den i de tunna filmerna erhålls genom mätningar av röntgenreflektivitet i kombination med GenX-anpassningar. Kristallstrukturen hos legeringen Co25 Pd75 undersöks genom röntgendiffракtion och texturanalys. De tunna filmerna har en kemisk sammansättning som ligger nära den avsedda sammansättningen, väll definierad skikt struktur och växer polykristallint i ytcenterad kubisk struktur med tillväxtriktning langs <001>.


Abstract

Magnetic metallic thin films have attracted interest for both fundamental science and industrial application, due to their unique magnetic properties arising from reduced dimensionality and broken symmetry at interfaces. The development of nanofabrication techniques enhances the possibilities to grow thin films with a high crystalline quality, which promotes the investigation of the mechanisms and dynamics of the magnetism discovered in magnetic metallic thin films.

This work investigates the crystal structure and magnetic properties of Co$_{25}$Pd$_{75}$ alloy thin films. The films are deposited at room temperature via direct current magnetron sputtering. Fe$_{25}$Pd$_{75}$ alloy thin films are fabricated as well in order to compare CoPd and FePd. The thickness of the thin films is varied in order to investigate the thickness dependence of the magnetic properties.

The actual chemical compositions are determined by Rutherford backscattering spectrometry. The thickness and roughness of the layers of the thin films are obtained from x-ray reflectivity measurements combined with GenX fitting. The crystal structure of the Co$_{25}$Pd$_{75}$ alloy is investigated via x-ray diffraction measurement and texture analysis. The thin films have a close to intended chemical composition, defined layering and grow textured polycrystalline in face centered cubic struture with growth direction along $<$001$>$.

Longitudinal and Polar magneto-optical Kerr effect measurements are performed to investigate the magnetic properties and anisotropy. The hysteresis loops indicate that the Co$_{25}$Pd$_{75}$ thin films exhibit perpendicular magneto-crystalline anisotropy while having no in-plane anisotropy. Besides, the hysteresis loops show evidence that the direction of magnetization at remanence ahhs in- and out-of-plane components, a so-called cone state. Absolute magnetic moment values are obtained from vibrating-sample magnetometry and are used to calculate the anisotropy energy. The anisotropy energy of the thicker films turns out to be lower than the thinner ones. The magnetic domains of the Co$_{25}$Pd$_{75}$ thin films are analyzed via magnetic force microscopy. Different domain morphology is observed when the films were magnetized in different directions.

This work builds the foundation for future investigations of magnetism of CoPd alloy thin films. One possible path is to tune the chemical composition and compare the contributions of cobalt and palladium atoms. Another possible path is to compare CoPd alloys with Co/Pd multilayers in order to investigate the interface anisotropy. Furthermore, the cone state and domain morphology differences with layer thickness observed in this work are worth further discussion.
## Contents

1 Introduction ........................................................................................................... 7

2 Theoretical Background ........................................................................................ 9

3 Methods .................................................................................................................. 12
   3.1 Sputtering ........................................................................................................ 12
   3.2 X-ray Reflectometry (XRR) ............................................................................ 13
   3.3 X-ray Diffractometry .................................................................................... 15
   3.4 Rutherford Backscattering Spectrometry ..................................................... 16
   3.5 Magneto-optical Kerr Effect Measurements ............................................... 16
   3.6 Vibrating-sample magnetometry .................................................................. 19
   3.7 Magnetic Force Microscopy (MFM) ............................................................ 20

4 Results and Discussion .......................................................................................... 22
   4.1 Chemical Composition .................................................................................. 22
   4.2 Layering and Crystal Structure .................................................................... 22
   4.3 Magnetic Properties ..................................................................................... 28
      4.3.1 Results of the MOKE Measurements .................................................. 29
      4.3.2 Results of the VSM measurements ..................................................... 33
      4.3.3 Magnetic Domains .............................................................................. 36

5 Conclusions ............................................................................................................ 39

6 Acknowledgement .................................................................................................. 40

References ............................................................................................................... 41
1. Introduction

Magnetic ultrathin metallic films has been investigated since the late 1950s and have been widely applied into industries in recent decades due to their unique magnetic properties [1]. Thin metallic films was first investigated due to a theoretical consideration that the reduced dimensionality and the appearance of interface could lead to different magnetic properties, including the magnetic domain structure, spin wave spectrum, magnetic anisotropy, etc. At first the theoretical prediction of the magnetism in thin films made significant progress. For example, C. Kittel predicted the spin waves in thin films and subsequently verified them in Permalloy films [2]. However, experimental limitations at that time hindered further investigation on this topic. For example, the thin film growth techniques in the early days can not produce thin films with a high quality crystal structure. The lack of structural and spectroscopic characterization techniques also hindered the detection the quality of thin films, such as crystalline structure, chemical constituents, impurities, interface quality, etc.

The situation changed when molecular beam epitaxy (MBE) appeared and was successfully applied to fabricate ultrathin semiconducting films [1]. The ability to obtain ultrathin films with high crystalline quality made it possible to perform experimental measurements on the high quality films and obtain reliable results. Besides, the development of characterization techniques (e.g. reflection high-energy electron diffraction) provided important tools in the study of thin film growth. In addition, the development of computer science also made theoretical calculations easier and more accurate. The first principles calculations of the modified magnetic moments in 2D systems were done in 1980s. Since then, magnetic ultrathin metallic films have attracted tremendous attention from academic reasearch and commercial applications.

The magnetic thin films based on \( R_xT_y \) (\( R = \) rare earths elements; \( T = \) 3d transition metals Mn, Fe, Co, Ni) metallic compounds exhibit unique magnetic properties (e.g. strong magnetization and magnetic anisotropy) due to the exchange interactions and magnetocrystalline anisotropy of \( R_xT_y \) alloys [3]. The exchange interactions exist between the unpaired spins in the 3d-4f system, which turns out to be strong in the Co- and Fe- based alloys. The magnetocrystalline anisotropy originates from the rare-earth ions and is transferred by the 3d-4f exchange interactions to the 3d sublattice. As an example is CoPd alloy thin films, which exhibit significant perpendicular magnetic anisotropy and become important materials for magnetic and magneto-optic storage. The anisotropy of CoPd was first discovered in Co/Pd compositionally modulated
multilayers in 1985 [4], and the anisotropy is named perpendicular magnetic anisotropy (PMA). Subsequently, other CoPd nanostructures fabricated via MBE, e-beam evaporation, or sputtering were found to exhibit PMA as well. These CoPd nanostructures include Co/Pd multilayers, CoPd alloyed films, and hybrid structure. In 2012, A. Vlachos et al. investigated the magnetic properties of textured CoPd nanocrystalline thin films [5]. They compared the CoPd alloy thin film with and without texture, prepared by radio-frequency magnetron sputtering. They found that the textured thin film exhibit stronger PMA.

This master thesis project focuses on Co$_{25}$Pd$_{75}$ alloy thin films prepared by sputtering. The aim of this project is to investigate the crystal structure and the magnetic properties of the Co$_{25}$Pd$_{75}$ thin films from an experimental perspective. The Co$_{25}$Pd$_{75}$ will be compared with Fe$_{25}$Pd$_{75}$ with similar film structures. The experimental methods used for sample preparation and characterization are summarized in the chapter "Methods". The results of experimental measurements and the discussions are presented in the chapter "Results and Discussion", including the chemical constituents, layering, crystal structure, hysteresis loops, and domain structures. The magnetic anisotropy and the anisotropy energy are also discussed with the help of hysteresis loops.
2. Theoretical Background

In this section, basic magnetism that are relevant to this study will be introduced. More comprehensive discussion of magnetism and magnetic materials might be found in other specialized books, for example [6, 7, 1].

