RASIC, GORAN. Nanoscale Surface Patterning and Coercivity Reduction in NiFe$_2$O$_4$ Thin Films. (Under the direction of Dr. Justin Schwartz).

Biaxially textured nickel ferrite (NFO) thin films were grown by chemical solution deposition on c-plane sapphire substrates. Crystal structure and chemical composition was evaluated using X-ray Diffraction. Nanoimprint lithography (NIL) technique using a polydimethylsiloxane (PDMS) stamp was used imprint the films. A method for large scale precise patterning of was demonstrated. Quality of the transferred pattern was evaluated using atomic force and transmission electron microscopies. Magnetic measurements were performed using superconducting quantum interference device (SQUID) and showed large decrease of coercivity in patterned samples. Probable causes for coercivity reduction have been investigated and surface patterning has been shown to be the direct cause of the coercivity reduction phenomena. Coercivity reduction has been shown to translate to thicker films with layer-by-layer manufacturing method yielding better results. The effect of changing the surface pattern on the topography, crystallography and magnetic properties was investigated and different trends were observed for the measurements done with the magnetic field parallel and perpendicular to the film surface. Coercivity reduction was shown to increase with increasing feature size in the case of magnetic field oriented perpendicular to the film surface. For the field parallel to the film surface the opposite was observed. In all cases, the coercivity was reduced relative to the unpatterned film and relative to the base layer onto which the patterned film was deposited. All films showed a similar magnetic response as indicated by similarities in the curve shape. Crystallography measurements
showed the imprint process did not affect the grain growth and orientation regardless of the surface feature size as indicated by all films having virtually identical diffraction patterns. The lower limit of surface patterning here was shown to be around 500 nm. Below 750 nm, the pattern quality degraded and the feature height reduced. The domain configurations of the plain and patterned films were investigated. Deviation from the expected domain configuration was found in the patterned films. The domain configuration of patterned films was similar regardless of the magnetic history of the sample. Micromagnetism and domain theory were used to investigate the energetics of different film configurations. Changing the domain sizes within values used in this study has been shown to have a very small effect on the energy of the system. Combining the theoretical prediction with the experimental measurements, the origin of the observed domain structure and coercivity reduction has been shown to be the surface topography induced change in the minimum energy configuration of the sample. This results in the minimization of the total sample magnetization through formation of stripe domains.
Nanoscale Surface Patterning and Coercivity Reduction in NiFe₂O₄ Thin Films

by

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DEDICATION

To my parents, whose hard work, sacrifice and strength of character allowed me to find my way, and whose wisdom and support helped me stay on it.
BIOGRAPHY

Goran Rasic was born on Feb. 6th 1986 in Zagreb, the capital of Croatia. He received his high school diploma in Computer Systems Engineering from Sesvete High School in 2004. He then enrolled in the University of Zagreb, a top Croatian university, where he received both B.S. and M.Sc. degrees in Physics. His thesis title was “Photoluminescent spectroscopy of semiconductor nanostructures.” Upon completing his Master’s degree in 2011 he came to US for his Ph.D. in Materials Science and Engineering at North Carolina State University under the direction of Dr. Justin Schwartz. He received his Ph.D. in April 2014.
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CHAPTER 1

Introduction

1.1. Motivation

As technology advances the demand for smaller and faster devices with reduced power losses becomes increasingly important. For high-frequency (>1 GHz) devices, such as antenna and sensors, two loss mechanisms are relevant, electrical and magnetic [1-3]. Electrical losses, arising from eddy currents, are reduced by forming laminate structures and/or choosing materials with high electrical resistivity [1-3]. Ferrites, combining high electrical resistivity with favorable magnetic properties, present attractive candidates [1-3]. Among these, ferrimagnetic transition metal-oxides with a general formula MO\(\cdot\)Fe\(_2\)O\(_3\), where M is a divalent ion such as Ni\(^{2+}\), Co\(^{2+}\), Fe\(^{2+}\), Mg\(^{2+}\) or Mn\(^{2+}\) are the most important. Nickel ferrite (NiFe\(_2\)O\(_4\), NFO), is one of the most important ferrites, with both high electrical resistivity and saturation magnetization. Combined with its inverse spinel cubic structure, high Curie temperature, and moderate magnetostriction, NFO is ideal for high-frequency [1, 2], microwave [4] or spin filter devices [5-7] and sensors [8], memory [9-13], and magnetoelectric composites [11, 12, 14-16].

While electrical losses have been minimized by use of electrically resistive materials such as ferrites and employing laminate structure, magnetic losses, arising from the magnetic hysteresis of the material, are intrinsic and increase proportionally to the frequency [9, 17]. At frequencies above 1 GHz, these losses become immense; they remain the limiting
factor for high-frequency (HF) device development. To reduce magnetic losses, the hysteresis losses must be reduced without losing desirable magnetic properties; reduced coercivity is needed, while retaining high saturation magnetization. At present, this is accomplished through doping and alloying [18-20], but a constraint on device manufacturing remains due to the limitations on material selection [1-3].

This study seeks to address this problem by reducing the magnetic losses in a material without changing its composition. Specifically, the coercivity is reduced by controlling magnetic domain formation on the surface of the material through surface patterning. Proper selection of surface pattern will alter the domain size and distribution through modification of energetically favorable domain configuration which in turn reduces the coercivity. This phenomenon was explored for textured thin and multilayered films with the same surface pattern for comparison. The effect of varying the surface feature size on the coercivity was also studied. Coercivity was shown to dramatically decrease for all films, while texture, curve shape and saturation magnetization remained similar. By affecting only the coercivity and retaining all other desirable properties, we are able to eliminate material selection constraints. This enables us to design devices starting with the most suitable material and then pattern the surface in order to achieve maximum performance.

To complement the experimental results, micromagnetism theory was used to look into the theoretically predicted favorable energy configurations and compare magnetostatic energies. Demagnetizing field was also considered as the origin of the coercivity reduction.
Chemical solution deposition (sol-gel) in combination with nanoimprint lithography was used as a quick and inexpensive method to deposit textured surface patterned thin films with reduced coercivity. Additional advantage of this method is its scalability and ease of implementation with current manufacturing technologies.

1.2. Dissertation structure

The intent of this dissertation is to find a solution to some of the current technological problems in the industry of magnetic materials. Specifically, magnetic losses in materials and loss of properties due to low coupling between different materials was addressed. For most part, the dissertation structure follows the research efforts, with some minor reorganization as to provide more coherent report.

Chapter 1 discusses the motivation and offers a brief introduction of research conducted.

Chapter 2 provides the basic background knowledge.

Chapter 3 discusses the sample manufacturing and equipment used.

Chapter 4 studies surface patterning of Nife$_2$O$_4$ thin films.

Chapter 5 examines the phenomena of coercivity reduction in surface patterned multilayered Nife$_2$O$_4$ films.

Chapter 6 explores the consequences of varying the feature size on the coercivity reduction phenomena.

Chapter 7 offers a theoretical study of the origin of the coercivity reduction.

Chapter 8 summarizes the conclusions and offers suggestions for future.
References


CHAPTER 2

Background

2.1. Basic magnetism

Magnetism is a physical phenomenon associated with motion of electric charge. Electrically charged particles will experience an attractive or repulsive force, depending on their relative direction of motion. This force is described as magnetic force. It is determined by the Lorentz force law:

\[ \vec{F} = Q(\vec{v} \times \vec{B}) \]  

(2-1)

where \( Q \) represents the total charge of the particle, \( v \) is the velocity and \( B \) is the magnetic field. The force on the particle acts in perpendicular direction to the plane given by \( B \) and \( v \). This is known as the right hand rule [1-5].

2.1.1. Magnetism in materials

In a magnetic material, this motion of charge is associated with electrons orbiting around nuclei and electrons spinning about their axes. For macroscopic purposes, these atomic scale current loops can be treated as magnetic dipoles [1, 2, 4]. The amount of magnetism of a material or “magnetization” is dictated by these magnetic dipoles and is given by [6]:

\[ M = \frac{N \cdot m}{V} \]  

(2-2)
Here $M$ is the magnetization per volume, $m$ is the magnetic dipole moment, $N$ is the number of magnetic dipoles, and $V$ is the volume of the material. Sometimes, for convenience, the magnetization is normalized to volume instead of the weight [1].

The response of a material when placed in a magnetic field ($H$), is termed its magnetic induction ($B$) and is given by [7]:

$$\vec{B} = \vec{H} + 4\pi\vec{M}. \quad (2-3)$$

2.1.2. Types of magnetism

Elementary magnetic moments are normally randomly oriented in a material giving the material a zero net magnetization. However, if we place the material in a magnetic field, the field will interact with the magnetic dipoles, causing them to orient themselves with respect to the direction of applied field. This orientation varies for different types of magnetic materials and dictates the type of magnetism. While a material can have more than one type of magnetic response simultaneously, the strongest one usually dominates the weaker ones and the materials are classified by the prevalent response to the magnetic field [1, 2, 4, 5].

2.1.3. Diamagnetism

Diamagnetism is the tendency of a material to oppose an applied magnetic field. When a diamagnetic material is placed in a magnetic field, extra currents are generated in the atoms by electromagnetic induction. The induction of currents is such as to oppose the field which created them, and so the induced magnetic moments will be directed opposite to the
applied field. This effect is linearly proportional to the applied field, as stronger field will induce stronger opposing magnetic moments (figure 2-1).

While diamagnetism is a property of all materials, it is very weak (except in superconductors), and thus easily overpowered by other forms of magnetism. However, if a material has no other magnetic response, diamagnetism is observed. This is true for materials where there is no net magnetic moment. This can be due to an atom having a closed electron shell as is the case in monoatomic noble gases He, Ne, Ar, etc. Polyatomic gases can also have closed-shell structures through molecule formation, as is the case of H₂, N₂, etc. In solids, diamagnetism can be found in materials with ionic bond (NaCl), covalent bond (diamond, Si, Ge) and most organic compounds [1]. A schematic magnetization curve for a diamagnetic material is given in figure 2-1.

2.1.4. Paramagnetism

Unlike diamagnetic materials, paramagnets have weakly coupled unpaired electrons. These electrons are free to align their magnetic moment in any direction and under normal conditions they will have random orientation due to thermal energy. When we apply a magnetic field, a portion of these free electrons will reorient themselves in the direction of the field. The number of magnetic moments oriented in the direction of the field is proportional to applied field strength. This effect is depended on the field and will disappear when the field is turned off.

Paramagnetism is usually exhibited in materials which have some spatial separation between the atoms with unpaired electrons, thus lowering the electron-electron interaction [1,
Some notable examples are salts of transition elements, where each transition-metal cation has a net magnetic moment resulting from its partially filled d-shell, but the cations are spatially separated by an anion weakening the interactions between the magnetic moments on neighboring cations. Other examples are rare-earth salts where the free electron is located in the highly localized f-shell which does not overlap with the f-shell of an adjacent ion. Some other examples include metals (Al) and gasses (O₂). A schematic of a magnetization curve for a paramagnetic material is given in figure 2-1.

Figure 2-1: Schematic magnetization curves for diamagnetic, paramagnetic and antiferromagnetic materials.
2.1.5. Ferromagnetism

Ferromagnetic materials are the most important class of magnetic material and most commonly referred to when we speak about magnetism [2]. In a ferromagnetic material, similar to a paramagnet, we also have unpaired electrons, but these electrons are strongly coupled. This strong coupling between the electrons causes them to orient their magnetic moments parallel to one another and to the direction of the applied field [1, 4]. As a consequence ferromagnets exhibit a substantially different response to magnetic field to that of a paramagnet. Unlike diamagnets and paramagnets, which have a very low response to the magnetic field, ferromagnetic materials have a very large response. This means that a large number of magnetic moments can be oriented in the direction of the field using very low field strength (i.e. low magnetic fields are required to achieve large magnetization of the material). This relationship is nonlinear and increasingly larger fields are required to achieve same increase in magnetization. Another difference is that while paramagnets and diamagnets have a response that grows proportionally to the applied field, a ferromagnetic material will have a maximum value of magnetization at specific field strength. This maximum value is called saturation magnetization as it refers to all of the magnetic moments pointing in the field direction, thus saturating the material. Increasing the field further will have no effect on the magnetization of the material. Another difference is that a ferromagnetic material will retain certain magnetization even after the magnetic field is removed. This is due to the magnetic moments interacting strongly with one another within the material. The extent to which a ferromagnet “remains” magnetic after the field is removed is called remnant magnetization or remanence (M_r). Remanence depends on many
factors, most notably the bond strength of the magnetic moments, which is related to the material itself. To reduce the magnetization of a material to zero, magnetic field must be applied in the opposite direction of the magnetization. The magnitude of the field required to reduce a materials magnetization to zero is called coercivity ($H_c$) of a material. Based on the magnitude of the coercivity, magnetic materials are divided into two classes – soft and hard [1, 2, 8].

Soft magnetic materials have smaller coercivity and are thus used for application where we want to quickly change the magnetization of a material, such as high frequency applications. Hard magnetic materials, on the other hand, are used in applications where we want the material to be very hard to demagnetize i.e. to have large magnetic moment without a magnetic field. This includes permanent magnets such as household magnets and memory devices [1, 2, 8].

As a consequence of it having remanence and coercivity, a ferromagnetic material will outline a hysteresis curve when cycled through a changing magnetic field [1-5]. A typical hysteresis loop for a ferromagnetic material is shown in figure 2-2. While ferromagnetic interaction is much stronger, a paramagnetic interaction can become dominant with increased temperature. Unlike ferromagnetic interaction which is a consequence of coupling of magnetic moment, a paramagnetic interaction is a competition between the applied magnetic field and thermal energy. This means there will be a point, called Curie temperature, where the thermal energy will overpower the cooperative ordering of the magnetic moments in the ferromagnet and the material will become paramagnetic.
Curie temperature defines the thermal operational range, and as such is a defining property of a magnetic material [1-3, 8].

Figure 2-2: Hysteresis curve for a ferromagnetic material.
2.1.6. Magnetic domains and domain walls

In a ferromagnet, exchange energy between elementary magnetic moments wants them to point in the same direction. This however increases the magnetostatic energy of a material. To lower the magnetostatic energy, the material wants the magnetic moments to point in the opposite directions. Competition between these two forces creates magnetic domains [1, 2, 8, 9]. The size and orientation of these domains is dictated by the competing forces to reach an energy minimum. Inside a magnetic domain, all the moments point in the same direction. At the boundary between the two domains however, the magnetic moments are oriented in such a way as to bridge the gap between them. This interface between two domains is called a domain wall. The creation of domain wall takes energy and so the material will split into domain only when the energy gain from reducing the magnetostatic energy is greater than the energy required to create a domain wall. The optimal energy configuration is one where closure domains are formed [1-3, 9, 10]. An example of closure domain is given in figure 2-3.
Figure 2-3: Formation of closure domains in a ferromagnetic material.

Based on the relative plane in which the moments rotate there are two types of domain walls – Bloch and Néel [1, 3]. In Bloch wall the moments reorient perpendicular to the plane of adjacent magnetic domains. This creates free poles at the material surface. An example of a Bloch wall is given in figure 2-4. When a material thickness becomes comparable to the domain wall thickness i.e. when we have a thin film, the energy associated with free poles in Bloch walls becomes huge. This leads to a change in the reorientation direction of magnetic dipoles as it becomes energetically favorable for magnetization to rotate in the plane the magnetic domains. This is called a Néel wall. In a Néel wall, the free
poles are inside the material, on the wall itself [1-3, 9]. Example of a Néel wall is given in figure 2-4.

Figure 2-4: Formation of Bloch and Néel walls.
2.1.7. Coercivity

Domain walls are crucial property of ferromagnetic materials, as they define the shape of the hysteresis curve. A normal ferromagnet will have magnetic domains distributed in a way as to minimize energy, as described previously. As we apply the magnetic field, the magnetic domain in the direction of the field will grow while the opposite one will shrink. This happens due to the reorientation of the magnetic dipoles in the direction of the field. This reorientation is caused by domain walls and can be thought of as domain wall movement. As the domain wall move across the material they reorient the magnetic dipoles.

Domain wall movement is the primary method of material magnetization, with domain rotation becoming dominant only when single domain is formed. The domain wall motion can however be hindered, as any inclusions will serve as a pinning center for the domain wall. These inclusions can be defects, vacancies, particles, surface roughness and even residual microstress [1, 2]. How easily a domain wall moves through a material will define its coercivity and in fact, any deviation from a perfect single crystal will act to increase it. Coercivity is defined as the magnetic field required to reduce the magnetization of previously saturated material back to zero.
Figure 2-5: Schematic of change in the domain structure during magnetization.
2.1.8. Antiferromagnetism

As the name suggests, adjacent magnetic moments in antiferromagnetic materials are aligned opposite to each other so as to completely cancel each other out. This can be viewed as two sublattices consisting of magnetic moments which have same magnitude but opposite orientation [1]. The response of antiferromagnetic materials in an applied magnetic field is similar to that of a paramagnet and it too becomes paramagnetic above a certain temperature, similar to a ferromagnet. The Curie temperature equivalent for an antiferromagnet is called Néel temperature [1-3].

2.1.9. Ferrimagnetism

A much more interesting class of materials are ferrimagnets. Looking at the arrangement of magnetic moments, ferrimagnets are very similar to antiferromagnets in that the adjacent moments are aligned opposite to each other. Unlike antiferromagnets, in ferrimagnets the two sublattices do not completely cancel each other out since the moments of the oppositely oriented sublattices are not same in magnitude (figure 2-6d). This results in the ferrimagnet having some residual net magnetization. As a consequence, a ferrimagnet behaves very similarly to a ferromagnet when placed in a magnet field. It will have saturation and remnant magnetization and it will trace out a hysteresis loop when cycled through a changing magnetic field. In addition, it also has a Curie temperature defining its thermal operational range [1, 2].

The key advantage of ferrimagnets over ferromagnets when it comes to device application is in their high electrical resistivity [1, 2, 11, 12]. Most ferromagnets are metals
and thus conductive, while ferrimagnets are oxides and behave as isolators. This combination of magnetism and electrical resistivity is crucial in applications where electrical conductivity would be detrimental [1].

Figure 2-6: Ordering of the elementary magnetic moments in (a) paramagnetic, (b) antiferromagnetic, (c) ferromagnetic and (d) ferrimagnetic materials.
2.2. Ferrites

Technologically most important class of ferrimagnets are transition metal oxides known as ferrites. Due to their high electrical resistivity they are used in applications where electrical conductivity would be detrimental. Most notably, high frequency applications where the alternating field induces eddy currents in conductive materials [13].

Cubic ferrites, a common group of ferrites, have a general formula XO·Fe2O3, where X is a divalent metal ion, such as Mn, Ni, Fe, Co and Mg [1-3]. Aside from cobalt ferrite, all other cubic ferrites are magnetically soft. Cubic ferrites have a spinel structure, named so after the mineral spinel (MgO·Al2O3). Large oxygen ions are close packed in a face-centered cubic arrangement, and the much smaller metal ions are occupying the spaces between. These spaces can be tetrahedral (A site) or octahedral (B site). However, only 1/8 of tetrahedral and ½ of octahedral sites are occupied. This nomenclature comes from the shape of the oxygen ions surrounding the site [1-3].

In ferrites with normal spinel structure, the divalent X⁺ ions are all on A sites and the Fe₃⁺ ions are all on B sites. Examples are ZnO·Fe2O3 and CdO·Fe2O3. [1-3].

The other possible type of structure of ferrites is an inverse spinel structure. In an inverse spinel structure all the divalent X⁺ ions move from A site to B site and the trivalent Fe₃⁺ ions are evenly divided between the A and B sites. Examples of such ferrites are NiO·Fe2O3, CoO·Fe2O3 and FeO·Fe2O3 [1-3]. However, these two types of structures should however be treated as idealized cases as most ferrites are a combination of both structures [1].
In both of these structures though, the trivalent Fe$_3^+$ ions are aligned antiparallel, canceling each other out. The divalent X$^+$ ions however, have their moments aligned parallel and they give the total moment of the material. The saturation magnetization is then just a product of the net spin magnetic moment of each divalent cation and their concentration [1, 2]. Values of calculated and measured moment per divalent ion for some common cubic ferrites are given in Table I. We see that the theoretically predicted values are very close to the experimentally determined ones. The small differences come from the fact that these simple calculations do not take into account that most ferrites diverge from a pure normal or inverse spinel structure.

In addition, ferrites can be prepared with two or more different divalent ions such as (Ni,Zn)O·Fe$_2$O$_3$. This can improve properties, and in fact, most of the commercially used ferrites are mixed ferrites [1-3].
Table 2-1: Theoretical and experimental values of magnetic moment per ion for some common ferrites [1-3].

<table>
<thead>
<tr>
<th>µH</th>
<th>Ferrite</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
<th>Zn</th>
<th>Mn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td></td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>0</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Measured</td>
<td></td>
<td>2.3</td>
<td>3.7</td>
<td>4.1</td>
<td>0</td>
<td>4.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Cubic ferrites are magnetically soft (sans cobalt) and thus easily magnetized and demagnetized. This, in combination with their high permeability, saturation magnetization and electrical resistivity, makes them ideal for high frequency applications [1-3]. One example would be inductor coil cores where their high permeability concentrates the magnetic flux density inside the coil and enhances the inductance, while their high resistivity reduces formation of eddy currents [14]. Basic material properties for some common ferrites are shown in Table 2-2.

Table 2-2: Material properties of some common ferrites [15].

<table>
<thead>
<tr>
<th>Material</th>
<th>a [nm]</th>
<th>ρ [g/cm³]</th>
<th>Mₛ [emu/cm³]</th>
<th>T_C [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO·Fe₂O₃</td>
<td>0.834</td>
<td>5.38</td>
<td>270</td>
<td>858</td>
</tr>
<tr>
<td>FeO·Fe₂O₃</td>
<td>0.839</td>
<td>5.24</td>
<td>480</td>
<td>858</td>
</tr>
<tr>
<td>CoO·Fe₂O₃</td>
<td>0.838</td>
<td>5.29</td>
<td>425</td>
<td>793</td>
</tr>
<tr>
<td>MnO·Fe₂O₃</td>
<td>0.85</td>
<td>5</td>
<td>400</td>
<td>573</td>
</tr>
<tr>
<td>MgO·Fe₂O₃</td>
<td>0.836</td>
<td>4.52</td>
<td>120</td>
<td>713</td>
</tr>
<tr>
<td>Fe</td>
<td>0.287</td>
<td>7.87</td>
<td>1714</td>
<td>1043</td>
</tr>
</tbody>
</table>
2.2.1. Nickel ferrite (NiFe$_2$O$_4$)

One of the most technologically important ferrites is nickel ferrite (NFO) in which Ni is the divalent metal ion [11, 16]. Nickel ferrite has an inverse spinel structure with Ni$^{2+}$ ions occupying octahedral sites and Fe$^{3+}$ ions evenly distributed between octahedral and tetrahedral sites. NFO is a soft ferrimagnet with a high Curie temperature, high electrical resistivity and large magnetostriction [1-3, 17, 18]. As such, it is suitable for a number of applications, including high frequency and microwave devices [13], spintronics [11, 19], sensors and antennas [20], as well as memory [21, 22] and magnetoelectric composites [20, 23, 24].

Based on the specific application, different values of saturation magnetization, magnetic response (field required to reach saturation magnetization), remnant magnetization, coercivity or magnetostriction may be required. The magnetic properties of a material are affected by number of parameters.

As most of device applications of soft magnetic ferrites (such as NFO) are high frequency devices [1-3], it is desirable to have high saturation magnetization with a large remnance, high permeability and low coercivity. If the intent is to use the ferrite as a magnetostrictive phase in a magnetoelectric composite, large magnetostriction is also desirable [1-3]. Since a lot of ferrites are polycrystalline, the degree of grain orientation (texture) becomes a significant parameter. As we increase the degree of grain orientation along the easy axis direction of a material, we lower the coercivity, increase the saturation magnetization and the
remnance, as well as improve the magnetic response. As a consequence we also improve the
magnetostrictive properties [1-3].

Similar to most other spinel cubic ferrites, the easy axis direction of NFO is in the
<111> direction, and the hard axis is in the <100> direction.

2.3. Magnetic anisotropy

Magnetic properties (shape of the hysteresis curve) are strongly dependent on the
magnetic anisotropy. Magnetic anisotropy refers to the dependency of the magnetic
properties on the direction in which they are measured. This anisotropy can be intrinsic, due
to chemistry of shape, or can be induced by processing parameters. There are many types of
anisotropies, most important of which we will consider in the following subchapters.

2.3.1. Magnetocrystalline anisotropy

Magnetocrystalline (or crystal) anisotropy refers to the tendency of magnetization to
align along a specific crystallographic direction. This is referred to as the magnetic easy axis
of a material. It is also the direction in which a material is easiest to magnetize (requires the
least amount of magnetic field to reach saturation) [1-3]. In addition, a material also has a
hard axis, which is the direction in which the field required to reach saturation is maximal. In
face-centered cubic crystals, such as NiFe$_2$O$_4$, the easy axis direction is <111>, while the
hard axis direction is <100>. Body-center cubic crystals however, such as CoFe$_2$O$_4$, have
inversed magnetization direction where easy axis is in <100> and hard is in <111> direction
Figure 2-8 shows a schematic of the magnetization curves for NFO along different crystallographic directions.

While the same value of saturation magnetization can be reached by magnetization in any direction, for most application it is desirable to do so using the smallest magnetic field possible and so the easy axis is the preferable magnetization direction.

Figure 2-8: Magnetization curves along different crystallographic direction for NiFe$_2$O$_4$ [1].
The origin of the magnetocrystalline anisotropy is related to the energy required to rotate the spin system of a domain away from the easy axis direction. In order to do so, we need to overcome the spin-orbit coupling [1-4, 25]. When we apply the magnetic field the spins want to orient in the direction of the field. This requires the orbit to reorient as well, however the orbit is strongly coupled to the lattice which results in the resistance to the reorientation. In figure 2-9 we see a schematic of reorientation of orbitals due to the applied magnetic field. As we reorient the spins away from the easy axis direction, the orbitals no longer have an energetically favorable overlap [25].

Figure 2-9: Interaction between spin and orbit degrees of freedom.
This resistance is usually weak in most materials due to weak spin-orbit coupling. In some materials however, this coupling is strong and can be used where permanent magnetism is desirable. Examples are rare-earth materials [1-3].

The work required by the magnetic field to rotate the magnetization away from the easy axis direction is called crystal anisotropy energy $E$, and is expressed as a series expansion of cosines of saturation magnetization relative to the crystal axes [1-3, 25]:

$$E = K_0 + K_1\left(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2\right) + K_2(\alpha_1^2\alpha_2^2\alpha_3^2) + \cdots$$ (2-4)

where $K_n$ are the magnetocrystalline anisotropy constants. For most practical applications higher order terms are too small to be important, and even $K_2$ can usually be neglected. $K_0$ is independent of angle and can be ignored as we are only interested in the difference in energy. This means that the easy axis direction is dictated by $K_1$. For positive $K_1$ this direction is $<100>$ while for negative $K_1$ it is $<111>$. The values of anisotropy constants are dependent on the temperature and reduce to zero near Curie temperature making the material paramagnetic. The values of anisotropy constants for some common ferrites are given in table 2-3.
Table 2-3: Anisotropy constants for some common ferrites [1-3].

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>$K_1$ [erg/cm$^3$]</th>
<th>$K_2$ [erg/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO·Fe$_2$O$_3$</td>
<td>Cubic</td>
<td>-0.7</td>
<td>/</td>
</tr>
<tr>
<td>FeO·Fe$_2$O$_3$</td>
<td>Cubic</td>
<td>-1.1</td>
<td>/</td>
</tr>
<tr>
<td>CoO·Fe$_2$O$_3$</td>
<td>Cubic</td>
<td>20</td>
<td>/</td>
</tr>
<tr>
<td>MnO·Fe$_2$O$_3$</td>
<td>Cubic</td>
<td>-0.3</td>
<td>/</td>
</tr>
<tr>
<td>MgO·Fe$_2$O$_3$</td>
<td>Cubic</td>
<td>-0.25</td>
<td>/</td>
</tr>
<tr>
<td>BaO·6Fe$_2$O$_3$</td>
<td>Hexagonal</td>
<td>33</td>
<td>/</td>
</tr>
<tr>
<td>Fe</td>
<td>Cubic</td>
<td>4.8</td>
<td>±0.5</td>
</tr>
</tbody>
</table>
2.3.2. **Shape anisotropy**

The origin of shape anisotropy lies in the demagnetizing field acting inside a material. If a polycrystalline material has no preferred orientation of the grains the net crystalline anisotropy will disappear. However, that doesn’t necessarily mean the sample will have the same magnetic response to the applied field in all direction. In fact this is only true for perfectly spherical samples. If the sample shape deviates from a sphere once again there will be a preferred direction of magnetization. In this case the easy axis of magnetization will lie along the longest axis. This phenomenon is known as shape anisotropy [1-3]. An example of how the shape anisotropy constant changes as we move further away from a spherical shape is given in figure 2-10.

From figure 2-10 we see that the anisotropy constant increases as we increase the ratio of the two axes i.e. we deviate more from a perfect sphere. This increase in anisotropy constant grows exponentially and can have enormous consequences on the magnetic response of a material [1-3].
Figure 2-10: Shape anisotropy constant in a prolate spheroid of cobalt [2].
2.3.3. Demagnetizing field

The demagnetizing field arises when we have shape anisotropy and is best explained by looking at the magnetic field lines. A schematic of magnetic field lines in and around a material are given in figure 2-11. When we place a material inside a magnetic field, the magnetic moments will reorient in the direction of the field so that we have a north and a south pole. The magnetic field lines originate at the north pole and sink at the south pole. Since the magnetic field lines have to form a closed loop, the direction of the magnetic field lines outside of the material will be in the opposite direction from the lines inside of a material. As a consequence the material itself forms a field opposite in the direction to the applied field. This internally created field demagnetizes the magnet and is called the demagnetizing field $H_d$ [1-3].

Figure 2-11: Magnetic field lines in and around a bar magnet.
The demagnetizing field is created by the magnetization of a material and as such is directly proportional and opposite in the direction to the magnetization [1-3]:

\[ H_d = N * M \]  \hspace{1cm} (2-5)

where N is the demagnetizing factor determined by the shape of the sample. Demagnetizing factors for some common sample shapes are given in table 2-4.

<table>
<thead>
<tr>
<th>Shape</th>
<th>Toroid</th>
<th>Cube</th>
<th>Sphere</th>
<th>Cylinder (l/d=20)</th>
<th>Cylinder (l/d=8)</th>
<th>Cylinder (l/d=1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demagnetization factor ( N/4\pi )</td>
<td>0</td>
<td>1/3</td>
<td>1/3</td>
<td>0.00617</td>
<td>0.02</td>
<td>0.27</td>
</tr>
</tbody>
</table>

From table 2-4 we can see that the demagnetization factor grows proportionally to the shape anisotropy of the sample, as expected.

The actual field acting on the material (i.e. the effective field magnetic dipoles in the material experience) is then the applied field reduced by the demagnetizing field and given by:

\[ H = H_{applied} - H_d \]  \hspace{1cm} (2-6)

For a long axis, where N is small, the field can be approximated as:

\[ H_{effective} = H_{applied} - H_d \approx H_{applied} \]  \hspace{1cm} (2-7)

and we can ignore the demagnetization field.

Along the short axis however, where N is large:

\[ H_{effective} = H_{applied} - H_d \ll H_{applied} \]  \hspace{1cm} (2-8)

demagnetization field will significantly affect the material response and has to be taken into account [1-3].
Sample geometry plays a crucial role for large sample anisotropies, where \( N \) is large and the field required to magnetize the sample can be huge.

### 2.3.4. Magnetostriction

When a ferromagnetic material is placed in a magnetic field, the reorientation of magnetic moments will cause a length change of a material. This change of length is called magnetostriction and calculated simply as:

\[
\lambda = \frac{\Delta l}{l} \tag{2-9}
\]

where \( \Delta l \) is change in length, and \( l \) is the original length [1-3]. Magnetostriction is usually calculated at magnetostriction and is denoted as \( \lambda_s \). This length change i.e. magnetostriction can be positive (as in iron) meaning the material elongates in the direction of applied field, or negative (as in nickel) if it shrinks. For most materials the change in length is very small, and so the saturation magnetostriction is on the order of \( \lambda_s \sim 10^{-5} \). It is nevertheless sufficient to influence domain structure and magnetic properties [1-3].

The origin of magnetostriction lies in spin-orbit coupling which is also responsible for magnetocrystalline anisotropy. A schematic picture of why magnetostriction occurs is given in figure 2-12.

As the electron clouds around a nuclei are forced to rotate under the influence of a magnetic field, the length of the material will change. This rotation will also mean that a material will elongate in some directions and shrink in others [1-3, 25].
Magnetostrictive materials can be used independently for applications such as sonars, ultrasonic sound generators and small displacement positioners, or in combination with other materials, such as piezoelectrics, for magnetoelectric composites.

Figure 2-12: Mechanism of magnetostriction.
2.3.5. Magnetoelectric composites

Magnetoelectric materials have generated much interest due to their ability to control and detect magnetic field with electronic devices and vice-versa [20, 23]. While the first discovery was in single phase magnetoelectrics i.e. a material that exhibits piezoelectricity and magnetostriction simultaneously, the effect is small and rare due to the mutually exclusive origins of the two phenomena [23, 27-29]. Much greater promise and better results was demonstrated in multiferroic materials where we join a ferroelectric with a ferromagnet [20, 23, 24, 30]. These materials can be joined together in several different configurations as shown in figure 2-13.

While the 0-3 connectivity is predicted to give best magnetoelectric response, preparation of such composites remains challenging. For that reason, 2-2 layered composites are more commonly used [2, 20, 23, 27, 31]. In 2-2 laminate structure, a piezoelectric and a magnetostrictive material are arranged in alternating stacks to maximize the coupling [23].

![Figure 2-13: Magnetoelectric composite for (a) 0-3, (b) 2-2 and (c) 1-3 connectivity.](image)
2.4. Thin film growth and patterning

While ferrites are traditionally manufactured using standard ceramic techniques, such as mixing together powders of NiO and Fe$_2$O$_3$ and heating them [1-3], many other approaches on synthesizing textured NFO thin films have recently been reported. Among these are pulsed laser deposition [16, 32-38], sputtering [39, 40], chemical vapor deposition [41-43] and others [44-46]. These methods require expensive equipment and processing materials; are time consuming and usually are not scalable. Recently, a chemical solution deposition approach was used to synthesize highly textured NFO thin films [47, 48]. This method is cost effective, quick and easily scalable to produce larger films. In addition, it was shown that the degree of texture was controllable through careful selection of the substrate to which the NFO was deposited [49]. In contrast, a chemical solution deposition (sol-gel) method has been reported to give biaxial texture at fraction of the cost [47]. Additional advantage of the sol-gel method lies in its compatibility with various soft lithography techniques [50]. Among these, nanoimprint lithography (NIL) provides a low-cost, high-throughput method for nanostructure fabrication in a precise, repeatable and scalable way [51-54]. Despite the numerous advantages of combining NIL with sol-gel deposition, the field of NIL has focused mostly on semiconductor [19, 55-58] and photonic applications [59-61]; minimal work has been reported on the patterning of magnetic materials via NIL. The few examples have reported fabrication of quantum dot arrays for high density magnetic recording with varying success [14, 62].
2.4.1. Chemical solution deposition

A highly flexible method for preparation of metal-oxide thin films is the chemical solution deposition (CSD). A CSD process starts with preparation of a suitable solution. Depending on the procedures used during solution preparation, the gelatin behavior of the deposited films, and reactions taking place during thermal treatment, the chemical routes for solution preparation can be roughly grouped into three main categories - classical sol-gel, metal organic decomposition and hybrid routes [63, 64].

A common method of solution preparation for CSD is sol-gel due to its relative simplicity, low cost and broad application. It can be used to manufacture thin film and fibers, protective coatings, nanoscale powders and dense ceramics [64].