Magnetization and Magnetic Materials

From the view of classical electrodynamics, electric current can lead to magnetism. A planar coil with a current can be assumed as a magnetic dipole, producing a magnetic field on the two sides of the coil. At the microscopic scale, the orbital angular momentum and spin angular momentum of electrons surrounding an isolated atom can be assumed as the counterpart of classical current-carrying wires and generate "magnetic dipoles" as well. If the net angular momentum of all the electron is non-zero, the atom would behave like a magnet, and the strength of such a magnet can be defined by the magnetic moment \( \mathbf{m} \). The physical meaning of the magnetic moment is the force between the gradient of magnetic field and the magnet. For a material consisting of a number of atoms, the contributions from all atoms form the total magnetic moment of the material. In fact, the actual cases are more complicated, because in most cases the magnetic moment of a non-isolated atom is influenced by the neighbouring atoms or ions. Some effects, such as quenching or the formation of energy bands, have a non-negligible impact on the magnetic properties of the entire material.

In the study of magnetic materials, it is difficult or even infeasible to measure the magnetic moment of each single atom, but easier to measure the total magnetic moments \( \sum \mathbf{m} \) of a material. For the same type of material, the ratio of the total magnetic moment to the sample volume \( V \) is a constant, named magnetization:

\[
M = \frac{\sum \mathbf{m}}{V} \tag{2.1}
\]

which is an important parameter to characterize the magnetic state of a material.

Magnetic materials can be classified into diamagnetic (DM) materials, paramagnetic (PM) materials, ferromagnetic (FM) materials, antiferromagnetic (AFM) materials, and ferrimagnetic (FiM) materials, according to their magnetic response to an external magnetic field. DM materials and PM materials...
exhibit weak induced magnetization when an external field is applied. The magnetization direction of DM materials is opposite to the applied field, while the magnetization direction of PM materials is the same as the applied field. FM, AFM, and FiM materials are magnetically ordered materials due to their significant exchange interaction. Magnetically ordered state means the magnetic moments can be aligned parallel or antiparallel depending on the materials. In FM materials the alignments are parallel, but in ATM materials the alignments are antiparallel. In FiM materials, the magnetic moments are still antiparallel ordered but the quantities of the opposite moments are unequal. However, magnetically ordered materials will lose their magnetic order if they are heated above a critical temperature. For FM materials the temperature is known as Curie temperature ($T_c$), and for AFM and FiM materials it is known as Néel temperature ($T_N$).

Hysteresis loop

![Hysteresis loop diagram](image)

*Figure 2.1. An example of a hysteresis loop. $M_s$, $M_r$, and $H_c$ are saturation magnetization, remanent magnetization, and coercive field, respectively.*

For FM and FiM materials, the induced magnetization ($M$) is not a linear function with respect to an applied field ($H$), but a curve called hysteresis loop. Hysteresis loop is used to characterize the magnetic properties of FM or FiM materials. Fig 2.1 gives an example of a hysteresis loop (M-H curve). Given a FM material in a demagnetized state, the net magnetization will be zero (the point O). If an increasing positive field is applied to the material, the magnetization increases at first (O→ A) and stops increasing at the saturation magnetization ($M_s$). Then if the applied field is reduced and becomes negative,
the magnetization does not follow the initial path but decreases along a different path (A → B → C), and vice versa (C → D → A). When the external field is removed ($H = 0$), the material still has a residual magnetization called remanent magnetization ($M_r$). And the field required to change the magnetization direction ($M = 0$) is called coercivity ($H_c$). The materials with small $M_r$ and $H_c$ are called soft magnetic materials, and the ones with large $M_r$ and $H_c$ are hard magnetic materials.

Magnetic Anisotropy

Magnetic Anisotropy refers to the directional dependence of the magnetic properties of a material [7]. Magnetic anisotropy can have different origins, thus can be classified into different types: magnetocrystalline anisotropy, shape anisotropy, interface anisotropy and induced anisotropy. Magnetocrystalline anisotropy arises from the intrinsic nature of a crystal. The magnetization tends to align itself along certain crystallographic directions. The direction in which the $M_s$ is achieved with the smallest (largest) external field is called easy (hard) axis. Shape anisotropy arises from the shape of a material. If a material is non-spherical, it is easier to magnetize the material along the longest axis. Interface anisotropy arises from the interface between two materials. The simplest example is the surface of a material. Interface anisotropy plays an important role in thin films or nanostructures due to a large interface-volume ratio. Induced anisotropy refers to the anisotropy induced from particular treatments or methods.

Magnetic anisotropy is crucial in the magnetic materials used for particular applications. For example, CoPd thin films are important for magnetic and magneto-optic storage due to their Perpendicular Magnetic Anisotropy (PMA) discovered on them [5]. PMA means the easy axis is perpendicular to the film surface while the hard axis is parallel to the film surface.

Magnetic Domains

Magnetic Dmoains are regions in FM materials within which the magnetic moments are aligned parallel to each other. Magnetic domains are formed in order to minimize the total energy, including exchange energy, magnetostatic energy, anisotropy energy, etc. The boundaries between two adjacent magnetic domain are called domain walls, where the directions of the magnetic moments change gradually. In a demagnetized state, different domains have different magnetization orientations, which may result in a zero total magnetization. The change magnetization process is to align the different domains into the same direction. During the magnetization process, the shapes and sizes of magnetic domains may change and therefore influence the hysteresis loop.
3. Methods

3.1 Sputtering

To investigate the structural and magnetic properties of Co$_{25}$Pd$_{75}$ thin films, 18 thin films were fabricated, as listed in table 3.1. Both Co$_{25}$Pd$_{75}$ and Fe$_{25}$Pd$_{75}$ (samples No.1 and 2) were fabricated in order to compared the difference between the two alloys. Also, the capping layer (Al$_2$O$_3$ and Pd) of the thin films are varied (samples No.1, 2, 3, and 7) in order to obtain the influence by the capping. Finally, the films have two different layer thickness (150 Å and 400 Å) in order to investigate the influence of the layer thickness on the properties (samples No.3, 7, 11, and 15). Fig 3.1 shows a schematic illustration of the layer structure of these thin films.

The thin films were deposited employing direct current magnetron sputtering in an ultra-high vacuum chamber. Four targets were used to fabricate the samples: Co, Fe, Pd, and Al$_2$O$_3$. The sample were deposited at ambient temperature and at an Ar pressure of 8 mTorr, except the Al$_2$O$_3$ capping which was deposited at 5 mTorr Ar. All samples were deposited on amorphous 10 mm × 10 mm × 0.5 mm SiO$_2$ substrates. The samples were rotated during deposition at 30 rpm to achieve uniform film thickness. Before the actual depositions, the deposition rates for all targets were calibrated. In order to achieve a similar chemical composition to the intended 25:75 ratio, Pd was sputtered at 50 W while Fe and Co were sputtered at 60 W applied power.

1All the sample were fabricated by Anna Ravensburg.

Table 3.1. The Co$_{25}$Pd$_{75}$ and Fe$_{25}$Pd$_{75}$ thin films used in this study.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Layering &amp; Description</th>
<th>Capping</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150 Å Co$<em>{25}$Pd$</em>{75}$</td>
<td>50 Å Al$_2$O$_3$</td>
</tr>
<tr>
<td>2</td>
<td>150 Å Fe$<em>{25}$Pd$</em>{75}$</td>
<td>50 Å Al$_2$O$_3$</td>
</tr>
<tr>
<td>3</td>
<td>150 Å Co$<em>{25}$Pd$</em>{75}$</td>
<td>50 Å Pd</td>
</tr>
<tr>
<td>4&amp;5&amp;6</td>
<td>Copies of No.3</td>
<td>50 Å Pd</td>
</tr>
<tr>
<td>7</td>
<td>150 Å Fe$<em>{25}$Pd$</em>{75}$</td>
<td>50 Å Pd</td>
</tr>
<tr>
<td>8&amp;9&amp;10</td>
<td>Copies of No.7</td>
<td>50 Å Pd</td>
</tr>
<tr>
<td>11</td>
<td>400 Å Co$<em>{25}$Pd$</em>{75}$</td>
<td>50 Å Pd</td>
</tr>
<tr>
<td>12&amp;13&amp;14</td>
<td>Copies of No.11</td>
<td>50 Å Pd</td>
</tr>
<tr>
<td>15</td>
<td>400 Å Fe$<em>{25}$Pd$</em>{75}$</td>
<td>50 Å Pd</td>
</tr>
<tr>
<td>16&amp;17&amp;18</td>
<td>Copies of No.15</td>
<td>50 Å Pd</td>
</tr>
</tbody>
</table>
Figure 3.1. A schematic image of the layer structure of the films.