Following preparation, the solution is dispersed (coated) onto the substrate. Common coating techniques include spin coating, spray coating and dip coating.

2.4.2. Spin coating of sol-gel solutions

Spin coating is a common technique for manufacturing thin films and protective coatings on flat substrates. A small amount of coating solution is placed on the substrate and then rotated at high speeds. The centrifugal force spreads the solution across the substrate in a thin layer. The excess solution is ejected from the substrate. This acts to reduce the thickness of this film until a balance is established between the centrifugal force and the force of viscosity. The final thickness of the spin coated films depends on the coating parameters and the viscosity of the solution [65, 66]. Using this technique, film thicknesses below 10 nm and above 1 μm have been demonstrated.
This wet coat of solution then dries forming a gel, which is transformed into an amorphous oxide film via thermal removal of organic species. Finally, the film is crystallized by heat treatment. Depending on the specific requirements this process can be repeat multiple times to achieve thicker films.

2.4.3. Nanoimprint lithography

Nanoimprint lithography (NIL) is a low cost, high throughput and high resolution method to create nanoscale structures [50-54]. While there are many variations such as thermal wafer scale NIL [67], UV wafer scale NIL [68, 69], UV step and repeat NIL [70, 71] and Roll-to-Roll printing [72-74], all NIL techniques have the same basic principle. In all cases, a stamp is created which is then pressed into a softer material or a solution, causing it to deform, taking the shape of the stamp [50, 53, 75, 76]. In addition, heat treatment is used to harden imprinted material, before removing the stamp. Since many of the materials are too hard to be imprinted directly, a layer of softer material is usually spin coated over a crystallized film of interest. After the soft layer has been imprinted, the pattern is transferred into the thin film via chemical or plasma etching. After the pattern has been engraved on the film of interest, the remaining soft layer is removed.
2.4.4. Interference lithography

Interference lithography is based on the fact that two coherent light beams will create an interference pattern which can then be recorded in the photoresist [77, 78]. While the precision of the imprinted pattern degrades with lowering the feature size, good patterns on the order of several tens of nanometers have been demonstrated [78, 79]. Lloyd’s mirror interference lithography (LIL) is an attractive version of interference lithography requiring minimal setup to manufacture periodic nanostructures [80-86]. It offers an advantage over traditional interference lithography by creating a virtual light source using a mirror, allowing the use of only one light source. In addition, it allows for passive disturbance rejection and easy period changes by adjusting the angle of the incident light. The principle of operation of LIL is given in figure 2-14. The incoming laser beam is split and simultaneously directed at the sample and the mirror. The beams will meet and create interference pattern on the sample.

The period of the interference pattern will depend on the wavelength of the light source $\lambda$, refractive index of the medium $n$ and the angle $\theta$ as:

$$T = \frac{\lambda}{2n \sin \theta}$$

(2-10)

The illumination time required to record the pattern in the photoresist is given by:

$$t = \frac{E}{P}$$

(2-11)

where $E$ is the required dose and $P$ is the power of the light source.
Figure 2-14: Schematic of Lloyd’s mirror interference lithography.
2.5. **Microscopy**

In order to view objects too small for an unaided eye, microscopes are used. Microscopes can be roughly divided into optical, electron and scanning probe [87-90]. Optical and electron microscopes use diffraction, reflection and refraction of light or electrons to obtain an image of the sample while the scanning probe microscope scans the sample with a probe and makes use of probes-sample interaction to obtain the image. To gain a more complete information about the sample of interest usually two or more microscopy method are combined.

2.5.1. **Scanning electron microscopy**

In a scanning electron microscope (SEM), the image is obtained by focusing a beam of electrons onto a sample. The typical SEM consists of an electron gun, condenser lens, objective lens, objective aperture, stigmator coils and sample chamber [91-93]. A schematic of an SEM is given in figure 2-15.

Starting point of an SEM is the electron gun where electrons are generated. There are two ways of generating electrons i.e. two types of electron guns – thermionic and field emission.

In a thermionic SEM the electrons are generated by passing current through a filament (usually tungsten). As the current passes it heats up the filament. This increase in thermal energy helps electrons overcome the work function of the filament, releasing the electrons.
In field emission SEM, the filament is sharpened into a needle. This amplifies the electric field, narrowing the potential energy barrier at the tip and allowing electrons to tunnel through.

To reduce the initial probe spot i.e. the beam of electrons coming from the electron gun a condenser lens is used. Modern SEMs will usually have several condenser lenses to increase the resolution. As we decrease the electron beam (spot size) the image resolution increases.

Finally, to form a probe an objective lens is used. Objective lens focuses the beam of electrons into a small spot on the sample. Both objective and condenser lenses use electromagnetic field to control the electron beam. Objective aperture serves to remove the off-axis electrons from the beam which will generally increase resolution, while stigmator coils are used to correct image astigmatism.

The detectors are placed inside the SEM sample chamber, which is operated under vacuum. While field emission SEMs have more resolution they are also more complicated and require ultra-high vacuum making them significantly more expensive. By contrast, thermionic SEMs are cheaper, require less vacuum and are usually sufficient for most practical imaging.

The image in an SEM is formed by scanning the beam of electrons over the region of interest on the sample. After hitting the sample the electrons are scattered and the information is collected in the detectors. The interaction of electrons with the sample is complex and can give different kinds of information about the sample based on the electrons we detect.
Most commonly however, we are interested in the secondary electrons. These electrons have low energy (usually 3-5 eV) and scatter inelastically upon hitting the sample. They give us information about the topography of the sample surface i.e. the image of the sample.

Figure 2-15: Principle of SEM operation.
2.5.2. Focused ion beam

The principal of operation for focused ion beam (FIB) is very similar to that of the SEM. In FIB however, in addition to an electron source there is also an ion source. Most commonly the ion source will be a liquid-metal ion such as gallium, gold and iridium [94]. While the ions can be used to image the sample, they are primarily used to sputter the sample surface. When a heavy ion is accelerated in a high electric field and impacted on the sample it will expel some of the material from the surface. By controlling the energy of the ions and the location at which it hits the surface, we can mill the surface with high precision. One of the prevalent practical uses of this is sample preparation for transmission electron microscope where the required sample thickness is generally less than 100 nm.

2.5.3. Transmission electron microscopy

The principle of operation of a transmission electron microscope (TEM) is very similar to that of a scanning electron microscope. The key difference is that the electrons are detected after passing through an ultra-thin specimen. This requires the sample to be thin enough to allow electron passage. This thickness is generally less than 100 nm. Since the image quality is affected by the sample thickness, for atomic level resolution sample thicknesses of less than 30 nm are required [95]. This makes TEM imaging substantially more difficult than SEM and puts some limitations on the applicability of the method. The benefit is that a TEM will generally have higher resolution than an SEM and will not have some of the problems with image collecting.
2.5.4. Atomic force microscopy

One of the most versatile and commonly used tools for high resolution surface imaging is the atomic force microscopy (AFM) [96, 97]. It falls under the category of scanning probe microscopy as it uses probes to obtain an image.

The probe consists of a cantilever with a very sharp tip. When the tip is brought into proximity of a sample, the tip and the sample will interact with some force. As the tip is scanned across the sample, this force will cause the cantilever to deflect according to the sample surface morphology. To record this change, a laser is used. A laser beam is reflected off the back of the cantilever and into the detector. As the cantilever is deflected, the laser beams will hit a detector at different positions. This change is then recorded and the image is formed. For precise movement of the sample a piezoelectric scanner is used [98]. The principle of AFM operation is shown in figure 2-16.

An AFM can be operated in two basic modes – contact and tapping. In contact mode the tip is in direct contact with the surface of the sample and the image is formed by continuous deflection of the cantilever as it is scanned across the sample surface [99].

In tapping mode the cantilever is held at a certain height above the sample and oscillated at a specific frequency by a small piezoelectric element mounted in the AFM tip holder. The image is then produced by imaging the force of intermittent contacts of the tip with the sample surface. There are a number of advantages to using taping mode and is commonly used whenever possible.

Based on the sample and the appropriate probe selection, the dominant force of interaction can be Van der Waals, magnetic, electric [100].
Figure 2-16: Principle of operation of atomic force microscope.
2.5.5. Magnetic force microscopy

Magnetic force microscopy (MFM) is a type of AFM where a magnetic probe is used to image the sample. By using a magnetic probe we are able to characterize the magnetic domains of the sample [100]. MFM is done in tapping mode using two-pass technique shown in figure 2-17. In the first pass, the tip is brought into close proximity to the sample and the surface topography is imaged. Then, the tip is lifted away from the sample and the same area is scanned again. This time the magnetic interaction between the tip and the sample is measured. The tip is kept at a constant distance from the sample using the stored topography image. This insures the Van der Waals force is eliminated from the measurements and we have an accurate ready of the domain size and distribution. While MFM is a great method to accurately determine the domain structure of a magnetic material, in practice there are a number of limitations to consider and special care has to be taken when interpreting the results. Some of the considerations include the tip shape, coating, magnetization direction and distance from the sample. In addition, the tip and sample can interact, reversing the magnetization direction i.e. rewriting the sample. These and other issues must be taken into account. This puts severe constraints on the type of samples and scanning conditions that can be used with MFM.
Figure 2-17: Two-pass measuring technique of magnetic force microscopy.
2.6. Crystallography

To determine the atomistic and molecular structure of a solid, crystallography techniques such as X-ray diffraction can be used. By measuring the angles and intensities of the signal diffracted from the crystal lattice three-dimensional picture of the density of electrons within the crystal can be extracted. From this we can extract information on the size and position of atoms, lengths and types of chemical bonds and atomic scale differences between materials [101, 102].

2.6.1. X-ray diffraction

An electromagnetic wave gives us different information about a material depending on the properties of the material and the wave. If this electromagnetic wave has a wavelength on the order of atomic spacing in the solid (few Å) it will diffract, giving us information about atomistic and crystal structure of a material [101-103]. Electromagnetic radiation a with wavelength between 0.01 and 10 nm is called X-radiation (or X-ray).

A schematic of the principle of diffraction is given in figure 2-18.

A beam of parallel, monochromatic and coherent X-rays is incident on two planes of a crystalline sample separated a distance d apart. A constructive interference (or diffraction) will occur when the beam satisfies the condition given by Bragg’s law [101, 102, 104, 105]:

\[ n\lambda = 2d \sin \theta \]  

(2-12)

where n is the order of reflection, \( \lambda \) is the wavelength of the incident beam and \( \theta \) is the angle between incident beam and the plane of the crystal.
The distance $d$ between two adjacent parallel planes is a function of Miller indices $(h,k,l)$ and lattice parameter. For a crystal structure with cubic symmetry it is given by:

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad (2-13)$$

where $a$ is the lattice parameter (edge length of a unit cell).

Figure 2-18: Principle of X-ray diffraction.
To determine at which angle diffraction occurs we use a diffractometer shown in figure 2-19. A beam is generated at point T and detected at point C. The sample is mounted at point S. The sample, X-ray generator and the detector are all coplanar. The detector is mounted on a movable carriage. The sample and detector are coupled in such a way that an angle change of $\theta$ of the sample is accompanied by an angle $2\theta$ of the detector with respect to the incident beam of X-rays. This insures that incident and reflection angles are maintained equal to one another. As the detector moves at constant angular velocity, the diffracted beam intensity is recorded as a function of $2\theta$, which is called the diffraction angle [104].

For a polycrystalline material with a completely random orientation of the grains, the X-rays will be diffracted equally in all directions. If however, there is some orientation of the grains (texture) along a certain crystallographic plane, it will be show up as a peak of higher intensity at an angle corresponding to that specific plane [101, 104, 105].

2.6.2. φ -scan

φ -scan is an X-ray crystallography technique where the intensity of a single peak is recorded while rotating the sample. It allows us to get information about the orientation of a specific set of diffraction planes in our material. We can probe the rotational symmetry and get information on texture and anisotropic strain/stress. In addition, we can distinguish overlapping film and substrate peaks [101, 102].
Figure 2-19: Schematic diagram of X-ray diffraction [104].
2.7. Magnetization measurements

While there are several methods to measure the magnetic behavior of a material a superconducting quantum interference device is the most common due to its ability to measure weak magnetic signals with high precision.

2.7.1. Superconducting quantum interference device

To measure extremely subtle magnetic fields, a superconducting quantum interference device (SQUID) is used. With careful experiment preparation and noise reduction, signals as low as $10^{-14}$ T have been measured [1-3, 106]. This also means that the SQUID is an extremely precise tool for measuring magnetic fields. The great sensitivity of a SQUID is associated with change of flux when a sample moves through superconducting magnetic coils. A measurement is performed by moving the sample through the superconducting detection coils using a vibrating sample magnetometer (VSM). This will induce a flux change in the Josephson junction, which acts as a detection coil. As the Josephson junction is under constant current bias, an induced flux change will induce a change of the persistent current proportional to the change in flux. Due to the quantization of flux, this relationship is very linear, allowing for great accuracy of the measurement [1-3]. Most commercially available SQUIDs have a temperature range between 500 mK and 400 K, and can generate fields of up to 7 Tesla.
2.7.2. Josephson junction

Josephson junction consists of two superconductors separated by a thin insulator. In this setup, quantum mechanical tunneling of Cooper pairs can occur without breaking up the pair. However, the current in Josephson junctions is changed by the presence of a magnetic field, increasing in one and reducing in the other. The SQUID uses this current change to detect magnetic fields [1-3]. A schematic of a Josephson junction is given in figure 2-20.

![Figure 2-20: Schematic of Josephson junction.](image)
2.7.3. Vibrating sample magnetometer

To induce a flux change in the detection coils, a sample is vibrated near it [1, 107]. This is achieved by attaching a sample to a long nonmagnetic rod connected to a mechanical vibrator. By moving the sample we effectively change the magnetic field which induces a flux change in the detector coils. A schematic of the VSM is given in figure 2-21.

Figure 2-21: Schematic of vibrating sample magnetometer.
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CHAPTER 3

Research methodology

3.1. Sample preparation

To grow and pattern NiFe$_2$O$_4$ thin films several preparation steps were required. NiFe$_2$O$_4$ solution with appropriate molarity and purity had to be prepared and the processing conditions had to be optimized. The patterning procedure had to be adapted as well. In addition, appropriate masters from which the pattern is to be transferred had to be made.

3.1.1. Preparation of NiFe$_2$O$_4$ sol-gel solution

All samples used in this research were prepared with a 0.2 molar NiFe$_2$O$_4$ solution. The solution was made using a recipe developed previously within the group [1, 2]. While the basic procedure was the same for all solutions made, the processing parameters have been slightly altered during the course of research to improve the quality as well as simplify the preparation of the solution. Initially, the solution preparation was done under nitrogen atmosphere and solution exposed to air only after the procedure was complete (figure 3-1(a)) [3]. This was found to be unnecessary as good quality solution was also produced in ambient conditions (figure 3-1(b)) [4]. Lastly, a purification step was added to remove precipitates from the solution. Purification was done using a high speed centrifuge spinning at 12000 RPM. The solution was initially centrifuged for 20 minutes, transferred to a clean vial, and
then centrifuged for additional 5 minutes. This has shown to give a highly pure good quality NFO solution.

![Figure 3-1: NiFe$_2$O$_4$ solution preparation procedure (a) under nitrogen atmosphere and (b) in air.](image)

Flowchart of the solution preparation procedure is given in figure 3-2. The solution was prepared using nickel(II) acetate tetrahydrate (C$_4$H$_6$NiO$_4$·4H$_2$O) and iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) powders from Sigma-Aldrich. To powders were dissolved in a 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH) solvent (also from Sigma-Aldrich). To prepare a 0.2 molar NiFe$_2$O$_4$ solution, 8.08 grams of iron(III) nitrate nonahydrate and 2.4884 grams of nickel(II) acetate tetrahydrate powders were mixed separately in two vials containing 20 mL of 2-methoxyethanol each. The two solutions were then stirred at 70°C for 2 hours before being mixed together for additional 15 minutes at room temperature.
Figure 3-2: NiFe$_2$O$_4$ solution preparation procedure.
3.1.2. Preparation of NiFe$_2$O$_4$ thin films

NiFe$_2$O$_4$ thin films were grown by spin coating 0.2 M NiFe$_2$O$_4$ sol-gel solution onto a sapphire substrate. The substrate used was a c-plane (0001) epi-polished sapphire (Al$_2$O$_3$) substrates from University wafer. Before film deposition the substrates was cleaned using organic solvents in sequence: methanol, acetone, isopropyl alcohol, followed by heating on a hot plate at 400°C for 60 seconds to remove organic contamination and water condensation. To create a film, NFO solution is dripped onto the substrate and spin coated using a WS-400BZ-6NPP/lite spin coater (Laurell Technologies Corp.) at 4000 RPM for 30 seconds. The film is then placed onto a hot plate (Corning PC-400D) at 400°C for 60 seconds to remove the organic species and create amorphous film. Finally the film is annealed in TF55030A-1 Lindberg/Blue M (Thermo Scientific) furnace at 750°C for 15 minutes to crystallize the film. The process can be repeated to create thicker films. This substrate, solution molarity and processing parameters were previously shown to give biaxially textured NFO thin film [5].

3.1.3. Surface patterning

To pattern the surface, a modified approach to nanoimprint lithography was used. Whereas a standard procedure consists of indirectly patterning the thin film by patterning a softer material first and then etching the pattern into the film [6], here a direct imprint method was used. In direct imprinting we imprint the film directly using a PDMS stamp. This method has shown to give as good, if not better pattern transfer as well as being simpler, quicker and less costly. A schematic of the direct imprinting procedure is shown in figure 3-
3. After the initial spin coating of the NFO thin film, a patterned polydimethylsiloxane (PDMS) stamp was pressed into the film as it was placed onto the hot plate for 60 seconds at 400°C. The stamp was then removed and patterned amorphous NFO film placed in the furnace for 15 minutes at 750°C to crystallize the film, as described previously.