3.2 X-ray Reflectometry (XRR)

Figure 3.2. An x-ray diffractometer used for XRR and XRD measurements.

X-ray reflectometry (XRR) is a method to probing length scales of the total thickness of a thin film. The experimental setting of XRR is similar to X-ray diffracometry (XRD), while the incident angles for XRR is smaller (below around 15 degrees). Both the XRR and XRD are performed through an x-ray diffractometer (figure 3.2).

More detailed discussion of XRR can be found in other books such as *Thin film analysis by X-ray scattering* [8]. For simplicity, the principles of XRR can be explained by the Bragg equation:
\[2d_{hkl} \sin \theta = n\lambda\]  

(3.1)

Where \(d_{hkl}\) is the distance between the lattice planes with Miller index \(hkl\), \(\theta\) is the incident angle of the x-rays, \(n\) is an arbitrary integer, and \(\lambda\) is the wavelength of the x-rays, respectively. The Bragg equation is used in x-ray analysis of materials by detecting the x-ray peaks in reflection mode.

\[\Delta_1 + \Delta_2 = 2d \cos(90^\circ - \theta) = 2d \sin \theta\]

Figure 3.3. Schematic illustration of x-ray diffraction resulting from a crystal with a simple cubic structure. \(\Delta_1\) and \(\Delta_2\) are the phase shift. \(d\) is the interplanar distance. \(\theta\) is the indicent angle of the x-ray. (The image is obtained from: Birkholz, Mario. Thin film analysis by X-ray scattering. John Wiley Sons, 2006.)

The Bragg equation is visualized and shown in Fig 3.3. The Bragg equation indicates that constructive interference occurs only if the the phase shift \(2d \sin \theta\) between the adjacent reflected beams is equal to a multiple of the wavelength \(n\lambda\). When the distance between lattice planes \(d\) increases, the \(\sin \theta\) term should be correspondingly reduced to a smaller value, in order to ensure that the Bragg equation still holds. Under such a scenario, the main reason for constructive interference is no longer the reflection of the lattice plane, but the reflection of the upper and lower film surfaces. This explains why the XRR is performed with a small incident angle.

In order to measure Bragg reflections, a commonly used scanning mode is the \(\theta / 2\theta\) scan. Figure 3.4 shows the schematic diagram of the \(\theta / 2\theta\) scan. During the scan, the incident angle and the reflected angle are equal (\(=\theta\)), thus the angle between the reflected beam and the extended incident beam is \(2\theta\). What the \(\theta / 2\theta\) reflectogram shows is the variation of the intensity of reflection \(I(2\theta)\) with the incident angle \(\theta\).

In order to obtain layer thicknesses and roughnesses of a thin film stack, a fitting software called GenX [9] is used. Figure 3.5 is an example of the x-ray reflectogram and the corresponding GenX fitting of a 150 Å thick Fe thin films with a 50 Å Pd cap. Once the GenX fitting is close to the XRR data, the layering of the film model in the GenX is considered to be the actual layering.
Figure 3.4. Schematic illustration of $\theta/2\theta$ scan mode. $\mathbf{K}_0$ and $\mathbf{K}$ are wave vectors of the incoming beam and reflected beam, respectively. $\mathbf{Q} = \mathbf{K} - \mathbf{K}_0$ is the scattering vector. $\mathbf{s}_i$ are sample coordinate vectors. (The image is obtained from: Birkholz, Mario. Thin film analysis by X-ray scattering. John Wiley Sons, 2006.)

Figure 3.5. An example of fitting with the GenX software. The blue curve is the normalized raw data and the red curve is the fitting curve calculated by the model in the GenX.

3.3 X-ray Diffractometry

X-ray Diffraction is a technique used to determine the atomic-scale structure of a material. A solid material can either be amorphous (having no long-range order of crystalline) or crystalline (having a crystalline long-range order, i.e. a periodic arrangement of the atoms). Crystals can be composed of one grain (single crystalline) or multiple crystal grains with different relative orientations (polycrystalline). However, polycrystalline materials can have a preferred growth direction for their grains which is called texture.

As is mentioned in the previous section, the experimental settings of XRD is close to XRR, but the incident angle $\theta$ is above $15^\circ$. The principle of XRD can be explained by the Bragg’s law as well. If a crystal is illuminated by x-rays, which are reflected and subsequently detected, the periodic arrangement of the atoms gives rise to positive interference of the incoming rays at specific incident angles. These angles are characteristic for reoccurring atomic distances in the crystal. The size of the incident angle $\theta$ where constructive
interference appears can be used to calculate the interplanar spacing \( d \) from the Bragg equation 3.1. And the crystal structure of a sample can be inferred from the interplanar distance.

In addition, another method called texture analysis, which is based on XRD in most cases, is used to investigate the crystal structure. Texture analysis can yield crystal structure and growth direction of a sample by the interpretation of pole figures.

3.4 Rutherford Backscattering Spectrometry

Rutherford backscattering spectrometry (RBS) is a technique to determine the chemical constituent of materials. The sample is impinged by a beam of high energy ions, and the the chemical composition can be obtained by analyzing the backscattered intensity and energy. Figure 3.6 shows the backscattered data from the RBS measurement and the corresponding simulations of the 150 Å Co\textsubscript{25}Pd\textsubscript{75} thin film.

\[ \text{Figure 3.6. An example of the RBS result of a 150 Å Co}_{25}\text{Pd}_{75} \text{ thin film. The red dots are the obtained results of the entire sample. The blue line is the simulated result of the entire sample, while the other lines are the contributions from different elements.} \]

3.5 Magneto-optical Kerr Effect Measurements

The magneto-optical Kerr effect (MOKE) measurements are a method to investigate magnetic properties of a surface or a thin film. The MOKE describes the rotation of a polarized light reflected from a magnetized surface. The phenomenon is highly sensitive to the surface magnetization, giving MOKE measurements an important role in the study of surface magnetism. By measuring
the magnitude of the rotation, one can obtain the relative surface magnetization \( M/M_s \) with respect to different magnetic field \( H \).

When a light propagates in an anisotropic medium, the dielectric permeability used to describe this material is no longer a number, but a tensor \( \varepsilon \). When the anisotropic material, such as a crystal, is demagnetized and is above the Curie temperature, the surface is symmetric. For a symmetric surface, the reflected light of a linear polarized incident light will still keep linear polarization. However, once the magnetization is not zero, the surface symmetry will be broken and the reflected light will in general become elliptically polarized. This can be understood as the magnetization \( M \) introduces non-diagonal terms in the dielectric tensor \( \varepsilon(M) \) [10], which is:

\[
\varepsilon(M) = \begin{pmatrix}
\varepsilon_0 & i\varepsilon_z & -i\varepsilon_y \\
-i\varepsilon_z & \varepsilon_0 & i\varepsilon_x \\
i\varepsilon_y & -i\varepsilon_x & \varepsilon_0
\end{pmatrix}
\]

where \( \varepsilon_0 \) the permittivity without magnetisation, \( Q \) the is Voigt magneto optical constant, \( M_i \) is the magnetization along i-axis, and \( M_s \) is the saturation magnetization, respectively. According to equation 3.2, the magnetization \( M \) changes the polarization state of the reflected light by altering the off-diagonal elements. The change of the polarization state consists in two parts: Kerr rotation \( \theta_K \) and Kerr ellipticity \( \eta_K \) [10]. The former describes the rotation of the major axis of the reflected elliptically polarized light, and the latter describes the ratio of the minor axes to the major axes of the reflected light.

\[
\varepsilon_i = \varepsilon_0 Q \frac{M_i}{M_s}, \quad i = x, y, z
\]

where \( \varepsilon_i \) is the permittivity with magnetization.

**Figure 3.7.** Polar, Longitudinal and Transverse configurations for MOKE measurements. The blue rectangles represent the sample surface, and the gray planes represent the plane of incidence. The white arrows indicate the direction of the magnetization. The red lines and arrows indicate the propagation of the light. (The image is obtained from: Stupakiewicz, A., Chizhik, A., Tekielak, M., Zhukov, A., Gonzalez, J., Maziewski, A. (2014). Direct imaging of the magnetization reversal in microwires using all-MOKE microscopy. Review of Scientific Instruments, 85(10), 103702.)