Figure 3-3: Patterning procedure of NiFe$_2$O$_4$ thin films.
3.1.4. Master preparation

To prepare the masters two different methods were used. Initially, a commercially available CD was used due to its availability and cost effectiveness. A DVD was also used. Both CD and DVD have consistent periodic features over large scale which allow for easy evaluation of the pattern transfer quality. The feature size of a CD is approximately 750 nm with a 1500 nm period. The feature size of a DVD is approximately half that of a CD and has a period of 750 nm. To access the features of the CD and DVD, the top aluminum layer of a CD and DVD were removed and the patterned polycarbonate plastic was cleaned and used for patterning.

In addition, a series of pattern masters with periods ranging from 300 nm to 1300 nm were prepared via laser interference lithography [7, 8]. To prepare the masters, silicon substrates were used. After cleaning, the silicon substrates were coated with 100 nm thick layer of antireflective coating (ARC) with a refractive index of \( n = 1.646 - 0.398i \) (i-CON-16 from Brewer Science). This reduces reflection from the silicon surface giving better more precise features. A 500 nm thick layer of PFI-88A2 photoresist (Sumitomo Chemical Corp.) with a refractive index of \( n = 1.72 - 0.04i \) was then coated to record the intensity pattern. The pattern was created by illuminating the photoresist with a dose of 50 mJ using a 325 nm wavelength laser. After exposure, the photoresist was developed in N-Methyl-2-pyrrolidone for 5 minutes.

The patterned was then transferred form the photoresist into the silicon substrate using reactive ion etching (RIE). The etching was done with Alcatel AMS 100 Deep Reactive Ion Etcher at room temperature in three steps. First, the underlying ARC layer was removed
using oxygen plasma at 250 W source/75 W bias for 30 seconds. Then, the pattern was etched into the silicon substrate by alternating sulfur hexafluoride (SF₆) and octafluorocyclobutane (C₄F₈) gas exposures for 3 and 1 seconds respectively. The total etch time was 40 seconds at 1200 W source/75 W bias. Finally, oxygen plasma was used to clean any remaining photoresist and ARC layers.

To attach the samples to a bare silicon wafer for etching, samples were thermally bonded using Cool grease from AI Technology.

3.1.5. Stamp preparation

To prepare the PDMS stamp, a Sylgard-184 Silicone Elastomer Kit from Dow Corning was used. The silicone base and curing agent were mixed in a 10:1 weight ratio for several minutes before being placed in the desiccator until there was no noticeable gas bubbles in the liquid. The liquid was the poured over the pattern master and placed in the desiccator until all gas bubbles were removed to insure the liquid penetrates completely into the features of the master. The master with the liquid is then placed in the furnace for 24 hours at 70°C to insure large molecules in the liquid have sufficient time to fully crosslink [9]. This will insure the stamp will retain its chemical and mechanical integrity during imprint. After curing, the PDMS stamp is removed from the master and cut into smaller pieces for patterning. Figure 3-4 shows cured PDMS stamps on different pattern masters.
Figure 3-4: Cured PDMS stamps of (a) CD and (b) silicon masters.
3.2. **Pattern evaluation**

To evaluate the quality and precision of the NFO thin film pattern atomic force microscopy and transmission electron microscopy were used. As a rough estimate, Olympus BX51M optical microscope with an SC30 digital camera (also Olympus) was used to look at the sample. While it does not give precise information about the pattern, it can be used to check if the pattern was indeed transferred from the stamp to the film as shown in figure 3-5.

![Optical microscopy image of patterned (left) and plain (right) regions of NiFe$_2$O$_4$ thin film.](image)

Figure 3-5: Optical microscopy image of patterned (left) and plain (right) regions of NiFe$_2$O$_4$ thin film.
3.2.1. Atomic force microscopy

To evaluate the surface morphology atomic force microscopy (AFM) was used. The images were taken in tapping mode using Cypher AFM by Asylum research. The images were taken with 512 lines at scan rate of 1 Hz. The scan angle of 90 degrees was used for best image quality. An AFM image of a NFO thin film is shown in figure 3-6.

Figure 3-6: Atomic force microscopy image of a NiFe$_2$O$_4$ thin film.
3.2.2. Transmission electron microscopy

Transmission electron microscope (TEM) was used for cross-sectional analysis of the surface features as well as to investigate microstructure. For this purpose JEOL 2000FX and JEOL 2010F were used. The electron source of the JEOL 2000FX microscope is lanthanum hexaboride (LaB6) with 0.28 nm point resolution, while the JEOL 2010F uses ZrO/W (100) Schottky type field emission gun as the electron source and is able to achieve 0.19 nm point resolution. Both microscopes were operated with accelerating voltage of 200 kV.

3.2.3. Focused ion beam

FEI Quanta three-dimensional (3D) FEG focused ion beam (FIB) was used to prepare the NFO samples for TEM imaging. To prevent the charging of the highly resistive NFO film and sapphire substrate the samples were carbon coated before starting the ion milling. The samples were prepared using 30 kV accelerating voltage for both electron and ion beams. For best viewing, standard mode was used, with 0.14 nA electron beam current and 10 pA ion beam current. Initial cut was made with 15 nA ion current and gradually reduced down to 50 pA to polish. An image of the sample cut from the film and lifted out is shown if figure 3-7.
Figure 3-7: Scanning electron microscopy image of FIB cut piece of carbon coated NiFe$_2$O$_4$ thin film.
3.3. **Texture evaluation**

Crystallography methods using X-rays provide an excellent tool to measure phases present, grain growth and orientation (texture). To measure the crystallographic properties of the samples used in this research, θ-2θ and φ-scanning X-ray diffraction measurements were done.

3.3.1. **X-ray diffraction**

To evaluate the texture and the phases present, θ-2θ X-ray diffraction (XRD) was used. Scans were performed from 15° to 60° using a Cu Kα radiation source with wavelength of \( \lambda = 1.5418 \) Å. The scans were done at room temperature with step size of 0.04 degrees and dwell time of 2 seconds. Rigaku Smartlab X-ray diffractometer was used to perform the scans. The peaks were identified using Bragg’s law and correlated with the reference PDF file (JCPDS File No. 003-0875).

In addition, φ-scanning XRD was done in a Panalytical Empyrean X-ray diffractometer with a pyrolytic graphite monochromator.
3.4. Magnetization measurements

To measure the magnetic properties of the whole samples, a superconducting quantum interference device was used. The specific domain structure within the samples was measured using magnetic force microscopy.

3.4.1. Superconducting quantum interference device

To look at the magnetic hysteresis curves a superconducting quantum interference device (SQUID) with a vibrating sample magnetometer (VSM) from Quantum design was used. Samples were measured at room temperature with magnetic field up to ±7 tesla. Peak VSM amplitude of 5 mm with 2 seconds averaging time was used to improve measurement precision, especially around zero magnetization. Before measuring, the magnet was oscillated from 7 to 0 T to minimize flux pinning. The samples were measured in two configurations – with the magnetic field parallel (in-plane) and perpendicular (out-of-plane) to the plane of the film. To reduce the background noise, the samples were mounted on a special quartz sample holder supplied by quantum design. For out-of-plane measurements, two smaller pieces of quartz were attached to the quartz holder. To attach the samples, as well as the two pieces of quartz, to the sample holder, a GE7031 varnish (Lake Shore Cryotronics) was used.
Figure 3-8: SQUID quartz sample holder for (a) in-plane and (b, c) out-of-plane measurements.
3.4.2. Magnetic force microscopy

To look at the magnetic domains on the sample, magnetic force microscopy (MFM) measurements were done on a MFP-3D AFM by Asylum Research. A non-magnetic head and low moment magnetic probes (ASYMFMLM by Asylum Research) were used to eliminate some of the possible MFM measurement issues discussed previously. To insure we stayed on resonance during measurements, frequency tracking via phase-lock loop was used.

The measurements were conducted in tapping two-pass mode. Example of magnetic force microscopy scan of a CoFe$_2$O$_4$ thin film is given in figure 3-9. A topography image is taken separately (figure 3-9a) from a magnetic force image (figure 3-9b). The topography is subtracted from the magnetic force image shown. The two scans can then be overlaid in a 3D image for clearer data interpretation. In figure 3-9c we can see a typical magnetic domain distribution with domains that cover multiple grains.
Figure 3-9: (a) AFM scan of CoFe$_2$O$_4$ thin film. (b) Surface topology subtracted image of magnetic domains on the same region of the film. (c) 3D overlay of the magnetic domains on surface.
References


CHAPTER 4

Surface patterning of textured NiFe$_2$O$_4$ thin films

Textured NiFe$_2$O$_4$ thin films were deposited at room temperature by chemical solution deposition onto c-plane sapphire substrates. A nanoimprint lithography technique using a polydimethylsiloxane (PDMS) stamp was used to transfer a pattern from a master to the thin film which was subsequently annealed to crystallize the NiFe$_2$O$_4$ films. Atomic force microscopy scans and cross-sectional transmission electron microscopy were used to evaluate pattern transfer. X-ray diffraction was used to evaluate the texture and composition of the grown films. Magnetic measurements were conducted to determine and compare the magnetic properties of NiFe$_2$O$_4$ films.

4.1. Motivation

Ferrites represent an interesting material for number of applications, particularly high frequency devices and magnetoelectric composites [1-6]. For virtually all applications, we want to achieve maximum magnetization with the least amount of applied field i.e. we want a material that has a large, easily achievable magnetization. As the direction in which material is easiest to magnetize (easy axis) lies along a certain crystallographic direction, we want the material to be highly textured along that particular direction. Sol-gel represents a quick, inexpensive and scalable method which has shown to produce highly textured NiFe$_2$O$_4$
(NFO) thin films. Larger texture will result in higher saturation magnetization, lower coercivity and better magnetic response. In addition it will improve magnetostriction.

When we consider multiferroic devices, such as magnetoelectric composites, it is not enough to simply look at properties of individual materials in the composite [6, 7]. We also have to consider the interaction between the materials. For example, a magnetoelectric composite of CoFe$_2$O$_4$ (CFO) and Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT) will yield a significantly lower magnetoelectric response than a similar composite containing NFO even though CFO has significantly larger magnetostriction. This is because the coupling coefficient between CFO and PZT is significantly lower ($k < 0.1$) than between NFO and PZT which have near perfect coupling ($k \sim 1$) [8]. Consequently we are limited in materials selection and processing by the coupling constant [9]. To overcome this issue a tongue and groove type of coupling is proposed. This would allow for a mechanical stress and strain to be transmitted more directly instead of relying purely on lattice matching for coupling. In addition, it would provide more surface area between the samples. Naturally, to get the full benefit of this improved coupling we have to be able to pattern the films with high degree of precision and do so without losing texture.

To create the pattern nanoimprint lithography (NIL) was chosen. NIL is a complementary method to sol-gel and our processing requirements, in that it is quick, cheap and scalable.

In this chapter the results of investigations on surface patterning of textured single phase NFO thin film grown by sol-gel deposition are presented. Surface topology, microstructure and magnetic properties have been investigated.
4.2. Experimental details

NFO solution was prepared by mixing iron(III) nitrate nonahydrate ($\text{Fe(NO}_3\text{)}_{3}\cdot9\text{H}_2\text{O}$) and nickel(II) acetate tetrahydrate ($\text{C}_4\text{H}_6\text{NiO}_4\cdot4\text{H}_2\text{O}$) in 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$) solvent (all from Sigma-Aldrich) under inert atmosphere. The solution was stirred at 80 °C for 40 minutes and allowed to cool to room temperature.

For comparison, and evaluation of the procedure, two sample configurations, plain and patterned, were used. For the plain samples, 0.2 molar NFO solution was spin coated at 5000 RPM for 30 seconds onto c-plane (0001) sapphire substrates. Samples were then pyrolyzed at 400 °C for 60 seconds to remove the solvent. Additional furnace annealing at 750 °C for 10 minutes was used to fully crystallize the film. Previous work revealed these to be the optimal processing parameters [10].

For the pattern master, a commercially available CD was selected due to its consistent periodic features over large scale which allow for easy evaluation of the pattern transfer quality. To access the features, the top aluminum layer of the CD was removed and the CD was cleaned using isopropyl alcohol.

A polydimethylsiloxane (PDMS) stamp was prepared using a Sylgard-184 Silicone Elastomer Kit (Dow Corning) by mixing together silicone base and a curing agent in a 10:1 weight ratio. After mixing, the PDMS was poured over the CD master, degased to remove the bubbles and allowed to cure at 80 °C for 24 hours, similar to procedures found in the literature [11]. After curing, the PDMS stamp was removed from the master and cut into smaller pieces for patterning.
Contrary to standard NIL procedure, the PDMS stamp was pressed directly onto the spin coated NFO thin film with immediate pyrolysis at 400 °C for 60 seconds. After pyrolysis, the stamp was removed and the patterned film placed in the furnace to crystalize the NFO according to the aforementioned procedure. Samples made with the intermediate patterning step were designated “patterned.”

4.3. Results and discussion

Surface morphology of the patterned NFO thin films was evaluated using a Cypher atomic force microscope (AFM) by Asylum Research in tapping mode (figure 4-1). For greater clarity, the AFM scans are also presented as three dimensional topography images to emphasize the quality of the pattern transfer in figure 4-2.

An AFM scan of the CD master shows consistent features with a periodicity of ~1.5 μm (figure 4-1a). The features were copied with a high degree of precision to the PDMS stamp (figure 4-1b) and to the NFO thin films (figure 4-1(c, d)). After demolding, the PDMS stamp had closely mimicked the features of the CD master (figure 4-1b). There were no noticeable deviations from the master pattern, such as uneven, collapsed or broken features, nor were there any gas bubbles present in the PDMS stamp. Good conformity between the CD master and the PDMS stamp resulted in good patterning of the entire PDMS stamp.

AFM scans of a patterned NFO thin film in two different magnifications are shown in Figure 4-1 (c, d). The lower magnification image shows that the pattern transferred over large areas without cracking, bending, misalignment, feature collapse, air gaps or other defects, which are commonly encountered with NIL techniques [12]. At higher magnification, the
high level of precision of the pattern and the individual grains making up the nanostructures are observed. Surface morphologies and pattern transfer are easily compared by looking at the roughness analyses also seen in figure 4-1. Feature height in the image from the CD (figure 4-1a) appears smaller than in the image from the PDMS (figure 4-1b); this is due to the insufficient aspect ratio of the AFM tip. In the PDMS, the tip is able to probe deeper due to the elasticity of the PDMS stamp. The feature height reduction observed in the NFO thin film (figures 4-1c and 4-1d) is a consequence of limited amount of material due to the NFO thin film thickness after spin coating. Further analysis of figure 4-1d shows that the features in the patterned sample are made up of individual grains, indicating that there was no growth disruption of the NFO thin film by the PDMS stamp during the patterning process.
Figure 4-1: AFM images of (a) CD master, (b) PDMS stamp and (c, d) patterned NiFe$_2$O$_4$ thin films grown on (0001) sapphire substrates.
Figure 4-2: 3D topography images of (a) CD master, (b) PDMS stamp and (c, d) patterned NiFe$_2$O$_4$ thin films grown on (0001) sapphire substrates.
To show the pattern was indeed transferred with high precision over large scale, an optical microscopy image taken at 50X magnification is shown in figure 4-3. While it does not offer conclusive evidence by itself, the facts it shows a uniform pattern over the entire sample and in combination with AFM topography images taken at different locations it is reasonable to assume the deviations from the topography shown in figures 4-1 and 4-2 are small, if any.

Figure 4-3: Optical microscopy image of the patterned NiFe$_2$O$_4$ thin film grown on (0001) sapphire substrate.
Transmission electron microscopy (TEM) images of the sample cross-sections were taken using a JEOL 2010F TEM. TEM sample preparation used focused ion beam (FIB) milling on a FEI Quanta 3D FEG microscope. Before ion milling, samples were carbon coated to prevent charging.

Cross-sectional TEM images of a patterned NFO thin film (figure 4-4) show that the film is 55 nm thick with 45 nm feature height and 1.5 μm periodicity. Surface features are sharp and precise with no apparent growth disruption by the PDMS mold. These results are consistent with the AFM results. No nucleation sites form at the NFO/PDMS interface during the patterning process, which is attributed to the insufficient thermal budget at the PDMS stamp/NFO interface during patterning.

An image of the plain sample (figure 4-4c) shows individual grains growing from the substrate indicating that the nucleation proceeds via an island growth (Volmer-Weber) mechanism [13]. Low lattice mismatch and favorable substrate orientation with the c-plane (0001) sapphire substrate cause the NFO thin film to crystalize preferentially in the easy axis <111> direction [10, 14]. If the thermal budget is optimum, nucleation from the substrate will fully crystallize the film before surface nucleation begins [15]. Comparing different samples (figure 4-4(b, c)), less grain orientation is observed and there is no evidence of substrate nucleation in the patterned sample (figure 4-4b), indicating the need for different processing conditions, i.e. an optimized thermal budget, for the patterned thin films.
Figure 4-4: TEM cross-sectional images of (a, b) patterned and (c) plain NiFe$_2$O$_4$ thin film grown on a (0001) sapphire substrate.
X-ray diffraction (XRD) was used to compare the crystal structure and chemical composition of plain and patterned films. XRD θ-2θ scans were performed from 15° to 60° using Cu Kα radiation (λ=1.5418 Å) in a Smartlab Rigaku X-ray diffractometer. XRD data for both configurations shows the NFO inverse spinel structure with no impurity phases (figure 4-5). The peaks were calculated using Bragg’s law and correlated with the reference PDF file [16]. In both cases, only peaks corresponding to the {111} family of planes are observed, confirming that the films are textured. This is in accordance with similar work on biaxially textured NFO thin films [14] and consistent with other reports on epitaxial grown NFO thin films [17, 18]. Comparing the peaks present and their intensity (figure 4-5), the texture in the patterned and plain films are the same; there is no noticeable grain misorientation or new phase formation in the patterned film. This confirms that there was no significant grain growth disruption by the PDMS stamp during the patterning process nor were there new nucleation sites formed at the NFO/PDMS interface.

The first sharp substrate peak seen in figure 4-5 is due to Cu X-ray target emitting Cu fluorescence lines plus a broad background called bremsstrahlung. We normally use a graphite monochromator crystal to select Cu Kα X-rays with wavelength λ=1.5418 Å (E=8.042 keV). However, a monochromator set at an angle for a particular wavelength (energy), will also reflect x-rays with wavelength λ/2 (twice the energy or 16 keV). Since the broad bremsstrahlung background is weaker than the characteristic lines and the detector electronics mostly discriminate against 16 keV X-rays, the λ/2 peaks are very weak, but are sometimes observable for strong substrate reflections.
Figure 4-5: X-ray diffraction patterns of (a) plain and (b) patterned NiFe$_2$O$_4$ thin films.
To evaluate the chemical composition of the film and investigate the phase purity elemental maps were collected using energy dispersive spectrometry system on an aberration corrected scanning transmission microscope (FEI Titan 80-300). Nickel, iron, oxygen and aluminum maps collected for plain and patterned sample are shown in figure 4-6. There is a clear sharp interface between the films and substrate for the nickel and iron atoms indicating there is no diffusion in the substrate. Oxygen atoms are found both in the films and substrate as expected. Finally, aluminum is found only in the substrate. Precise spatial separation between the films and the substrate indicate the films to be pure single phase and sapphire to be a good substrate for producing high quality NiFe₂O₄ films as it does not interact with the films.
Figure 4-6: Elemental maps of plain (left) and patterned (right) NFO thin films. Elemental nickel (red), iron (green), oxygen (blue), aluminum (yellow) as well as the composite image are shown separately.
Magnetic properties were measured at room temperature using a Quantum Design superconducting quantum interference device (SQUID) with the magnetic field parallel to the thin film surface and magnetic field up to ±7 T. The substrate contribution to the measured magnetic data was removed and the data was normalized to the NFO thin film volume; the resulting magnetic hysteresis curves for the plain and patterned samples are shown in figure 4-7. For comparison, magnetic data for an area of film that was not patterned is also shown.

Saturation magnetization (M_s) values of plain and nonpatterned samples are similar, 120 and 118 emu/cm^3, respectively, and somewhat smaller than the results reported elsewhere [14]. This reduction is attributed to using a lower molarity solution, 0.2 M, compared to 0.5 M reported previously. The saturation magnetization of the patterned sample is reduced to 67.5 emu/cm^3, a ~44% reduction as compared to the plain samples. As the AFM, TEM and XRD measurements show no evidence of reduced crystallinity or damage in the patterned film, this is attributed to a larger surface to volume ratio. This in turn results in larger porosity and reduced long range magnetic order in the patterned film [19].

Coercivity differences are seen in the magnetic hysteresis curves shown in figure 4-7b. Comparing the coercivity (H_c) of plain and nonpatterned samples, they again have similar values, 230 Oe and 210 Oe, respectively. The patterned sample, however, shows a significantly smaller value of 25 Oe, a reduction of ~89%. Typically one expects an increase in coercivity with higher surface roughness due to changes in domain wall movement [20, 21]. Instead the opposite is observed. Here, the dominant factor is not the domain wall movement but the change in the energy minimum configuration induced by the anisotropy of surface morphology [22-24]. This causes and antiparallel orientation of domains which
reduces the coercivity by close to 90% of the initial value. This result may be of significant technological importance, as the approach may facilitate tuning of the coercivity.
Figure 4-7: Magnetization hysteresis measurements of plain, patterned and nonpatterned NiFe$_2$O$_4$ thin films. The inset shows the significant reduction in coercivity in the patterned film.
To further evaluate these results, patterned NFO film was annealed for additional 5 minutes at 750 °C, followed by 10 minute anneal at 850 °C. This should provide more than enough thermal budget to be able to confidently evaluate if coercivity reduction seen in figure 4-6 is due to lack of crystallinity in the patterned film. SQUID measurements on the additionally anneal sample (designated Patterned+RTA) is shown in figure 4-8. For comparison the magnetic measurement results of plain and patterned samples, as well as a different part of the patterned sample are also shown.

Looking at the magnetic hysteresis curves in figure 4-8 we see that the saturation magnetization of patterned sample will reach that of the plain sample with additional annealing. This reveals there to be some discrepancy between the optimal processing parameters for the plain and patterned samples even if this difference is not seen in any other characterization methods. To verify these results are not an anomaly or location specific another part of the patterned sample (Patterned-2) was measured and shows almost identical results to the originally measured patterned sample.

Higher magnification image shown in figure 4-8b confirms the coercivity reduction is indeed a physical phenomenon and not a product of insufficient film crystallization. The small differences in the coercivity values can be explained by small variations in the film, pattern and flux pinning of the SQUID magnet. These differences are negligible when compared to plain films value. Moreover, the coercivity of a thin film is expected to increase with increased annealing, contrary to what is seen. This serves as further confirmation that the coercivity reduction seen in the patterned samples is not related to any material or processing specific property.
Figure 4-8: (a) Hysteresis curve of additionally annealed NFO thin film. (b) Higher magnification image centered on the origin.
4.4. Conclusion

NFO thin films were sol-gel deposited onto a c-plane sapphire substrate and surface patterned using a modified NIL technique. The pattern from the master was transferred completely and with high degree of precision over large areas. XRD revealed similar texture between plain and patterned films. The process of patterning did not affect nucleation, grain growth or texturing due to insufficient thermal budget at the PDMS interface. Thus, we were able to grow textured films while simultaneously modifying the surface. This was confirmed with cross-section TEM. The reported patterning method represents a fast, inexpensive, easy, versatile and scalable method for large scale surface design of sol-gel derived textured thin films.

By growing textured surface patterned thin films with we can improve the coupling between materials previously thought to be incompatible, thus opening an interesting new research front. Highly precise large scale pattern was also demonstrated. This control over the pattern parameters allows for imprinting of different shapes tuned to specific requirements. The feature transfer precision shown is comparable to or better than state-of-the-art results. However, retention of crystallographic texture after patterning is better [25]. In addition, the patterning was done without using a photoresist as a mediator, thus simplifying the procedure. In addition to eliminating extra steps, this method removes some of the constraints on the imprinting process.

Magnetic measurements showed a large reduction of coercivity in patterned thin films. Additional experiments confirmed this was not a consequence of changed materials properties but directly related to the surface patterning. The coercivity reduction is attributed
to a change in the minimal energy configuration of the sample due to surface morphology anisotropy. This means the coercivity of the films can be tuned by surface modification at the nanoscale, making them particularly interesting in high frequency applications where further reduction in the power losses can be obtained.
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CHAPTER 5

Coercivity reduction in multilayered NiFe$_2$O$_4$ thin films

Here the coercivity reduction in surface patterned multilayered NiFe$_2$O$_4$ films is studied. Room temperature chemical solution deposition is used to grow multilayered NiFe$_2$O$_4$ thin films on c-plane (0001) sapphire substrates. For comparison, the films were made in “layer-by-layer” and “bulk” annealed variants. Prior to final crystallization the surface was patterned with polydimethylsiloxane stamp using a nanoimprint lithography technique. Good feature transfer to the thin film surface was confirmed both in atomic force microscopy and transmission electron microscopy images. X-ray diffraction showed both variants to produce single phase inverse spinel nickel ferrite, with increased texture in layer-by-layer samples. In both variants, magnetic measurements showed substantial reduction in coercivity in the patterned samples.

5.1. Motivation

NiFe$_2$O$_4$ (NFO), a spinel ferrite, with high electrical resistivity and favorable magnetic properties, is an interesting material for high-frequency signal and power electronic applications [1-5]. For all high frequency devices, however, lowest possible coercivity is desired. The coercivity represents losses of a magnetic material. These losses grow
proportional to frequency and become material defining property at GHz frequencies [6, 7].

So far, all attempts to lower the coercivity have focused on doing so by doping and alloying [1, 2, 8-10]. This materials constraint is further amplified by the fact that no new soft magnetic materials (sans amorphous alloys) have been developed since the 1950s [1]. The method of reducing coercivity studied in previous chapter and published in 2013 [11] offers a solution to this problem as well as offering interesting new possibilities.

Chemical solution deposition in combination with nanoimprint lithography was shown to be a low-cost, quick and scalable approach to grown textured surface patterned NFO thin films [11]. The feature transfer and texture were comparable to state-of-the-art results [12], while simultaneously eliminating extra steps. However, the coercivity reduction effect was only studied for single layered thin films. For surface patterning to become a widely used coercivity reduction method, aside from effectiveness, low cost and scalability are crucial. Study on the effect of surface patterning on the coercivity of magnetic film as the thickness is increased is needed. In addition, how the pattern transfer and texture are affected needs to be explored.

In this chapter the magnetic behavior of relatively thick (>100 nm) surface patterned multilayered NFO thin films is reported. The effect of increased film thickness on topography and crystallographic properties is also examined.
5.2. Experimental details

A 0.2 molar NiFe$_2$O$_4$ (NFO) sol-gel solution was prepared by separately mixing 8.08 grams of iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) and 2.4884 grams of nickel(II) acetate tetrahydrate (C$_4$H$_6$NiO$_4$·4H$_2$O) in two vials each containing 20 mL of 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH) solvent (all from Sigma-Aldrich). The two solutions were stirred at 70 °C for 2 hours in ambient conditions, mixed together for additional 15 minutes and allowed to cool.

All samples were made by spin coating three layers of 0.2 molar NFO solution onto a c-plane sapphire substrate at 4000 RPM for 30 seconds. After spin coating, each layer was pyrolyzed at 400 °C for 60 seconds to remove the solvent and solidify the film. The films were then crystallized at 750 °C in two different variants. For the layer-by-layer (“L”) variant, samples were pyrolyzed and annealed for 15 minutes after the deposition of each layer. For the bulk (“B”) variant, samples were annealed for 45 minutes following the deposition and pyrolysis of all three layers.

Due to its sharp periodic features over large scale, a commercially available CD was selected as the pattern master. This facilitates evaluation of the pattern transfer quality and comparison with previous work. The CD was prepared using a method described previously [11]. A polydimethylsiloxane (PDMS) stamp was used to transfer the features from the CD master to the NFO thin films. The stamp was prepared with Dow Corning Sylgard-184 Silicone Elastomer Kit by mixing the silicone base and the curing agent in a 10:1 ratio and cured for 24 hours at 70 °C [11, 13]. Finally, the cured PDMS stamp was cut into sample-size pieces. Films were then patterned after spin coating of the third and final layer of NFO.
For patterning, the PDMS stamp was pressed onto the NFO and immediately pyrolyzed at 400 °C. After 60 seconds, the stamp was removed and the surface patterned film was placed in the furnace to crystallize. For comparison to the patterned (“P”) films, unpatterned (“U”) films were also produced.

5.3. Results and discussion

Atomic force microscopy (AFM, Cypher by Asylum Research in tapping mode) was used to evaluate the surface morphology of the patterned NFO thin films; AFM images are seen in figure 5-1. Surface scans of LP and BP samples show good feature transfer from the PDMS stamp. The features were copied without noticeable deviations or gas bubbles across the whole stamp confirming good conformity between the stamp and the samples. Closer examination of the sample morphology shows smooth feature planes and sharp features with periodicity of ~1.5 μm, similar to the CD master. Roughness analysis (also in figure 5-1) reveals the feature height to be ~45 nm for both the LP and BP samples, which is significantly smaller than in the PDMS stamp (~140 nm). The feature height difference is attributed to the relatively small film thickness after annealing which limits the imprint depth. Similar feature height in patterned sample types reveals the imprint conditions to be similar. The images show that both films are crystallized after annealing; individual surface grains are observed, but neither bending, cracking nor deformation is seen. In addition, there are no signs of crystalline damage or grain growth disruption by the process of NIL imprinting, similar to results for single layers of NFO [11].
Figure 5-1: AFM images and corresponding surface roughnesses of (a) bulk patterned and (b) layer-by-layer patterned NiFe$_2$O$_4$ thin films.
Optical microscopy image, of the area separating the patterned and unpatterned part of the same film is shown in figure 5-2. Looking at the left side of the image we see the pattern was transferred over large area with high degree of precision. There is no evidence of defects or gas bubbles in the pattern. Comparing the patterned (left) and unpatterned (right) side of the image there is a clear distinction and visible separation line of the PDMS stamp.

Figure 5-2: Optical microscopy image of patterned (left) and unpatterned (right) area of NiFe$_2$O$_4$ thin film.
Figure 5-3 shows TEM (JEOL 2010F) cross-sectional images of the four sample types. Samples were carbon coated and prepared using a FEI Quanta 3D FEG focused ion beam for thinning. The images of the BU and LU films show that both variants are well crystallized with 125 nm and 113 nm film thicknesses, respectively. Similar results are found in the two patterned variants, with the BP film having a thickness of 160 nm compared to 115 nm thickness for the LP film. The larger thickness in the BP film is a result of increased porosity which is seen in the TEM image. The features are smooth, confirming that there was no growth disruption by the PDMS stamp. These results are consistent with the AFM data and show no nucleation sites formed at the PDMS/NFO interface during imprinting. This was previously attributed to the insufficient thermal budget at the interface during imprinting.

Lastly, in both patterned films, there is a clear distinction between the first two layers and the final, imprinted, layer. The final layer has larger porosity as a result of the imprinting process due to limited amount of material which must be shifted to create the features.
Figure 5-3: Cross-sectional TEM images of the (a) bulk unpatterned, (b) layer-by-layer unpatterned, (c) bulk patterned and (d) layer-by-layer patterned NiFe$_2$O$_4$ thin films grown on c-plane sapphire substrates.
θ-2θ X-ray diffraction (XRD, Smartlab Rigaku, Cu Kα radiation) was used to evaluate the crystal structure and grain orientation (texture) of the samples. The peaks were identified using Bragg’s law and reference PDF (JCPDS File No. 003-0875). XRD results in figure 5-4 show all variants produce pure phase inverse spinel NFO with preferential orientation along the <111> direction. Using the Scherrer equation [14] we estimate the grain size to be ~30 nm in all samples. Examination of the peaks and their intensities reveals all samples to be textured without noticeable grain misorientation or unwanted phases, indicating that grain nucleation and growth were not significantly affected by the imprinting process. Due to higher film thickness, the BP film shows weaker peak intensities and somewhat reduced texture. Lower film thickness allows for more uniform heating and crystallization of the sample, resulting in a larger percentage of grains nucleating at the film/substrate interface and thus following the substrate dictated growth direction [15].
Figure 5-4: 0-2θ X-ray diffraction patterns of NiFe$_2$O$_4$ thin films. The first two layers of “L” samples (not shown) have same texture as the final layer.
To further investigate the texture of the NFO films, φ-scans were done Panalytical Empyrean X-ray diffractometer with a pyrolytic graphite monochromator. The φ-scans were done on the NFO (440) plane (2θ=63.5°). Layer-by-layer grown samples were scanned as they showed better texture in the θ-2θ scans. Both samples show six discrete peaks around <111> crystallographic direction indicating 6-fold in-plane symmetry. However, the NFO (111) plane has a 3-fold symmetry. The observed 6-fold symmetry is explained by two in-plane alignment variants, namely 60° and 180° ones. The in-plane epitaxial relationship is created by matching (111) NFO planes in two variants rotated by 30° with respect to the hexagonal lattice of the (0001) sapphire as:

- [110] NFO || [1010] Al₂O₃
- [110] NFO || [1100] Al₂O₃

where [111] NFO || [0001] Al₂O₃ in both variants [5, 15]. The observed epitaxial relationship is similar to reports on other spinel thin films on same substrate [16, 17] and are described in more detail in previous work [5, 15].
Figure 5-5: $\phi$-scans of layer-by-layer grown plain and patterned films.
A Quantum Design superconducting quantum interference device (SQUID) was used to measure room temperature magnetic properties with the magnetic field parallel (in-plane) and perpendicular (out-of-plane) to the sample surface up to ±7 T. The magnetic behavior, shown in figure 5-6, is normalized after removing the substrate contribution.

The out-of-plane magnetization hysteresis, normalized to 4 T values, show all samples except the BP film have similar shape indicating similar texture. The hysteresis of the BP film is less square, an indication of the reduced texture seen in the XRD results. The BP sample also shows significantly smaller saturation magnetization, ~40% of the other films, as a result of reduced texture and larger sample thickness. Note that the larger sample thickness is related to increased porosity which reduces the saturation magnetization by reducing the long-range magnetic order in the film [18].

The inset in Figure 5-6a shows the very low field portion of the magnetization hysteresis and thus the coercivity. Similar values for both unpatterned films are seen, consistent with the XRD and TEM results, whereas the patterned films have much lower values. This is quantified in figure 5-6b, which shows the coercivity as a function of film thickness for in-plane (dashed lines) and out-of-plane (solid lines) measurements. For the L films, the hysteresis is measured after the processing of each individual layer; the coercivity increases with film thickness. For the LU film, the coercivity continues to increase with the addition of the third layer, whereas for the LP film the coercivity decreases sharply due to the patterning of the third layer. As a result, the out-of-plane coercivity of the final LP film is ~80% lower than that of the LU film. The same trend is observed in the BU and BP films, but with an even greater reduction in coercivity, clearly showing that the coercivity reduction
is attributable to the surface patterning.

The magnitude of the coercivity reduction reported here is comparable to previous results and ranges from ~50% for the in-plane measurements on L films to ~90% for out-of-plane measurements of B films. The coercivity reduction with surface patterning is particularly interesting since increasing surface roughness usually increases coercivity through domain wall pinning [1, 2, 19]. These results further strengthen the previous study and the conclusion that the coercivity reduction is a direct consequence of patterning the surface.

Saturation values are 106 emu/cm$^3$ for the layer-by-layer unpatterned (LU) film, 101 emu/cm$^3$ for the layer-by-layer patterned (LP) film, 102 emu/cm$^3$ for the bulk unpatterned (BU) film, and 43 emu/cm$^3$ for the bulk patterned (BP) film. The similarities between the values of saturation magnetization for the LP, LU and BU films indicate the process of patterning did not affect the magnetic properties or the grain growth and texture of the films. The lower saturation magnetization value of the BP film indicates that the layer-by-layer manufacturing method to be superior to bulk manufacturing. The very low value of the saturation magnetization is also indicative of the need for optimized processing conditions for the patterned films similar to what is found in the previous study.
Figure 5-6: (a) Magnetic hysteresis measurements of NiFe$_2$O$_4$ thin films. Higher magnification images of the coercivity are shown in inset. (b) In-plane (dashed) and out-of-plane coercivities.
5.4. Conclusion

Multilayered NFO thin films were sol-gel deposited onto c-plane sapphire in layer-by-layer and bulk film variants. Both variants were patterned using NIL and compared to unpatterned films. The pattern was transferred over large areas without noticeable defects or nucleation and grain growth disruption. Insufficient thermal budget at the PDMS/NFO interface results in textured samples despite the surface patterning.