The MOKE measurement can be performed principally in three different geometric configurations: polar, longitudinal and transverse configurations,
Figure 3.8. The settings of the P-MOKE measurement. The red lines and arrows illustrate the propagation path of the light. The A, B, and C are the x-ray generator, the sample holder, and the analyzer, respectively.

Figure 3.9. The settings of the L-MOKE measurement. The red lines and arrows illustrate the propagation path of the light. The A, B, and C are the x-ray generator, the sample holder, and the analyzer, respectively.
which are illustrated as figure 3.7. The three configurations can be abbreviated as P-MOKE, L-MOKE, and T-MOKE, respectively. In P-MOKE, the magnetization is parallel to the incidence plane but perpendicular to the sample surface. In L-MOKE, the magnetization is parallel to both the incidence plane and the sample surface. In T-MOKE, the magnetization is perpendicular to the incidence plane but parallel to the sample surface. In order to study the perpendicular anisotropy of a sample, one has to obtain both in-plane magnetization and out-of-plane magnetization, and compare the hysteresis loops in the two directions. Hence, the combination of P-MOKE and L-MOKE is used within the scope of this work to investigate perpendicular anisotropy.

Within the scope of this work, the L-MOKE and P-MOKE measurements are applied to the aforementioned thin films. Figure 3.9 and 3.8 show the setting for the L-MOKE and P-MOKE measurements, respectively. In the L-MOKE measurement, the external magnetic field scan speed is 15 mT/s. In order to determine whether the samples have in-plane anisotropy, each sample is measured four times by rotating the sample by 0°, 45°, 90°, and 135° in the plane of the film. In the P-MOKE measurement, the scan speed of the external magnetic field is 15 mT/s as well.

3.6 Vibrating-sample magnetometry

![Figure 3.10. An illustration of the background removal process. The example used here is the out-of-plane VSM result of the 400 Å Co$_{23}$Pd$_{77}$ thin film. The two grey ellipses indicate the data that can be used to calculate the slope of the background.](image)

Vibrating-sample magnetometry (VSM) is a method to measure the absolute value of the magnetic moment as a function of an external applied magnetic field. The basic principle of VSM is to detect the electric field induced by a vibrating magnetic sample in an changing magnetic field. The magnetic sample is fixed on a sample holder and is put between two pickup coils. The magnetic moment of the sample induces a voltage in the coils if the sample moves up and down, which relates on the magnetic moment of the sample.
Figure 3.10 shows how to obtain the hysteresis loop of a sample from the raw data obtained from VSM. The original data obtained from the VSM (see figure 3.10a) contain two contributions: the contribution from the magnetic sample and a diamagnetic background. The backgrounds interfere with the analysis of the magnetic contribution from the Co$_{23}$Pd$_{77}$ or Fe$_{18}$Pd$_{82}$ layers, hence the backgrounds must be removed. Figure 3.10 shows an example of the background removal process. The diamagnetic background (see figure 3.10b) can be calculated from the slope of the magnetisation in saturation, since the magnetic contribution of the sample is supposed to be constant at saturation. Then, the calculated background can be stripped from the raw data to obtain the sole contribution from the magnetic sample (see figure 3.10c).

3.7 Magnetic Force Microscopy (MFM)

Magnetic Force Microscopy is a method used to map the structure of tiny magnetic domains of a magnetic surface, which is based on tapping mode of Scanning Probe Microscopy. Figure 3.11 shows the magnetic force microscope used in this study. A tip attached to a cantilever scans over the magnetic surface and vibrating slightly at a frequency close to its resonant frequency. The tip does not contact the surface directly, but maintains a fixed tip-surface distance of about 20 µm - 100 µm. The tip used for MFM is coated with a ferromagnetic thin film, which induces a magnetic force between the tip and the magnetic domains. In the sample, changes in magnetic force will affect the vibration of the tip, therefore resulting in a phase change which is measured.
The resolution of MFM is limited to approximately 20 nm [11], which is because the magnetic forces are long-range but the atomic forces are short-range. Higher resolution requires the tip to be closer to the surface. Once the tip is close to the surface at a small distance, the atomic forces dominate and the image will be affected by the surface topography. Besides, for some soft magnetic materials with perpendicular anisotropy, the magnetic force from the tip may destroy the domain structure when the tip scans at a very small distance, which means the magnetization of such materials may change to a new state during the scan, and the properties of the sample are altered.

![Image](image1.png)

*Figure 3.12.* The magnetic domains of the in-plane saturated 150 Å Co\textsubscript{23}Pd\textsubscript{77} film: (a) the original image and (b) the filtered image. The original map is obtained directly from the MFM, and the filtered image is obtained from the software Gwyddion.

Figure 3.12a shows an example of the MFM map (original image) of an in-plane magnetized 150 Å Co\textsubscript{23}Pd\textsubscript{77} thin film. A software called Gwyddion [12] is used to remove noise and polynomial background, and obtain the filtered image (figure 3.12b). In this study, all investigations and discussions are based on the filtered images, thus all the MFM images presented in the next chapter are filtered images. Besides, fast Fourier transform spectrum (FFT spectrum) of the MFM map are obtained from the Gwyddion as well. The FFT spectrum shows the magnetic domain distribution in terms of the frequency distribution.
4. Results and Discussion

This chapter contains the results of the measurements employing the methods described in the previous chapter. The following sections will present and discuss the results on the chemical composition, layering, crystal structure and magnetic properties of the films.

4.1 Chemical Composition

The chemical compositions of the films were determined by the RBS measurement\(^1\). The chemical compositions are listed in table 4.1. For Co\(_{25}\)Pd\(_{75}\) layers, the sample used in the RBS measurement is the Al\(_2\)O\(_3\)-capped 150 Å Co\(_{25}\)Pd\(_{75}\) thin film (the sample No.1), since the Pd cap can interfere with the measurement of the Pd elements. The Al\(_2\)O\(_3\)-capped 150 Å Fe\(_{25}\)Pd\(_{75}\) film (the sample No.2) is used for the same reason. The actual chemical compositions of the two samples turn out to be Co\(_{23}\)Pd\(_{77}\) and Fe\(_{18}\)Pd\(_{82}\), with a deviation of 2 % and 7 % from the 25:75 ratio, respectively. For other Co\(_{25}\)Pd\(_{75}\) thin films, the chemical compositions are assumed to be the same as Co\(_{23}\)Pd\(_{77}\), since the power of the Co and Pd targets is the same. Similarly, all Fe\(_{25}\)Pd\(_{75}\) thin films are assumed to be Fe\(_{18}\)Pd\(_{82}\). Hereafter, I will refer all thin films by their actual chemical compositions Co\(_{23}\)Pd\(_{77}\) or Fe\(_{18}\)Pd\(_{82}\), in order to avoid confusion.

**Table 4.1.** The chemical compositions of the Al\(_2\)O\(_3\)-capped 150 Å Co\(_{25}\)Pd\(_{75}\) and 150 Å Fe\(_{25}\)Pd\(_{75}\) thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Film Thickness (10(^{15}) atoms/cm(^2))</th>
<th>Pd (%)</th>
<th>Co (%)</th>
<th>Fe (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>113.2</td>
<td>77</td>
<td>23</td>
<td>-</td>
</tr>
<tr>
<td>No.2</td>
<td>99.3</td>
<td>82</td>
<td>-</td>
<td>18</td>
</tr>
</tbody>
</table>

4.2 Layering and Crystal Structure

The layering of the thin films were obtained by fitting the XRR data using the software GenX. Figure 4.1a and b show the x-ray reflectograms and the corresponding GenX fitting curves of the Al\(_2\)O\(_3\)-capped 150 Å Co\(_{23}\)Pd\(_{77}\) and Fe\(_{18}\)Pd\(_{82}\) thin film, respectively. Owing to length constraints, the results of

---

\(^{1}\)The RBS measurement was performed by Eleni Ntemou.
(a) XRR raw data and fitting of the Al$_2$O$_3$-capped 150 Å Co$_{23}$Pd$_{77}$ thin film.

(b) XRR raw data and fitting of the Al$_2$O$_3$-capped 150 Å Fe$_{18}$Pd$_{82}$ film.

Figure 4.1. The XRR reflectograms (raw data) and GenX fitting of the 150 Å Co$_{23}$Pd$_{77}$ and Fe$_{18}$Pd$_{82}$ thin films with Al$_2$O$_3$ capping. The y-axis (intensity) are logarithmic. FOM refers to figure of merit, which indicates the error between the raw data and fitting.

other films are not shown. The layer thickness and roughness are collected and listed in the table 4.2. For the 150 Å thick thin films, the actual thickness of Co$_{23}$Pd$_{77}$ or Fe$_{18}$Pd$_{82}$ layer has a deviation of no more than 5 Å, compared to the desired values. For the 400 Å thick thin films, the deviation is less than 10 Å. The actual layer thicknesses of 400 Å Co$_{23}$Pd$_{77}$ and Fe$_{18}$Pd$_{82}$ layers are both slightly thinner than 400 Å. The thickness of Al$_2$O$_3$ capping is approximate to 50 Å , and the Pd capping is around 40-42 Å. Since the deviations of the actual thicknesses from the intended layer thicknesses are considered small, hereafter I will continue to refer to the intended layer thicknesses for simplicity. Besides, the layer roughness $\sigma$ is from around 10 Å to around 20 Å.
Table 4.2. The layering of the films determined from the XRR measurements with GenX fitting. $t$ and $\sigma$ refer to the layer thickness and layer roughness of the corresponding layer, respectively. For the copied samples, only one copy was measured. All data are in Å. The errors on the thicknesses and roughnesses are assumed to be within +/- 2 Å.

<table>
<thead>
<tr>
<th>Sample - capping</th>
<th>$t_{\text{Co$<em>{23}$Pd$</em>{77}$}}$</th>
<th>$\sigma_{\text{Co$<em>{23}$Pd$</em>{77}$}}$</th>
<th>$t_{\text{Fe$<em>{18}$Pd$</em>{82}$}}$</th>
<th>$\sigma_{\text{Fe$<em>{18}$Pd$</em>{82}$}}$</th>
<th>$t_{\text{cap}}$</th>
<th>$\sigma_{\text{cap}}$</th>
<th>$\sigma_{\text{sub}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 Å Co$<em>{23}$Pd$</em>{77}$ - Al$_2$O$_3$</td>
<td>151</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>49</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>150 Å Fe$<em>{18}$Pd$</em>{82}$ - Al$_2$O$_3$</td>
<td>-</td>
<td>-</td>
<td>145</td>
<td>12</td>
<td>47</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>150 Å Co$<em>{23}$Pd$</em>{77}$ - Pd</td>
<td>154</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>41</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>150 Å Fe$<em>{18}$Pd$</em>{82}$ - Pd</td>
<td>-</td>
<td>-</td>
<td>150</td>
<td>13</td>
<td>42</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>400 Å Co$<em>{23}$Pd$</em>{77}$ - Pd</td>
<td>393</td>
<td>27</td>
<td>-</td>
<td>-</td>
<td>41</td>
<td>17</td>
<td>4</td>
</tr>
<tr>
<td>400 Å Fe$<em>{18}$Pd$</em>{82}$ - Pd</td>
<td>-</td>
<td>-</td>
<td>391</td>
<td>16</td>
<td>40</td>
<td>20</td>
<td>5</td>
</tr>
</tbody>
</table>

The crystal structure of the films is investigated by analyzing the XRD results. Figure 4.2a and b show the diffractograms of the Al$_2$O$_3$-capped 150 Å thick Co$_{23}$Pd$_{77}$ and Fe$_{18}$Pd$_{82}$ thin films, respectively. Within the range of 2$\theta$ from 35° to 70°, peaks are observed only at around 50.6° for both thin films. Figure 4.3a gives the zoom-in on the peak of the Co$_{23}$Pd$_{77}$ sample. The zoomed-in diffractogram shows that the peaks are composed of a major peak at 50.59° and a secondary peak at 50.73°, which is because the x-ray generator have not only pure Cu $K - \alpha - 1$ radiation ($\lambda = 1.5406$ Å) but also a part of Cu $K - \alpha - 2$ radiation ($\lambda = 1.5444$ Å). This can be verified by calculating the interplanar distance $d$ using the Bragg equation 3.1: first set 2$\theta = 50.59°$ and $\lambda = 1.5406$, and second set 2$\theta = 50.6°$ and $\lambda = 1.5444$. Both yield the same result $d = 1.803$ Å, indicating the dual peaks arise from the same constructive interference but different radiation. The same phenomenon is observed in the Fe$_{18}$Pd$_{82}$ thin film, and the interatomic distance $d = 1.802$ Å.

Figure 4.3b shows the rocking curve of the Co$_{23}$Pd$_{77}$ sample at 2$\theta = 50.6°$. The full width at half maximum (FWHM) of the rocking curve is 0.0612°, indicating that the growth of the Co$_{23}$Pd$_{77}$ grains are textured. The same method is performed on the 150 Å Fe$_{18}$Pd$_{82}$ thin film (Al$_2$O$_3$-capped) and the FWHM shows that the Fe$_{18}$Pd$_{82}$ grains are textured grewed as well.

The crystal structure and growth direction of the thin films can be obtained by comparing the experimental XRD results with theoretical XRD patterns calculated by density functional theory (DFT). Materials Project [13] provides the crystal structure of cubic Co$_{25}$Pd$_{75}$ lattice (figure 4.4a) and hexagonal Co$_{25}$Pd$_{75}$ lattice (figure 4.4b), as well as the corresponding calculated XRD patterns (figure 4.4c and d). According to the theoretical patterns, the cubic Co$_{25}$Pd$_{75}$ are expected to have intensive peaks at 2$\theta = 40.36°$ or 46.95°, resulting from the diffraction of [111] and [200] planes, respectively. And the hexagonal Co$_{25}$Pd$_{75}$ are expected to exhibit peaks at 2$\theta = 43.09°$, correspond to [2021] planes. None of the theoretical results matches the experimental results of the diffractogram in figure 4.3a. For the Fe$_{18}$Pd$_{82}$ thin film, the theoretical pattern does not match the experimental results either.
Figure 4.2. The x-ray diffractograms of the 150 Å Co$_{23}$Pd$_{77}$ and Fe$_{18}$Pd$_{82}$ films capped with Al$_2$O$_3$. The range is from 35° to 70°.
The x-ray diffractogram (2θ = 48° to 52°) of the Al₂O₃-capped 150 Å Co₂₃Pd₇₇ thin film. (b) The rocking curve of at 2θ = 50.6°.

Figure 4.3. (a) The x-ray diffractogram (zoomed in on the peak) and (b) the rocking curve of the peak (2θ = 50.6°) of the Al₂O₃-capped 150 Å Co₂₃Pd₇₇ film.

Therefore, texture analysis was performed in order to obtain both growth direction and crystal structure of the Co₂₃Pd₇₇ and Fe₁₈Pd₈₂ thin films in this work. The texture analysis revealed that the Co₂₃Pd₇₇ and Fe₁₈Pd₈₂ grains both have face centered cubic crystal structure, and the peaks at 50.6° correspond to a [001] texture of the grains. The differences between the experimental results and the theoretical results are probably from the deviations of the chemical compositions. The theoretical XRD patterns adopted Co₂₅Pd₇₅ and Fe₂₅Pd₇₅ as their models for calculation, while the actual chemical compositions are Co₂₃Pd₇₇ and Fe₁₈Pd₈₂. Besides, another possible reason is that the texture analysis was performed by Anna Ravensburg.
(a) The crystal structure of cubic Co$_{25}$Pd$_{75}$.

(b) The crystal structure of hexagonal Co$_{25}$Pd$_{75}$.

(c) Calculated XRD patterns of cubic Co$_{25}$Pd$_{75}$.

(d) Calculated XRD patterns of hexagonal Co$_{25}$Pd$_{75}$.