Magnetic measurements reveal that the LU, BU and LP films have similar hysteresis curve shapes and saturation magnetization values, and the LU and BU films have coercivities comparable to other reports. As a result of surface patterning, the NFO thin films show a large reduction in coercivity attributed to a change in minimum energy configuration. By combining NIL with sol-gel deposition we have shown an easy and inexpensive method for large scale precise surface modification and coercivity reduction while retaining desirable crystallographic and magnetic properties. The results on thicker films equaled those in previous chapter, showing this to be a viable pathway for coercivity reduction independent of film thickness, opening this to implementation in current technologies. This new, interesting and technologically useful phenomenon allows for loss reduction desirable in high-frequency applications.
References


CHAPTER 6

Effects of feature change on coercivity reduction in surface patterned NiFe$_2$O$_4$ thin films

Here the effect of varying the feature size on topography, crystallography and magnetic properties is studied. Surface patterned NiFe$_2$O$_4$ films were deposited on c-plane sapphire substrates using chemical solution deposition. Nanoinprint lithography, using a polydimethylsiloxane stamp, was used to transfer the features from the masters to the films. In addition to the standard CD and DVD, patterning masters with feature sizes varying from 500 nm to 1300 nm in 200 nm increments were made using laser interference lithography. Atomic force microscopy showed good feature transfer for all samples. X-ray diffraction images showed all samples to be pure single phase inverse spinel nickel ferrite and to have similar texture. Magnetic measurements showed patterning did not affect the magnetic response of the samples. All patterned samples showed coercivity reduction as compared to the unpatterned samples. The dependence of coercivity reduction on feature size was shown to have opposite trends for the in-plane and out-of-plane magnetized samples. Saturation magnetization of the patterned films was not affected by feature size changes. Magnetic force microscopy images confirmed the origin of coercivity reduction to be shape-anisotropy-forced alternating domain formation.
6.1. Motivation

Spinel nickel ferrite (NiFe$_2$O$_4$) is a promising material for next generation high-frequency and spin filter devices due to its intrinsic high electrical resistivity [1-8]. A key issue to be addressed is the magnetic loss which grows proportional to frequency and becomes substantial at frequencies above 1 GHz [7, 9]. Earlier, coercivity reduction through surface patterning in single [10] and multilayered [11] NiFe$_2$O$_4$ films was studied. For comparison all samples were patterned using the same readily available master. However, to get the whole picture, the effect of changing the surface pattern on the magnetic and crystallographic properties remains to be studied. Also, the limits of the procedure need to be explored. This will not only offer a better understanding of the phenomena of coercivity reduction, but is also an important parameter if the intent is to improve coupling in composites [12-17].

Chemical solution deposition (sol-gel) was used as an inexpensive and scalable method to deposit textured thin films. In combination with nanoimprint lithography it presents a low-cost, quick and easy method to manufacture textured, surface patterned thin films. A series of pattern masters with periodic features was made using interference lithography.

In this chapter the effect of changing the feature size and period on coercivity reduction is studied. The effect on the pattern precision and crystallography is also examined. Finally, the magnetic domain structure is measured.
6.2. Experimental details

A sol-gel solution of 0.2 molar NFO was prepared by separately mixing 2.4884 grams of nickel(II) acetate tetrahydrate (C$_4$H$_6$NiO$_4$·4H$_2$O) and 8.08 grams of iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) in 20 mL of 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH) solvent each (all from Sigma-Aldrich). The solutions were stirred at 70 °C in ambient conditions for 2 hours before being mixed together for 15 minutes and allowed to cool to room temperature.

Samples were made by spin coating the solution onto c-plane sapphire substrates. Spin coating was done at 4000 rpm for 30 s followed by pyrolysis for 60 s at 400 °C to remove the solvent. Finally the film was annealed at 750 °C for 15 minutes to crystalize the NFO phase.

Initially, two layers were spin coated, pyrolyzed and crystallized on a wafer (“Base”) according to the aforementioned procedure. The wafer was then cut into smaller pieces and the final (third) layer was deposited and imprinted. For control, a final layer without imprint was made (“Plain”).

To evaluate the effect of geometric variations on coercivity, a series of lithography masters with different periods was prepared. For control, and comparison with previous work [11], a standard CD and a DVD master were used. The CD and DVD were prepared by carefully removing the protective aluminum layers, exposing the features. The feature periods are 1500 nm for CD and 750 nm for DVD.

The series of lithography master patterns were prepared via laser interference lithography [18-20] using a 325 nm wavelength laser. To prepare the masters, silicon substrates were first coated with a 100 nm thick antireflective coating layer (ARC, Brewer
Science i-CON-16, \( n=1.646-0.398j \) to reduce reflection from the silicon, allowing for higher precision and feature quality. The samples were then coated with 500 nm thick layer of photoresist (PFI-88A2, \( n=1.72-0.04j \)) to record the intensity pattern. Finally, samples were exposed with a dose of 50 mJ and developed in N-Methyl-2-pyrrolidone for 5 minutes. Feature sizes ranged from 500 nm to 1300 nm in 200 nm increments and were varied by changing the angle of the incident beam [20].

Reactive ion etching (RIE) was used to transfer the pattern from the photoresist to the silicon substrate. The etching was performed at room temperature in three steps on an Alcatel AMS 100 Deep Reactive Ion Etcher. First, the ARC layer was removed using oxygen plasma (250 W source/75 W bias) for 30 s. Second, the pattern was transferred to the silicon substrate by alternating sulfur hexafluoride (SF\(_6\)) and octafluorocyclobutane (C\(_4\)F\(_8\)) gas exposures for 3 and 1 s respectively. The total etch time was 40 s at 1200 W source/ 75 W bias. Finally, oxygen plasma was used to clean any remaining photoresist and ARC layer of the samples. To attach the samples to a bare silicon wafer for etching, samples were thermally bonded using Cool grease from AI Technology.

A polydimethylsiloxane (PDMS) stamp was used to transfer the features from the masters to the films. The PDMS stamp was prepared using a Dow Corning Sylgard-184 Silicone Elastomer Kit. Silicone base and the curing agent were mixed in a 10:1 ratio, poured over the masters and degassed to remove the bubbles. Finally, the PDMS was cured for 24 hours at 70 °C to assure good crosslinking in the polymer [21]. After curing, the PDMS was removed from the masters and used for imprinting.
To imprint the samples, nanoimprint lithography (NIL) was used as a compatible low-cost high-throughput method for surface patterning [22]. The PDMS stamp was pressed onto the spin coated films as the samples were pyrolyzed. After pyrolysis the stamp was removed and the film was annealed.

To determine if observed coercivity reduction is a result of the imprinting process itself, a sample was partially imprinted with a flat PDMS stamp (stamp) and compared with the part of the sample that was not imprinted (plain). In addition, to test the effect of shape anisotropy, the samples were cut with 1.38 (Plain) and 1.40 (Stamp) aspect ratios of long to short edge. Measurements done with the long edge of the samples parallel to the field (Plain, Stamp) were done first, followed by measurements with the long edge perpendicular to the field (Plain-2, Stamp-2).

6.3. Results

The surface morphology of patterned films was evaluated by atomic force microscope (AFM, Cypher by Asylum Research) in tapping mode; images are shown in figure 6-1. Surface roughnesses and feature heights are given in table 6-1. Distinct, one-dimensional periodic features are seen in all patterned samples without noticeable deviations or gas bubbles, indicating successful pattern creation and good feature transfer between master/stamp and stamp/film. The features were uniformly copied over large areas indicating good conformity between the stamp and the films.

The images also show feature quality slightly deteriorating as the feature size decreases. This is a result of smaller features and higher aspect ratios, increasing the
difficulty of imprinting as the feature size decreases. Table 6-1 shows that the feature height decreases with feature size. As the feature size becomes smaller it is more difficult for the PDMS stamp to penetrate the material, reducing the feature height. All films appear to be fully crystallized and no sign of crystalline or feature damage is observed. In addition, and corresponding to previous study, there is no indication of grain growth disruption [10, 11].
Figure 6-1: AFM scans of patterned NiFe$_2$O$_4$ thin films with (a) 1500 nm, (b) 1300 nm, (c) 1100 nm, (d) 900, (e) 750 nm, (f) 700 nm and (g) 500 nm feature size and the (h) plain sample.
Table 6-1: Magnetic and topographical values of NiFe₂O₄ samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>Feature height [nm]</th>
<th>Coercivity [Oe]</th>
<th>Saturation [emu/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>In-plane</td>
<td>Out-of-plane</td>
</tr>
<tr>
<td>Base</td>
<td>1.94</td>
<td>118</td>
<td>290</td>
</tr>
<tr>
<td>Plain</td>
<td>2.98</td>
<td>155</td>
<td>483</td>
</tr>
<tr>
<td>1500 (CD)</td>
<td>45</td>
<td>104</td>
<td>194</td>
</tr>
<tr>
<td>1300</td>
<td>60</td>
<td>124</td>
<td>173</td>
</tr>
<tr>
<td>1100</td>
<td>50</td>
<td>97</td>
<td>208</td>
</tr>
<tr>
<td>900</td>
<td>60</td>
<td>89</td>
<td>225</td>
</tr>
<tr>
<td>750 (DVD)</td>
<td>30</td>
<td>88</td>
<td>223</td>
</tr>
<tr>
<td>700</td>
<td>30</td>
<td>92</td>
<td>252</td>
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<tr>
<td>500</td>
<td>20</td>
<td>85</td>
<td>244</td>
</tr>
</tbody>
</table>
X-ray diffraction (XRD) was used to evaluate the crystal structure and grain orientation (texture) of the films; results are seen in figure 6-2. θ-2θ scans were performed using Cu Kα radiation (λ=1.5418 Å) from 15° to 60° in a Smartlab Rigaku X-Ray diffractometer and the peaks were identified using reference PDF (JCPDS File No. 003-0875) and confirmed with Bragg’s law. Figure 6-2 reveals all samples to be pure phase inverse spinel NFO with preferential orientation along the <111> direction and the degree of texture comparable to previous study [10, 11, 23]. Similar texture between plain and patterned samples confirms there was no noticeable nucleation and/or growth disruption by the imprinting process and that changing feature size does not affect crystallographic properties. In addition, all samples have similar grain size as evidenced by the similar FWHM of the peaks [24].

Maximal similarity between samples is assured by growing the first two layers on a single large wafer. As a result, the possible measurement errors resulting from external factors such as growth, ambient and processing conditions, as well as crystallographic and structural properties, are minimized.
Figure 6-2: 0-2θ X-ray diffraction patterns of NiFe$_2$O$_4$ thin films.
A superconducting quantum interference device (SQUID, Quantum Design) was used to measure the magnetic properties. Magnetization hysteresis was measured with the magnetic field parallel (in-plane) and perpendicular (out-of-plane) to the samples. Measurements were performed at room temperature with magnetic field ranging between ±7 T. Magnetic measurement results are normalized to 4 T after removing the substrate contribution; hysteresis loops are shown in figure 6-3 and summarized in table 6-1. Due to the slight shift in the hysteresis curves, the coercivities are calculated as the average between the coercivity in the positive and negative field direction.

The out-of-plane magnetic hysteresis curves in figure 6-3a show that all samples have similar curve shape, indicating that the imprinting process did not alter the magnetic response significantly. This is indicative of similar texture as confirmed by XRD and in agreement with previous work [11]. In-plane magnetic hysteresis curves in figure 6-3b show a similar trend as the out-of-plane curves, with all the samples having similar curve shape as expected.
Figure 6-3: Normalized hysteresis curves of patterned NiFe$_2$O$_4$ thin films measured (a) perpendicular and (b) parallel to the sample surface. The insets show higher magnification plots of the hysteresis curves.
The out-of-plane coercivities in figure 6-4 show, starting from the base sample, a small but steady reduction in coercivity as the feature size increases. Comparing the base and plain films, the coercivity in the plain film is higher due to larger sample thickness. As the thickness increases, the coercivity behaves less like a thin film and more like a bulk film, i.e. the coercivity increases. For out-of-plane measurements, patterning the surface reduces the film below the coercivity of the base layer. Note that the coercivities for the base, plain and CD samples are in accordance with previous work [11], indicating good consistency.

Figure 6-4: Coercivity values of patterned NiFe$_2$O$_4$ thin films measured perpendicular to the film surface. Feature heights are shown above the coercivity values.
The variation of coercivity with feature size for the in-plane measurements, seen in figure 6-5, however, shows the opposite trend. Starting from the base sample, decrease in coercivity is found in the 500 nm sample, with coercivity increasing with the feature size. This could be attributed to weakening of the effect governing the coercivity reduction as well as an increased number of pinning centers as the feature size increases. In-plane coercivity values for base, plain and CD samples are again similar to previous results [11].

![Figure 6-5: Coercivity values of patterned NiFe$_2$O$_4$ thin films measured parallel to the film surface. Feature heights are shown above the coercivity values.](image-url)
Saturation magnetization values at 4 T are given in table 6-1 and plotted in figure 6-6. The saturation magnetization of the plain film is comparable to previous reports (~190 emu/cm³) [25], and only 29% less than that of the bulk NFO (270 emu/cm³) [1]. Comparing the base and plain samples, the saturation magnetization increases significantly, due to larger sample thickness and increased density resulting from the additional 15 minutes of annealing of the first two layers in the plain sample as compared to the base sample. Saturation magnetization values of the patterned samples, while lower than the plain samples, are larger than the base sample. By patterning, the sample surface to volume is increased. Since the amount of material is dictated by the spin coating parameters and solution viscosity, which is identical for all samples, this results in larger sample porosity, reducing the long range magnetic order in the patterned films and lowering the saturation magnetization as compared to the plain sample [11, 26]. The similar saturation magnetization value of all patterned films indicates that they are of comparable thickness and porosity.

The average coercivity reduction in patterned samples can be calculated from table 6-1. For the out-of-plane measurements, the patterned samples have, on average, a 25% reduction as compared to the base sample and 55% reduction as compared to the plain sample. For the in-plane measurements, the patterned samples have, on average, a 18% reduction as compared to the base sample and 38% reduction as compared to the plain one, similar to previous report [11].
Figure 6-6: Saturation magnetization values of patterned NiFe$_2$O$_4$ thin films normalized to volume. Feature heights are shown above the saturation magnetization values.
Looking at the magnetization measurements in figure 6-7a similar behavior is observed in all cases. The slightly larger saturation magnetization in the imprinted sample (Stamp) is likely due to the small inhomogeneities in the film resulting from the manufacturing process. More important is the behavior exhibited by the samples showing similar magnetization curves and saturation magnetization values. In both cases, however, a slightly larger value of saturation magnetization (~3 %) is observed due to the shape anisotropy of the sample. In both cases, the orientation of long sample edge perpendicular to the field yields larger saturation magnetization values. Although this effect is small, it is worth noting.

A higher magnification image of the magnetization data, shown in figure 6-7b, reveals all samples to have similar coercivity values, comparable to the results obtained for the plain film shown in figure 6-5. Thus the observed coercivity reduction in this study is not a result of the process of imprinting.
Figure 6-7: (a) Hysteresis curves of NiFe$_2$O$_4$ thin film imprinted with a flat PDMS stamp measured with the long edge parallel (Stamp) and perpendicular (Stamp-2) to the magnetic field. (b) Higher magnification image centered on the origin.
In addition, the effect of different feature orientation with respect to the magnetic field for in-plane measurements was studied. The measurements, seen in figure 6-8, were done on the 1100 nm sample due to high quality of features. The sample was cut with an aspect ratio of 1.09 with features parallel to the long axis.

Magnetization measurements, seen in figure 6-8a, show both sample orientations have similar magnetic response. The value of saturation magnetization for the features (and the long axis) oriented perpendicular to the magnetic field is slightly larger, in accordance to what is seen in the plain film (figure 6-7a). This shows that there is no significant influence of the feature orientation to the field direction on the saturation magnetization of the sample.

Looking at the values of coercivity in figure 6-8b, we observe a similar response for both sample (feature) orientations with respect to the magnetic field. This indicates that the orientation of the features is not a significant contributor to the coercivity. While the coercivity is shown to be affected with high aspect ratio nanoscale shapes such as wires and dots, here the features are not isolated but are only a surface modification of a thin films. Thus, the total magnetic response comes not only from the features, but from the sample as a whole, where the features are only on the surface.
Figure 6-8: (a) Hysteresis curves of 1100 nm sample measured with the features parallel and perpendicular to the magnetic field. (b) Higher magnification image centered on the origin.
To better understand the physical phenomenon leading to coercivity reduction, magnetic domains of a patterned sample are imaged using magnetic force microscopy (MFM) and compared to the plain film. MFM measurements were done on a MFP-3D AFM by Asylum Research. To eliminate machine-sample interactions, a non-magnetic head and low moment magnetic probes (ASYMFMLM by Asylum Research) were used. Before imaging, the probe was magnetized using a permanent magnet. The measurements were done with frequency tracking via a phase-lock loop to assure that all measurements remained on resonance. All measurements were conducted under same conditions for maximal comparability. The film patterned with CD master was chosen for MFM imaging due to the large feature and period size, allowing for greater reliability of the acquired data. MFM measurements of the CD sample magnetized in-plane, out-of-plane and non-magnetized are shown in figure 6-9. For comparison, MFM measurement of a non-magnetized plain sample is also shown.