*Figure 4.4.* Illustrations of crystal structures and calculated XRD patterns of Co$_{25}$Pd$_{75}$ crystals. (a) and (c) are cubic Co$_{25}$Pd$_{75}$. (b) and (d) are hexagonal Co$_{25}$Pd$_{75}$. The data are obtained from the Material Project database (version 2020_09_08) [13].
Figure 4.5. (a) The x-ray diffractogram and (b) the rocking curve at 50.6° of the Al₂O₃-capped 400 Å Fe₁₈Pd₈₂ thin film.

DFT calculations are performed at 0 K whereas the measurements in this work are performed at room temperature.

For the Pd-capped 150 Å thick films and the Pd-capped 400 Å thick films, their x-ray diffractograms show the same peaks. Hence, the crystal structures and growth directions of these films are assumed to be the same. The peak of the 400 Å Fe₁₈Pd₈₂ film was not observed in the diffractogram at first, but was found in the cocking curve when 2θ = 50.6° and θ = 25.69°, as shown in figure 4.5. The value of θ is not the half of 2θ, indicating that the surface of the 400 Å Fe₁₈Pd₈₂ film is tilted.

4.3 Magnetic Properties
This section shows the magnetic properties of Co₂₅Pd₇₅ films, including hysteresis loops (in-plane and out-of-plane), magnitude of magnetization, and domain structure. The hysteresis loops are measured from both longitudinal and polar MOKE measurement. The magnitude of magnetization is obtained from
Figure 4.6. The in-plane hysteresis loops of the (a) 150 Å Co$_{23}$Pd$_{77}$, (b) 150 Å Fe$_{18}$Pd$_{82}$, (c) 400 Å Co$_{23}$Pd$_{77}$, (d) 400 Å Fe$_{18}$Pd$_{82}$ thin films, obtained from the L-MOKE measurements. For the 150 Å thick films, both the Al$_2$O$_3$- and Pd-capped samples are measured. While for the 400 Å only the Pd capped film is measured.

the VSM measurement. The magnetic domain structure is obtained from the MFM.

4.3.1 Results of the MOKE Measurements

Results of the L-MOKE Measurement

The in-plane hysteresis loops of the Co$_{23}$Pd$_{77}$ and Fe$_{18}$Pd$_{82}$ thin films are shown in the figure 4.6. The hysteresis loops of the Co$_{23}$Pd$_{77}$ and the Fe$_{18}$Pd$_{82}$ exhibit different shapes. The 150 Å Co$_{23}$Pd$_{77}$ films (figure 4.6a) exhibit near-parallelogram like hysteresis loops. In contrast, the shape of the hysteresis loops of 150 Å Fe$_{18}$Pd$_{82}$ films (figure 4.6b) are almost a distinct step. The 400 Å Co$_{23}$Pd$_{77}$ and 400 Å Fe$_{18}$Pd$_{82}$ films exhibit the similar difference, shown as figure 4.6c and 4.6d. Although the hysteresis loop of the 400 Å Co$_{23}$Pd$_{77}$ film is severely deformed, it still tends to exhibit a parallelogram-like shape. The severe deformation may be attributed to the setting of the MOKE measure-
ment. When the applied magnetic field is increased to produce a larger interaction with the film, the sample surface or the sample holder may be twisted slightly, resulting in a disturbance of reflection. This may also explain the asymmetry observed in the hysteresis loops: when the applied magnetic field is negative, the hysteresis loops beyond the saturation point still have a small slope, whereas they are almost horizontal when the applied field is positive. Besides, no significant difference is found between the Al$_2$O$_3$ and Pd capping, indicating that the magnetization from the capping is assumed to be negligible.

In addition, the Co$_{23}$Pd$_{77}$ films exhibit a bigger in-plane coercivity and saturation magnetization than the Fe$_{18}$Pd$_{82}$ films. The Co$_{23}$Pd$_{77}$ films show a coercivity of around 100 to 200 mT and a saturation field of approximately 300 mT for 150 Å and more than 700 mT for 400 Å thick layers, indicating that Co$_{23}$Pd$_{77}$ is a good candidate for hard magnetic materials. In contrast, the coercivity of both 150 Å or 400 Å Fe$_{18}$Pd$_{82}$ films is smaller than 1 mT, hence significantly smaller than the Co$_{23}$Pd$_{77}$ counterpart. And the saturation field of Fe$_{18}$Pd$_{82}$ is of the same order as the coercivity.

**Results of the P-MOKE Measurements**

While the shape of the hysteresis loops of the Fe$_{18}$Pd$_{82}$ indicate a full in-plane magnetization, a partly out-of-plane magnetization of the Co$_{23}$Pd$_{77}$ would match the shape of loops observed here. Hence, P-MOKE measurements were performed on these samples to investigate this.

Figure 4.7 shows the results of the P-MOKE measurement of Co$_{23}$Pd$_{77}$ films. The results of Fe$_{18}$Pd$_{82}$ films are not shown because Fe$_{18}$Pd$_{82}$ films exhibit no out-of-plane magnetization. The in-plane and out-of-plane hysteresis loops of the Co$_{23}$Pd$_{77}$ exhibit significantly different shapes. For the 150 Å thick film, the out-of-plane hysteresis loop exhibit a coercivity of around 20 mT and a saturation field of around 120 mT. Both are significantly smaller than

![Image](image_url)

(a) The Al$_2$O$_3$-capped 150 Å Co$_{23}$Pd$_{77}$. (b) The Pd-capped 400 Å Co$_{23}$Pd$_{77}$.

**Figure 4.7.** The out-of-plane hysteresis loops of the (a) 150 Å Co$_{23}$Pd$_{77}$ (b) 400 Å Co$_{23}$Pd$_{77}$ thin films, obtained from the L-MOKE measurements. The raw data of the 400 Å thick film have been smoothed, shown in subfigure (b).
the results obtained from the in-plane hysteresis loops. The same observation is made for the 400 Å Co$_{23}$Pd$_{77}$ film. The differences between the in-plane and out-of-plane results indicate that Co$_{23}$Pd$_{77}$ films exhibit significant perpendicular magnetic anisotropy.

Furthermore, an interesting phenomenon is observed: the 400 Å Co$_{23}$Pd$_{77}$ film exhibits a butterfly-shaped hysteresis loop, whereas such a shape is not found in the 150 Å thick films. The remanence of the 400 Å thick film is smaller than the 150 Å thick films, corresponds to only a small fraction of the magnetic moments of the 400 Å thick film remaining in the perpendicular direction after the external magnetic field is removed. This may be explained by a phenomenon called cone state [14]. Sone state is defined as the magnetization orientation is not exactly perpendicular to the surface but inclined to the surface. In other words, part of the out-of-plane components of the magnetization becomes the in-plane components. The cone state appears when the shape and surface anisotropy are balancing each other. Therefore, the cone state is observed in the 400 Å thick film probably because the increasing layer thickness results in weaker shape anisotropy.

![Hysteresis loops](image)

(a) The Al$_2$O$_3$-capped 150 Å Co$_{23}$Pd$_{77}$.

(b) The Pd-capped 150 Å Co$_{23}$Pd$_{77}$.

(c) The Pd-capped 150 Å Fe$_{18}$Pd$_{82}$.

(d) The Pd-capped 400 Å Fe$_{18}$Pd$_{82}$.

Figure 4.8. The in-plane hysteresis loops with the sample rotated by different angles. The films are (a) Al$_2$O$_3$-capped 150 Å Co$_{23}$Pd$_{77}$ (b) Pd-capped 150 Å Co$_{23}$Pd$_{77}$ (c) Pd-capped 150 Å Fe$_{18}$Pd$_{82}$ (d) Pd-capped 400 Å Fe$_{18}$Pd$_{82}$, respectively.
Figure 4.9. The in-plane and out-of-plane hysteresis loop of the same 150 Å Co$_{23}$Pd$_{77}$ thin film (Al$_2$O$_3$-capped).

**Anisotropy**

Figure 4.8a and b show the in-plane hysteresis loops (having different rotation angles) of the 150 Å Co$_{23}$Pd$_{77}$ films with Al$_2$O$_3$ and Pd capping, respectively. The magnetic field is applied in different in-plane directions with an interval of 45°. No significant difference with rotation angles is observed, indicating that the magnetization is isotropic in-plane. No significant difference between the Al$_2$O$_3$ and Pd capping is observed. The 400 Å Co$_{23}$Pd$_{77}$ thin films have not been measured due to the deformation. Figures 4.8c and d show the counterpart hysteresis loops of the 150 Å and 400 Å Fe$_{18}$Pd$_{82}$ films, respectively. Still no significant difference with rotation angles is observed. Hence, the magnetisation of Fe$_{18}$Pd$_{82}$ films is assumed to be isotropic in-plane as well.

The in-plane isotropy indicates that the microstructure of these films are in-plane long-range disordered. The isotropy also matches the results from XRD and texture analysis: both the Co$_{23}$Pd$_{77}$ or Fe$_{18}$Pd$_{82}$ films consist of multiple crystal grains which grow [001] textured, i.e. with a preferred out-of-plane orientation while the in-plane orientation of the unit cells seem to be randomly distributed.

In order to investigate the perpendicular anisotropy, the in-plane and out-of-plane hysteresis loops of the same 150 Å Co$_{23}$Pd$_{77}$ thin film are compared, shown in Figure 4.9. The shapes of the in-plane and out-of-plane are significantly different, indicating that the 150 Å Co$_{23}$Pd$_{77}$ thin films exhibit strong perpendicular magnetic anisotropy. The saturation field of the in-plane of is larger than the out-of-plane, meaning the easy axis is not entirely in-plane. The data of the 400 Å Co$_{23}$Pd$_{77}$ thin film are not shown, due to the deformation of
the in-plane hysteresis loop mentioned before. But the VSM results (shown in the next section) indicate that the 400 Å thick films exhibit perpendicular magnetic anisotropy as well. The Fe$_{18}$Pd$_{82}$ films only exhibit in-plane magnetization, and no out-of-plane magnetization is obtained for the Fe$_{18}$Pd$_{82}$ thin films.

4.3.2 Results of the VSM measurements

Although the MOKE measurements show the shape of the hysteresis loops, the absolute value of the magnetic moments can not be obtained with L- or P-MOKE measurements. Hence, VSM measurements were performed on the following thin films$^3$: 150 Å Co$_{23}$Pd$_{77}$ (Al$_2$O$_3$ capping), 150 Å Fe$_{18}$Pd$_{82}$ (Al$_2$O$_3$ capping), 400 Å Co$_{23}$Pd$_{77}$ (Pd capping), and 400 Å Fe$_{18}$Pd$_{82}$ (Pd capping). The four films were cut into 5 × 5 mm$^2$ pieces (figure 4.10) in order to fit the sample holder.

Figures 4.11a and c show the hysteresis loops obtained from the VSM measurements of the 150 Å and the 400 Å Co$_{23}$Pd$_{77}$ thin films, respectively. For both the Co$_{23}$Pd$_{77}$ thin films, the in-plane and the out-of-plane hysteresis loops were recalibrated according to the SQUID results, because the original VSM results show that the in-plane saturation moment does not equal to the out-of-plane value of the same sample. Hence, a SQUID was applied to remeasure to the saturation magnetic moments$^4$, and the hysteresis loops were corrected according to the SQUID results. The VSM results of the 150 Å and 400 Å

---

$^3$Anna Ravensburg and Daniel Hedlund also contributed the VSM results.
$^4$The SQUID was performed by Fernand Denoel.
Fe18Pd82 films are shown in figure 4.11b and d, respectively. Since no out-of-plane magnetization of Fe18Pd82 is observed, only the in-plane hysteresis loops were measured. The difference between Co23Pd77 and Fe18Pd82, the thickness dependence of magnetization, and the direction dependence of magnetization are observed in the VSM results as well. Besides, no significant difference between Al2O3 and Pd capping is observed. These findings agree with the results obtained from the MOKE measurement. In addition, the in-plane hysteresis loop of the 400 Å Co23Pd77 thin film, which is deformed in the L-MOKE result, is obtained here.

However, the hysteresis loops obtained from the VSM and the MOKE measurement are not exactly the same. For example, the in-plane hysteresis loops of the 150 Å Co23Pd77 thin film show a significant difference between the VSM and MOKE (figure 4.11c and figure 4.9). The L-MOKE result exhibits...
a significant in-plane hysteresis while the VSM result does not. Besides, the VSM result shows an in-plane coercivity of around 25 mT, which is significantly smaller than the value obtained from the L-MOKE result. This phenomenon can be explained by the important difference between the VSM and MOKE: L- and P-MOKE only measure a point in the center of the film where the polarized light is reflected, but VSM measures the entire film. The differences between the VSM results and the MOKE results indicate that there may exist difference magnetic behaviours between the film center and the film edges.

Table 4.3 lists the maximum magnetic moment ($m_{\text{max}}$), the layer volume ($V_{\text{layer}}$), and the saturation magnetization ($M_s$) for each thin film. The maximum magnetic moments were obtained from the VSM results. The layer volume refers to the volume of a Co$_{23}$Pd$_{77}$ or Fe$_{18}$Pd$_{82}$ layer, and is estimated by taking the product of the film area (figure 4.10) and the layer thickness (table 4.2). The saturation magnetization was calculated by dividing $m_{\text{max}}$ by $V_{\text{layer}}$ for each thin film. The $M_s$ of a Co$_{23}$Pd$_{77}$ layer is about 7-10 times larger than a Fe$_{18}$Pd$_{82}$ layer of the same thickness. The difference come from mainly the intrinsic difference of the Co and Fe elements and partly the proportion difference of the Co/Fe atoms. Furthermore, for the same type alloy, the 400Å films exhibit larger maximum magnetic moments but smaller saturation magnetization than the 150Å films. One possible reason is the thickness dependence of the magnetization. Thicker grains have a smaller surface-to-volume ratio, thus the broken symmetry near the surface may lead to a different magnetic properties from the interior. Another possible reason is the deviations between the calculated layer volume and the actual layer volume. In the calculations, the layer thickness is assumed to be a constant at any position, while the actual layers are tilted.

Table 4.3. The saturation magnetic moment $m_{\text{max}}$, layer volume $V_{\text{layer}}$, and saturation magnetization of the thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$m_{\text{max}}$ (emu)</th>
<th>$V_{\text{layer}}$ ($\times 10^{-7}$ cm$^3$)</th>
<th>$M_s$ (emu/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 Å Co$<em>{23}$Pd$</em>{77}$</td>
<td>$1.46 \times 10^{-4}$</td>
<td>3.626</td>
<td>402.6</td>
</tr>
<tr>
<td>150 Å Fe$<em>{18}$Pd$</em>{82}$</td>
<td>$2.07 \times 10^{-5}$</td>
<td>3.626</td>
<td>57.1</td>
</tr>
<tr>
<td>400 Å Co$<em>{23}$Pd$</em>{77}$</td>
<td>$2.40 \times 10^{-4}$</td>
<td>8.712</td>
<td>275.5</td>
</tr>
<tr>
<td>400 Å Fe$<em>{18}$Pd$</em>{82}$</td>
<td>$2.36 \times 10^{-4}$</td>
<td>8.712</td>
<td>27.1</td>
</tr>
</tbody>
</table>

The anisotropy energy of the Co$_{23}$Pd$_{77}$ thin films can be calculated from hysteresis loops obtained from the VSM. The area enclosed between the in-plane and out-of-plane loops is exactly the anisotropy energy. In the calculation, the two hysteresis loop branches are averaged, in order to remove the hysteresis and obtain a single branch to calculate the anisotropy energy. The anisotropy energy density of the 150 Å Co$_{23}$Pd$_{77}$ is $3.77 \times 10^5$ erg/cm$^3$, and the 400 Å is $2.5 \times 10^5$ erg/cm$^3$. The lower anisotropy energy density of the
400 Å thick film probably come from the reduced shape anisotropy as the thickness increases.