The MFM image of the plain sample in figure 6-9d shows small (~150 nm), random domains covering multiple grains on the surface. The images of the patterned sample in figure 6-9a-c show large (~750 nm) ordered domains following the pattern topography and covering numerous grains. The similarity between the domain structure of the patterned sample indicates that the domain formation is dictated by the surface anisotropy. Uniform magnetization and domain orientation of the features indicates that the domain distribution is a consequence of the features themselves. In addition, the “trenches” between the features have a uniform magnetization and domain orientation as well, but opposite in direction to the domains in the features.
Figure 6-9: Magnetic force microscopy images of patterned NiFe$_2$O$_4$ thin films (a) without magnetization and magnetized (b) in-plane and (c) out-of-plane magnetized. (d) Image of the plain NiFe$_2$O$_4$ thin film.
MFM scan performed on a plain sample using a non-magnetic probe shown in figure 6-10 was used to assure the observed domain structure is not an artifact of the sample topography or the sample-probe interaction. The scan of the magnetic domains in figure 6-10b can be misleading by itself, therefore it is necessary to compare it with a scan of the topography shown in figure 6-10a. The two images can be overlaid to provide an accurate three-dimensional representation of the sample shown in figure 6-10c. From the perfect overlap of topography and magnetic domains and the fact that the domains appear to be one grain in size it is easy to conclude that we are not measuring the actual domain structure. In the absence of magnetic force, Van der Waals interaction becomes dominant. Since that is the same force we measure the topography with, the resulting scans are the same.
Figure 6-10: Magnetic force microscopy image of a plain sample taken with a nonmagnetic probe.
Hard disk drive shown in figure 6-11 was used as a standard to test the reliability of the measurements and the probe. Low surface roughness in figure 6-11a and large magnetic response in figure 6-11b assure reliable and repeatable measurements. The information is recorded in discrete domains, which makes for easy evaluation of the probes magnetic response.

Figure 6-11: Magnetic force microscopy image of a hard disk drive used as a standard.
6.4. Discussion

The AFM data in figure 6-1 shows the imprint transfer to be of high quality and without noticeable defects over large scale. The PDMS stamp showed reduced imprint depth, starting at around 900 nm with a cut-off around 500 nm. The XRD data in figure 6-2 confirms texture in all samples. The similarity of the peak position and FWHM in the plain and patterned samples reveals that the crystallography of the thin films is not affected by imprinting or feature size/period change. This, combined with the AFM data, confirms NIL to be effective method for surface patterning sol-gel deposited thin films.

The magnetic data in figure 6-3 shows similar curve shapes for all samples, indicating similar sample response. This indirectly confirms similar texture between the samples. Saturation magnetization of the patterned samples, while lower than in the plain sample, is still relatively high and larger than the base sample. The saturation values of the patterned samples do not vary significantly indicating that the reduction is not affected by the feature size but the imprinting process itself which reduces the density of the top film layer.

Out-of-plane coercivity values of the patterned samples in figure 6-4 show reduction compared to the base and plain samples. The out-of-plane coercivity decreases with increase in feature size. This trend can be explained by corresponding increase in feature height as the feature size increases. By increasing the feature height we reduce the thickness of the layer underneath, lowering the coercivity.

For the in-plane coercivity in figure 6-5 the opposite trend is observed. After the initial sharp reduction in coercivity for the 500 nm patterned film as compare to the base, a slight trend towards higher coercivity is seen with increasing feature size and period. The
Coercivities show a slow and steady increase, approaching the value of the base sample. This is explained by the weakening of the effect of coercivity reduction. As the domain size increases, the energy required to have a single domain increases. Another possible explanation is an increased number of pinning defects with increased feature size.

Coercivity reduction in patterned samples is a consequence of the alternating arrangement of domains pointing in the opposite directions. Oppositely oriented domains are similar in size, so the effective magnetization at the sample surface approaches zero, lowering the film coercivity. Reducing the coercivity below that of the base layer is a consequence of this domain arrangement penetrating into the base layer, lowering its coercivity as well. The overall coercivity reduction of the film is a combination of near zero magnetization of the patterned layer and the penetration depth of the domain arrangement into the base layer.

Alternating domain arrangement of the patterned films is a direct consequence of the surface morphology. With all the magnetic moments pointing in the same direction, the magnetostatic energy of the sample becomes substantial. The formation of magnetic domains would reduce the magnetostatic energy, leading to a minimum energy configuration. By patterning nanoscale size features on the sample surface the minimum energy configuration is affected by the surface topography of the films and the new minimum magnetostatic energy configuration is one where domains in the trenches are oriented in the opposite direction to the feature domains [1]. This configuration also reduces the sample coercivity.
6.5. Conclusion

Sol-gel deposited NFO thin films were deposited on c-plane sapphire and surface patterned using NIL. Pattern masters of different sizes were manufactured and used as templates for PDMS stamps. NIL, in combination with chemical solution depositions is shown to be a reliable method for consistent high quality surface patterning of textured thin films. Imprint depth was reduced with decreasing feature size and the limit for pattern size was determined to be 500 nm. All films showed comparable texture with preferential orientation along the <111> direction. Magnetic measurements showed the magnetic field response in the patterned samples to be unchanged as compared to plain samples, indicating there was no loss in magnetic properties. Similarly, the patterned samples showed appreciable and consistent saturation magnetization values. The coercivity of all samples showed significant reduction as compared to the plain samples. In addition, two distinct regimes were identified. For the out-of-plane measurements, the coercivity reduction increases with increasing feature size, whereas for the in-plane measurements the opposite is observed. These polar trends for the in-plane and out-of-plane measurements allow us to further fine tune the material for specific applications by not only controlling the feature size but also the orientation of the film with respect to the field. Finally, the origin of the coercivity reduction was shown to be the surface morphology anisotropy by MFM measurements. Magnetic domains were shown to be strongly affected by the surface features and oppositely oriented, reducing magnetostatic energy and leading to coercivity reduction.
References


CHAPTER 7

Theoretical considerations

To better understand the coercivity reduction phenomena observed in patterned NiFe$_2$O$_4$ thin films and offer an explanation, as well as provide a more complete report, theoretical study was done. The most likely origins of the phenomena were explored and compared to other reports. The possible change of the demagnetization factor with change in surface topography was investigated and shown not to be a likely explanation. The effect of changing the film thickness and domain size on the equilibrium energy density was studied. While the relative energy density was shown to sit in a stable equilibrium position, the energy increase for domain sizes equaling that of pattern films in this study was small. Finally, the new domain structure in patterned NiFe$_2$O$_4$ films was explained within the domain wall theory.

7.1. Motivation

The coercivity reduction method reported in this study offers a new scientific breakthrough. Reducing losses in magnetic material used in high frequency applications is of paramount technological importance [1-6]. With smaller losses devices with less power consumption and heating can be manufactured. This would serve to increase efficiency and performance, with improved signal to noise ratio [1-3].
Before any serious technological implementation can be done, the origin of the observed phenomena needs to be resolved. This would serve to better understand the science behind the results, as well as allow for purpose specific device design. The novelty of the conducted research makes comparison with other reports difficult. In addition, a rigorous theoretical framework has not been developed.

In this chapter the standard physical effects behind coercivity as well as the most likely origins of coercivity reduction are explored. Changes in the demagnetization factors, domain size and film thickness are studied. Finally, an explanation for the observed phenomena is offered.

7.2. Demagnetization factors

When considering the magnetic properties of a material, the shape must be considered. The shape dictates the demagnetization field, given by eq. 2-5, and the shape dependence of the magnetic properties is quantified by the demagnetization factor, \( N \), as described in chapter 2.

Demagnetizing factors for different shapes have been studied for over a century. While calculations for ellipsoids [7] and cylinders [8] are relatively simple, and their demagnetization factors are readily reported in the literature [1, 2, 4], thin films present a greater challenge. Part of the problem lies in the fact that the demagnetizing field in a non-ellipsoidal body is not uniform but a function of location within the body. Therefore, in order to define a constant demagnetizing factor, it is necessary to define some sort of averaging
field. This problem was solved by Aharoni [9] for a prism extending over the volume

\[-a \leq x \leq a, \quad -b \leq y \leq b \quad \text{and} \quad -c \leq z \leq c\]

as shown in figure 7-1.

![Figure 7-1: Coordinate system and field direction used for calculations of the demagnetization factors [9].](image)

For magnetic field applied in the z direction the following equation is obtained:

\[
\pi \times D_z = \frac{b^2 - c^2}{2 + b + c} \times \log \left[\frac{\sqrt{a^2 + b^2 + c^2} - a}{\sqrt{a^2 + b^2 + c^2} + a}\right] + \frac{a^2 - c^2}{2 + a + c} \times \log \left[\frac{\sqrt{a^2 + b^2 + c^2} - b}{\sqrt{a^2 + b^2 + c^2} + b}\right] + \frac{b}{2 + c} \times \log \left[\frac{\sqrt{a^2 + b^2 + c^2} - a}{\sqrt{a^2 + b^2 + c^2} + a}\right] + \\
\frac{a}{2 + c} \times \log \left[\frac{\sqrt{a^2 + b^2 + c^2} - b}{\sqrt{a^2 + b^2 + c^2} + b}\right] + \frac{c}{2 + a} \times \log \left[\frac{\sqrt{b^2 + c^2} - b}{\sqrt{b^2 + c^2} + b}\right] + \frac{c}{2 + b} \times \log \left[\frac{\sqrt{a^2 + c^2} - a}{\sqrt{a^2 + c^2} + a}\right] + 2 \times \\
\arctan \left[\frac{a + b}{c \sqrt{a^2 + b^2 + c^2}}\right] + \frac{a^2 + b^2 - 2 + c^2}{3 + a + b + c} \times \arctan \left[\frac{a + b}{c \sqrt{a^2 + b^2 + c^2}}\right] + \frac{a^2 + b^2 - 2 + c^2}{3 + a + b + c} \times \arctan \left[\frac{a + b}{c \sqrt{a^2 + b^2 + c^2}}\right] + \frac{c}{a + b} \times \arctan \left[\frac{a + b}{c \sqrt{a^2 + b^2 + c^2}}\right] + \\
\sqrt{b^2 + c^2} - \frac{(a^2 + b^2)^{\frac{3}{2}} + (b^2 + c^2)^{\frac{3}{2}} + (c^2 + a^2)^{\frac{3}{2}}}{3 + a + b + c}
\]

(7-1)

where \(D_z = N/4\pi\) is the demagnetization factor in the z direction. The demagnetization factors in other directions obey the relation:
\[ D_x + D_y + D_z = 1 \]  \hspace{1cm} (7-2)

and indeed for eq. 7-1 they do.

Demagnetization factors for a thin film magnetized perpendicular to the film surface as a function of the film thickness is plotted in figure 7-2. The demagnetization factor \( D_z \) was calculated from 10 nm to 1 mm. The film was assumed to square with a 1 mm\(^2\) area. The demagnetization factor for a thin film is approximately equal to unity, which is in accordance to the values reported in literature [1, 2, 4]. As the film thickness increases, the relative thickness compared to the other two dimensions gets smaller, and the demagnetization factor reduces exponentially. If the film thickness increases to 1 mm, so that it equals the other two dimensions, the demagnetizing factor becomes 1/3, exactly equal to the values reported in the literature for a cube [1, 4]. The demagnetization factor for a cube, through symmetry, must be equal in all three dimensions and from eq. 7-2 must be 1/3.
Figure 7-2: Out-of-plane demagnetization factor as a function of film thickness.

Similarly, the demagnetization factor values for a thin film magnetized parallel to the film surface are plotted in figure 7-3. As expected, for very thin films the demagnetization factor is vanishing and the demagnetizing field can be ignored. As the sample thickness increases to 1 mm, the demagnetizing factor rises exponentially to value of 1/3 again, equaling the result expected for a cube.
Figure 7-3: In-plane demagnetization factor as a function of film thickness.

These calculations show that the calculation of demagnetizing factors for a rectangular object is possible, albeit not simple. While this method works well for flat thin films, it is difficult to adapt it to account for surface inhomogeneities. As we increase the surface roughness, the magnetic field of a sample becomes difficult to calculate. The self-field of individual features, their mutual interactions as well as interactions with the film, are just some of the factors to consider. Nevertheless, it can be seen that the demagnetizing factors depend exponentially on the shape, and that changing the surface will inevitably affect the effective field the sample feels, i.e. the demagnetization field. However, the value change in the demagnetization factors is not significant for small changes in shape, even up to several times the sample thickness. It certainly is not sufficient to explain such drastic
changes in coercivity. Other authors have derived similar results for magnetic thin films with rough surfaces [10-12]. Furthermore, the demagnetization field is dependent on the magnetization of the films, which for ferrites is not sufficiently large to significantly affect the results. Lastly, the demagnetization factor affects the squareness (i.e. the remnant magnetization) of the hysteresis curve, but not the coercivity as when \( M = 0 \rightarrow H_d = -NM = 0 \). This means the applied field is equal to the field felt by the sample. An example with \( N = 10 \) for a NFO thin film measured out-of-plane is shown in figure 7-4. This indicates the origin of the reduced coercivity must be elsewhere.
Figure 7-4: Measured (black) and demagnetization field (N=10) subtracted (red) magnetic hysteresis curves. The inset shows a higher magnification image of the x-y axis intercept.
7.3. Micromagnetism and domain theory

The origin of magnetism in magnetic materials is connected to the electron spins and their interactions which is ultimately responsible for the observed large scale magnetic phenomena. This atomistic level of description is governed by the quantum theory of solids. However, this description becomes inadequate when we look at the magnetic behavior at an increased length scale. To transition to larger, more practical length scales micromagnetism theory was developed by Landau and Lifshitz in 1935 [13]. Micromagnetism moves away from discrete and into a continuous representation of the magnetic structure. The theory is based on a variational principle, searching for the magnetization distribution with the smallest energy. From this, a set of equations (micromagnetic equations) is derived. In the original work by Landau and Lifshitz [13], these equations were developed for only one dimension. Later, Brown extended the equations to three dimensions [14, 15] and included the stray field effect [16]. The micromagnetic equations are complicated and difficult to solve analytically. To resolve this problem, domain theory was developed by Kittel [17] using the same principles originally introduced by Landau and Lifshitz [13]. Domain theory treats the magnetic structure as magnetic domains separated by domain walls.

The micromagnetic equation results from minimization of the total free energy:

$$E_{total} = E_{exchange} + E_{anisotropy} + E_{zeeman} + E_{stray field} + E_{stress} + E_{magnetostriction}$$

$$= \int \left[ A(\nabla m)^2 + F_{an}(m) - H_{ex} * J + \frac{1}{2} H_d * J - \sigma_{ex} * \varepsilon^0 + \frac{1}{2} c * (p_e - \varepsilon^0)^2 \right] dV. \quad (7-3)$$

As we are only interested in the energy difference between various domain arrangements without an external applied field, this equation can be greatly simplified. In this case the main contribution to the magnetic field energy is the magnetic field generated by the
magnetized body itself. This energy is called stray field or magnetostatic energy. In a uniformly magnetized sample, a magnetic field is created by the resulting reorientation of magnetic moments in the direction of the applied field $H_{\text{applied}}$. This creates a magnetic field known as the demagnetization field ($H_d$) oppositely oriented to $H_{\text{applied}}$. Energy associated with this field can then be calculated as [4, 18]:

$$E_d = -\frac{1}{2} \int (H_d \ast M) \, dV$$

(7-4)

After the sample is saturated and $H_{\text{applied}}$ removed, the total resulting magnetic field is the one generated only by the sample ($H_d$) so that

$$H_d = -4\pi M_s.$$  

(7-5)

plugging this into eq. 7-6 we get

$$E_d = -\frac{1}{2} H_d \ast M_s = 2\pi M_s^2$$

(7-6)

where $E_d$, depending on the literature used, is called the demagnetization, dipolar, magnetostatic or stray field energy density. As all of the magnetic moments are pointing in the same direction, it is a measure of the maximum energy density of a material per volume. As this represents a highly unfavorable arrangement, oppositely oriented magnetic domains are formed to lower the total energy of the system. The energy reduction is approximately proportional to the number of domains created, $N$, and is connected to a reduction of long range ordering in the material [17]. This division process however, will not continue indefinitely, as there is an energy cost associated with creating addition interfaces (domain walls) between the domains. The final domain structure is then an energy minimum.
configuration of energy reduction from domain splitting and energy gain from additional interfaces.

### 7.3.1. Domain walls

The interface (boundary) between two oppositely oriented magnetic domains is called a domain wall. The domain wall describes the transition region between the two domains. There are two types of walls, Bloch and Néel, depending on the plane in which the rotation of magnetization occurs. Néel has shown that in very thin films it is energetically more favorable to reorient the moments in the film plane [19]. The change between Bloch and Néel walls is gradual and thickness dependent.

In the case of a Bloch wall for a relatively thick ferromagnetic material with uniaxial anisotropy the domain wall width $\delta_w^B$ is given as:

$$\delta_w^B = \frac{\pi}{|K_u|} \sqrt{A}$$

(7-7)

where $A$ is the exchange stiffness and $K_u$ is the uniaxial anisotropy constant. The exchange stiffness $A$ can be calculated as:

$$A = \frac{k_B T_m}{a} \left(1 - \frac{T}{T_m}\right)$$

(7-8)

where $k_B$ is the Boltzmann constant and $a$ is the lattice constant.

The energy density $\sigma_w^B$ of a Bloch wall is then

$$\sigma_w^B = 4\sqrt{A |K_u|}.$$  

(7-9)

In a Bloch wall, the small amount of surface charges due to the rotation of the magnetic moments can safely be neglected.
For a thin film, however, surface charges have a much larger contribution and must be taken into account. The domain wall width in this case is then

$$\delta_N = \frac{\pi \sqrt{A/2\pi M_s^2}}{2\pi M_s^2}$$

(7-10)

where $\delta_N$ is Néel wall width. The energy density $\sigma_N$ is given as

$$\sigma_N = 4\sqrt{A * 2\pi M_s^2}.$$ 

(7-11)

We can see that the magnetostatic energy in a Néel wall has the same role as the anisotropy constant in Bloch wall. The ratio of the anisotropy constant to magnetostatic energy is called the quality factor Q and indicates magnetic hardness. While this would suggest the type of wall in the material will be affected by the magnetic hardness, the key variable is film thickness. Naturally, in real materials, the situation is more complicated and intermediate structures can form.