4.3.3 Magnetic Domains

The images of the magnetic domains of the Co$_{23}$Pd$_{77}$ thin films were obtained from the MFM mapping. In order to investigate the magnetic domains of Co$_{23}$Pd$_{77}$ thin films, MFM mapping were performed on a 400 Å thick Pd-capped films in three different states: demagnetized, in-plane magnetized, and out-of-plane magnetized. Besides, a demagnetized 150 Å thick Pd-capped Co$_{23}$Pd$_{77}$ films was also measured in order to compare the difference between

![MFM map](image1)

(a) The MFM map (10µm × 10µm) of the 150 Å Co$_{23}$Pd$_{77}$ film (demagnetized).

![MFM map](image2)

(b) The MFM map (10µm × 10µm) of the 400 Å Co$_{23}$Pd$_{77}$ film (demagnetized).

![FFT spectrum](image3)

(c) The FFT spectrum of the 150 Å Co$_{23}$Pd$_{77}$ film (demagnetized).

![FFT spectrum](image4)

(d) The FFT spectrum of the 400 Å Co$_{23}$Pd$_{77}$ film (demagnetized).

Figure 4.12. a) The domain map and c) the corresponding FFT spectrum of the demagnetized 150 Å Co$_{23}$Pd$_{77}$ film. b) The domain map and c) the corresponding FFT spectrum of the demagnetized 400 Å Co$_{23}$Pd$_{77}$ film.
the two thicknesses. The Fe_{18}Pd_{82} films have not been mapped and will not be discussed here.

Fig 4.12a and b show the MFM images of the demagnetized 150 Å and 400 Å Co_{23}Pd_{77} films, respectively. Both the films exhibit maze-like domain patterns and a near-uniform magnetization distribution. The domain size of the 150 Å Co_{23}Pd_{77} film is estimated to be around 0.15 μm, and to be around 0.16 μm for the 400 Å film. The corresponding FFT spectrums are shown in fig 4.12c (150 Å) and d (400 Å). In both the FFT spectrums, white pixels (highest density) were distributed to a four-fold region, forming a four-leaf-clover-like shape with the symmetry center at the origin. Such a distribution corresponds to the maze-like domain morphology observed in the two films. No significant difference between the 150 Å and 400 Å thick layers is found.

For Co_{23}Pd_{77} thin films in in-plane magnetized state, the MFM images of the 150 Å and 400 Å films are shown in fig 3.12b and fig 4.13a, respectively. Unlike the demagnetized films, the two in-plane magnetized films exhibit stripe-patterned domains. The domain size of the 150 Å in-plane magnetized film is around 0.14 μm, which is similar to the demagnetized film. In contrast, the domain size of the 400 Å film is 0.08 μm, almost half of the demagnetized film. Fig 4.13b shows the FFT spectrum of the 400 Å in-plane magnetized Co_{23}Pd_{77} film. In contrast to the demagnetized films, white pixels were distributed to two regions, corresponding to the stripe-domain morphology and in-plane distributed magnetization.

For the Co_{23}Pd_{77} thin films in out-of-plane magnetized state, the MFM image of the 400 Å film is shown in Fig 4.12a. The film exhibits maze-like domains, with a domain size of around 0.15 μm. Compared to the demagnetized films, the domain morphology is closer to a "standard" maze. In order
(a) The MFM map (5μm × 5μm) of the 400 Å Co\textsubscript{23}Pd\textsubscript{77} film (out-of-plane magnetized).

(b) The MFM map with a blue mask.

(c) The FFT spectrum of the 400 Å Co\textsubscript{23}Pd\textsubscript{77} film (out-of-plane magnetized). The insert is a zoom-in of the spectrum.

Figure 4.14. a) The MFM map, b) the masked MFM map, and c) the FFT spectrum of the out-of-plane magnetized 400 Å Co\textsubscript{23}Pd\textsubscript{77} film. The black spot appearing in a) and b) arises from a dust or a defect on the surface.

to illustrate the domain morphology further, the map was covered by a blue mask (fig 4.14b). The corresponding FFT spectrum is shown in fig 4.14c, where white pixels were distributed in a cross-like region. Such a distribution corresponds to the special maze-like domain morphology. Also such a distribution means the magnetization remains in-plane component even in the out-of-plane magnetized state. This might correspond to the cone state found in the hysteresis loops.
5. Conclusions

In this work, the crystal structure and magnetic properties of Co$_{25}$Pd$_{75}$ alloy thin films are investigated, and the comparison between Co$_{25}$Pd$_{75}$ and Fe$_{25}$Pd$_{75}$ is made. The films are deposited via sputtering under room temperature, and the actual chemical composition turned to be Co$_{23}$Pd$_{77}$ and Fe$_{18}$Pd$_{82}$. The films have two different thicknesses: 150 Å and 400 Å. Both the Co$_{25}$Pd$_{75}$ and Fe$_{25}$Pd$_{75}$ films are textured polycrystallines in face centered cubic structure. The growth direction of the textured grains is along <001>. The Co$_{25}$Pd$_{75}$ thin films show both in-plane and out-of-plane magnetization, and exhibit perpendicular magnetic anisotropy while having no in-plane anisotropy. In contrast, the Fe$_{25}$Pd$_{75}$ thin films only exhibit in-plane magnetization. No significant difference between the Al$_2$O$_3$-capped and Pd-capped samples is found. In the 400 Å Co$_{25}$Pd$_{75}$ films the cone state is observed, while in the 150 Å thick films no obvious evidence of the cone state is found yet. The anisotropy energy of the 400 Å Co$_{25}$Pd$_{75}$ films is lower than the 150 Å thick films, corresponding to a reduced anisotropy from the layer thickness. In addition, the differences between the MOKE results and the VSM result indicate that the magnetic properties probably vary in different film positions. Magnetic domains exhibit maze-like morphology in the demagnetized and out-of-plane magnetized 400 Å Co$_{25}$Pd$_{75}$ films while exhibit stripe-like morphology in the in-plane magnetized film. The domain structures correspond to the perpendicular anisotropy and the cone state observed in the hysteresis loops.

At present, there are still works deserving further study. Firstly, the Co$_{25}$Pd$_{75}$ can be compared with other chemical compositions (Co$_x$Pd$_{1-x}$), in order to investigate the composition dependence of the structural and magnetic properties. This is also an important part that is unfinished in this project due to the limited time and the constraints of the sputter system. Secondly, the reason and mechanism of the cone state appearing in the 400 Å Co$_{25}$Pd$_{75}$ films is not entirely clear. Thirdly, it is worth to repeat the MOKE and VSM measurement in order to figure out why they show different hysteresis loop for the same sample. Furthermore, The alloy thin films can be compared with other nanostructures, such as multilayers or hybrid structures.
6. Acknowledgement

I would like to thank everyone who contributed this work and helped me during my master thesis project.

Firstly, I would like to thank Anna Ravensburg for her help in every aspect in this master thesis project, including scheduling the plans, fabricating the samples, guiding me the presentations, and help me with the thesis writing. She is the important person who teaches me the XRR, XRD, GenX basics, L-MOKE measurement, and P-MOKE measurement. And she always gives me encouragement when I have difficulties in this project.

Secondly, I would like to thank Vassilios Kapaklis for involving me in this interesting topic, providing me the theoretical backgrounds and helping me with the experimental settings. He is the important person who helps me to understand the unexpected outcomes.

Furthermore, I would like to thank Christina Vantaraki for her introduction to the MFM measurements and providing me the book about magnetic domains.

Besides, I would like to thank Daniel Hedlund for teaching me the VSM measurements.

Next, I would like to thank Gunnar Karl Pálsson for help me convert the XRD files.

Also, I would like to thank Roméo Beignon for teaching me the MFM measurement and Gwyddion basics.

Then, I would like to thank Björn Erik Skovdal for his help in the MFM measurements.

Next, I would like to thank Matias Pablo Grassi for his help in the cutting of the samples.

And, I would like to thank Eleni Ntemou for the help of the RBS measurements.

Also, I would like to thank Fernand Denoel for the help of the SQUID measurements.

In addition, I would like to thank Petra Jönsson for introducing me to this project.

Finally, I would like to thank all the people who gives me support and encouragement during my two years of study in Sweden!
References