### 7.3.2. Stripe domains

We now consider the energy of a stripe domain structure [1, 4, 17, 20, 21]. The domains are assumed to be uniformly magnetized and separated by domain walls of width $\delta_w$. The total energy of this configuration is given as the sum of the magnetostatic and domain wall energies. In case of a thick film, the calculation is straightforward and yields [17]:

$$E_{ms} = 0.8525 * M_s^2 * D$$

(7-12)

where $E_{ms}$ is the magnetostatic energy density per unit area for a stipe domain configuration and D is the domain size. From this we can calculate the domain size by minimizing the total
energy given as:

\[ E_{total} = E_{ms} + E_w \]  (7-13)

with respect to domain size. \( E_w = \sigma_w \times t/D \) is the domain wall energy density per unit area and \( t \) is the thickness of the film. From this it follows that

\[ D = \left( \frac{\sigma_w \times t}{0.85M_s} \right) \]  (7-14)

Unfortunately, this relatively simple calculation breaks down in cases where the film thickness is smaller or comparable to the domain width. In this case the magnetostatic energy is a function of thickness \( t \) and is found by expanding the magnetic potential in a double Fourier series [22]:

\[ E_{ms} = \frac{16M_s^2D}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{2n} \left[ 1 - \exp \left( -\frac{2\pi nt}{D} \right) \right] \]  (7-15)

In the limit of thick films the exponential is negligible and we return to the result by Kittel [17] shown in eq. 7-12. In the limit of thin films \( (t \ll D) \) the exponential can be expanded to the first order so that the equation reduces to:

\[ E_{ms} = 2\pi M_s^2 t. \]  (7-16)

From this we can see that, in the thin film limit, the magnetostatic energy is dependent on the thickness. Analytical study of the system in the thin film limit was done by Kaplan and Gehring [23] by using a 2\textsuperscript{nd} order Taylor expansion of \( t/D \). The derived expression for magnetostatic energy is given as:

\[ E_{ms} = 2\pi M_s^2 t \left( 1 - 0.67 \frac{t}{D} + \frac{2t}{\pi D} \ln \frac{t}{D} \right) \]  (7-17)

The numerical solution was calculated by Speckmann [24] and is shown in figure 7-5.
Figure 7-5: Domain width as a function of film thickness going from thick to thin film regime. The axes are normalized to the minimum domain width [24].

In the limit of thick films the curve follows the prediction of Kittel [17]. The minimum is obtained by decreasing the film thickness until the charges of the two surfaces begin to interact. Again the domain size is obtained by minimizing the total energy and yields:

$$D(t) = 0.95 \times t \times e^{\frac{\pi D_0}{2t}}$$

where $D_0 = \sigma_w / 2\pi M_s^2$ is the characteristic dipolar length.

In the limit of thick films the gain in magnetostatic energy due to the formation of closure domains is large enough to guarantee the stripe domain configuration is lower in energy than a single domain state. By lowering the film thickness, the gain in energy from
forming closure domain reduces and becomes comparable to the wall energy resulting in less
efficient domain formation. The calculations shown here assume perfectly parallel alternating
domains. In reality that is not the case, as can be seen from the MFM image of a plain sample
shown in figure 6-9. Numerical studies of dipolar sums predict that a parallel stripe domain
structure should be energetically favorable over the observed domain structure (sometimes
referred to as labyrinth or maze) [25]. The experimentally observed deviation from the
parallel stripe pattern is due to the imperfections in real materials. Defects, inclusions and
surface anisotropy provide energetically favorable domain wall locations, altering the domain
structure [1, 2, 4]. Furthermore it was demonstrated that the domain pattern is strongly
dependent on the magnetic history of the sample and the demagnetization procedure used
[25, 26].
7.3.3. Results

The relevant magnetic properties for the samples in this work can now be calculated. The films used in this study have an average thickness of around 100 nm and that value will be used as the “standard.” While for thicknesses of a 100 nm we expect Bloch walls, we are close to the changeover thickness between Bloch and Néel walls. For this reason the consideration of the relevant magnetic properties will be conducted for both Bloch (thick film regime) and Néel walls (thin film regime).

- Thick film regime

Using the known values of Curie temperature \( T_C = 858 \, K \) and lattice constant \( a = 0.834 \, nm \) for NiFe\(_2\)O\(_4\), the room temperature exchange stiffness is calculated from eq. 7-8 as

\[
A = \frac{k_B T_C}{a} \sqrt{1 - \frac{T}{T_C}} = 1.145 \times 10^{-6} \, \text{erg cm}.
\]  

(7-19)

From this, the Bloch domain wall width is

\[
\delta_w^B = \pi \frac{A}{|K_u|} = 127 \, nm.
\]  

(7-20)

Comparing with the MFM image in figure 6-9, this is a reasonable value for the width of the domain walls in the samples. The energy density of the domain wall is then

\[
\sigma_w^B = 4\sqrt{A \times |K_u|} = 1.13 \, \text{erg cm}^2.
\]  

(7-21)

The domain size is calculated from eq. 7-15

\[
D = \sqrt{\frac{\sigma_w^B + t}{0.85M_s^2}} = 135 \, nm
\]  

(7-22)
which is in good agreement with the observed results. The total energy density of this configuration is then calculated by plugging the domain size into the eq. 7-13.

In this study, only the relative change of the energy density between the samples is of interest, hence the total energy density has been normalized to the thickness value of 100 nm which is taken to be the approximate average film thickness.

The change in normalized total energy density with film thickness for the thick film regime is plotted in figure 7-6. It is clear that the relative energy density changes very little going from the lower (60 nm for plain single layer NFO) to upper limit (150 nm for patterned multilayered NFO) of film thicknesses studied (figure 7-6a). How small the change in energy really is becomes even more obvious when considering the film with thicknesses in the micrometer range (figure 7-6b). The graph increases linearly and the energy densities increase by two orders of magnitude. The film thickness is thus not the driving force behind the observed differences in the domain structure.
Figure 7-6: Relative change in the energy density as a function of film thickness for (a) thin and (b) thick films in the thick film regime.
As the change of energy density is minimal for the film thicknesses of interest, the average value of the film thickness (100 nm) is used to examine how the normalized energy density changes with domain size. This time, the energy was normalized to the equilibrium domain size (135 nm) calculated in eq. 7-22. The plots are shown in figure 7-7. Now the change in energy is more severe, as expected, since the domain size directly affects the total energy of the system. However, the change from the equilibrium domain size for the plain film (135 nm) to the largest domain size in the patterned NFO films (750 nm) is still relatively small (figure 7-7a). Once again, for a significant change in the energy density, orders-of-magnitude differences are required.

Looking at the shapes of the curves (figure 7-7) a clear energy minimum corresponding to the equilibrium domain size is observed. Any change in the domain size will result in a higher energy configuration. However, the energy dependence on domain size differs depending how the domain size is changed. Reducing the domain size will induce a sharp exponential jump in the energy due to a large number of new domain walls created. On the contrary, increasing the domain size above the energy minimum value, the increase in the energy density of the material is slow and linear. The increase in the energy density with increasing domain size from the energy minimum value to the maximum value in our patterned films (750 nm) is relatively small. This helps explain the observed change in the domains as the films are patterned.
Figure 7-7: Relative change in energy density as a function of domain size for (a) nanometer and (b) micrometer sized domains in the thick film regime.
- **Thin film regime**

Theoretical predictions for the thin film limit also need to be considered providing greater insight and serving as a verification of the results.

Using the calculated value for exchange stiffness in eq. 7-19 and the known saturation magnetization value of NiFe₂O₄, the Néel domain wall width is calculated from eq. 7-10

\[
d_\text{w}^N = \frac{\pi \sqrt{A/2\pi M_s^2}}{2} = 49.7 \text{ nm.} \tag{7-23}
\]

The energy density is then

\[
\sigma_w^N = 4\sqrt{A \cdot 2\pi M_s^2} = 2.897 \frac{\text{erg}}{\text{cm}^2}. \tag{7-24}
\]

Using the results in eq. 7-24, the domain size from eq. 7-18 becomes:

\[
D(t) = 0.95 \cdot t \cdot \exp\left(\frac{\pi D_0}{2t}\right) = 256.5 \text{ nm} \tag{7-25}
\]

for the average film thickness (100 nm) value. The domain size obtained here is somewhat larger than the average domain size measured with the MFM on the plain sample in figure 6-9, but still reasonable. The similarity between the results for two different regimes confirms that 100 nm is in the range of the changeover film thickness.

The total energy density is obtained by inserting the result from eq. 7-25 into eq. 7-17 where the total energy density is given by eq. 7-13. Again, only the relative change in the energy between films is of interest. The resulting change in the normalized energy density with film thickness for the thin film regime is shown in figure 7-8. As before, the energy density values are normalized to the value for a 100 nm thick film which is used as the average film thickness in this study. Looking at film thicknesses in the range of those in this study (60-150 nm), very little energy change is seen as the thickness is varied (figure 7-8a).
This result is almost identical to the one calculated in the thick film regime (figure 7-6a) and clearly demonstrates that the thickness variation between the films does not explain the observed domain structure. Looking at the energy change for micrometer film thicknesses (figure 7-8b), a huge increase in the energy density is seen, virtually identical to what is seen for bulk film calculations (figure 7-6b).
Figure 7-8: Relative change in the energy density as a function of film thickness for (a) thin and (b) thick films in the thin film regime.
Finally, the relative change in the energy density with varying domain size is studied (figure 7-9). The energy density values are normalized to the value for the energy density minimum domain size from eq. 7-25. The relative energy density changes very little with increasing the domain size from the equilibrium value (256.5 nm) to the maximum domain size in the patterned thin films (750 nm). The slope has a slow growth which plateaus at relatively small energy change as seen for the case of micrometer-sized domains. The energy change in the thin film regime is even smaller than for the thick film calculations (figure 7-7). The equilibrium value in the thin film calculations for a 100 nm thick film is almost identical to the domain size in the patterned films with the smallest features (250 nm) used in this study. Going to micrometer sized domains, a saturation of energy density is observed (figure 7-9b), as expected, for an ultra-thin film, as a single domain state is expected.
Figure 7-9: Relative change in energy density as a function of domain size for (a) nanometer and (b) micrometer sized domains in the thin film regime.
7.4. Discussion

The origins of the coercivity reduction measured experimentally have been studied. The few available experimental reports on similar phenomena attributed the “anomalous” coercivity reduction to the change in the demagnetization factors [27]. In addition, some theoretical work on magnetic materials with a single rough boundary showed there is a possibility of coercivity reduction for a specific surface morphology [10]. Even though the change of the demagnetization factor reported was only a few percent, it validated consideration and further investigation was needed. It was shown that for the case of the films studied here, the coercivity change is minimal with surface patterning. While the specific surface morphology was not included in the calculations, it is clear that for the nanoscale film thicknesses, the change in the demagnetization factor is very low, due to the other two dimensions being orders of magnitude larger. It also seems improbable that the same effect would be seen for films measured both perpendicular and parallel to the plane of the film. To verify the accuracy of the equations, the film thickness was increased up to the value of the other two dimensions and demagnetization factor of 1/3 was obtained, exactly as expected. Finally, a rather large demagnetization factor was used to examine the effects on the measured magnetic properties. The demagnetization factor affects the shape of the hysteresis curve, namely the remnant magnetization, but it does not change the coercivity. This shows that the changes in the demagnetization factors are not the origin of the coercivity reductions observed.

To gain greater insight in the driving force behind the coercivity reduction and the altered domain structure, the relevant energetics of the system were examined. For this,
micromagnetism and domain theory developed for stripe domain structure was used. The original theory was developed for bulk materials and has shown good correlation down to the predicted crossover limit where the material is considered to be a thin film. This crossover is material dependent and is around 40 nm for NiFe$_2$O$_4$. However, this transition is gradual and hard to calculate. The film thicknesses used in this study (60 – 150 nm) are expected to be within the “thick” film regime, however due to the proximity to the crossover limit, study was conducted within the framework developed for thin films also.

The first study was done within the theoretical framework developed for bulk films. The calculated domain size for a 100 nm thick film used as a standard agrees well with the domains sizes observed experimentally using MFM. The estimation of the Bloch domain wall in this scenario seems reasonable and in agreement with the measurements. The relative changes in energy with thickness for the films used in this study are small, with significant energy increase only for micrometer film thicknesses. This indicates that the small differences in thicknesses for the NiFe$_2$O$_4$ film used in this study do not significantly affect the energy density of the system. With this in mind, the relative change in the energy density with varying domain size was examined. The calculations show there is a clear energy minimum with substantially different curve behavior on two sides of the equilibrium position. Lowering the domain size induces a sharp exponential increase in energy due to the creation of large number of new domain walls. This is a very energetically unfavorable scenario. Increasing the domain size past the equilibrium position however, has a very slow and linear effect on energy density.
Results obtained using the theory developed for thin films show somewhat larger than observed domain sizes for a 100 nm thick film. This confirms that the films used in this study are relatively well described within the bulk film regime. The results, however, are similar, indicating proximity to the crossover point and that both regimes must be considered to gain a more complete understanding of the phenomena. Looking at the change in the relative energy density with film thickness reveals very small differences going from the thinnest (60 nm) to the thickest (150 nm) films used in this study. This result is virtually identically to the one obtained using bulk film theory and confirms that the change in the film thickness is not a significant contributor to the observed change in the magnetic domain structure for the samples used in this study. It is only after considering much larger (micrometer) differences in film thicknesses that the effect on the energy density must be considered. This allows use of a 100 nm film thickness as a standard to examine the change in the relative energy density as the domain size varies. Once again, there is a clear energy minimum with two distinctly different behaviors on either side of the curve. Lowering the domain size past the equilibrium value induces a sharp exponential increase in the energy density, while increasing the domain size results in a slow, linear increase similar to what is observed within the framework of bulk film theory. The distinction, however, is that the increase in energy with increasing domain size is much lower as compared to the bulk film theory and in fact even for the case of the maximum observed domain size (750 nm) it constitutes only a ten percent increase. Increasing the domain size up to micrometer scale results in an asymptotic approach to a maximum value, indicating the limits of the theory, which is to be expected as single domains are expected for ultra-thin films.
What is most important is the similarity between results of theories developed for both bulk materials and thin films within the limits of this study. The results clearly demonstrate that changing the domain size from the observed and calculated values for plain films to the maximum observed values in patterned films used in this study does not significantly change the energy density of the system, i.e. the energy required to alter the domain size is relatively small. While the energy required is small, this process will not happen spontaneously and a driving force is needed.

The external “driving force” for the observed change in the domain size is the energy preference of domain walls. A domain wall always seeks to minimize its total area, and so it will remain in valleys where the sample is thinnest [1, 4, 21, 28]. In the case of random surface roughness this effect evens out. If there is a continuous hill or trench running through the sample, however, it will affect the domain structure [1, 2, 4]. In addition, it can easily be shown that the domain wall-inclusion energy is minimal when the inclusion is positioned directly at the center of the wall [1, 4]. The decrease in domain wall energy is proportional to the size of the inclusion and can be large. By patterning the samples, preferential locations for domain wall positions have been created. This has altered the energy minimum domain wall configuration of the samples. The energetically favorable domain wall positions are now at the interface between the film and the protruding feature. Patterning the sample with parallel equidistant features stretching the length of the sample induces an energetically favorable domain wall position along the length of the feature/film interfaces. This is similar to the energy minimization associated with magnetic vortex pinning by defects in
superconductors [29]. This is in accordance with the MFM measurements of the patterned film (figure 6-9), with domain walls formed at the feature/film (hill/trench) boundary.

The MFM measurements on patterned films show that the areas between the boundary domain walls (i.e. hills and trenches) are a single domain. From the theoretical considerations it is seen that the energy cost of stretching the domain from the equilibrium value to the maximum value used in this study (750 nm) is rather low. Taking into account this low energy cost of increasing the domain size, the relatively high energy cost of creating new domain walls and the fact that the material already has a preferential domain wall location, feature sized single domains are expected. These equidistant antiparallel magnetic domains stretching the length of the sample effectively form a parallel stripe domain structure, reducing the coercivity, as observed in the magnetic hysteresis measurements.
7.5. Conclusion

The most likely origins of the change in the domain structure and coercivity observed in the patterned NFO films have been investigated. Demagnetization factors were calculated and the results were validated through comparison with known values. Contrary to some reports in the literature, the change in the demagnetization factor of the material has been ruled out as the source of the coercivity reduction. It was shown that the relative change in the film morphology due to surface patterning has a minimal effect on the demagnetization factor. This is explained by the fact that for thin film, the size change with surface patterning is negligible compared to its surface area. The effects of patterning were evaluated within both the bulk and thin film frameworks of micromagnetism and domain theory. The predicted values of the domain and wall size were shown to be in good agreement with the experimental results for the case of plain films. In both cases, small variations in the film thickness used in this study have been shown to have minimal effect on the energy density of the system. Changing the domain size, however, has a larger impact and any deviation from the equilibrium domain size is energetically unfavorable. While the energy expense to reduce a domain size grows exponentially, stretching a domain has a slow linear dependence on energy. This low energy cost of stretching a domain and relatively high energy cost of creating a new domain wall in combination with the film/feature interface creating an energetically favorable location for domain wall explains the observed stripe domain structure seen in patterned films. The observed coercivity reduction phenomena can then be explained by minimization of the total sample magnetization through stripe domain formation.
References


CHAPTER 8

Conclusions and future work

8.1. Conclusions

This study represents a systematic report on a novel method to reduce the coercivity in magnetic materials and improve coupling in multilayered thin films by patterning the surface. Nickel ferrite thin films were grown on a c-plane sapphire substrate via spin coating a sol-gel solution. Nanoimprint lithography was used as a complementary method to pattern the surface prior to final crystallization. In chapter 4 a modified nanoimprint lithography technique was used to create large scale surface patterned thin films with texture equaling that of the plain films. The feature transfer from the master was precise and without noticeable defects. As a result, the coercivity had been substantially lowered. In chapter 5 coercivity reduction phenomenon was further investigated by extending the study to thicker films grown by the deposition of multiple layers. Different methods to grown thicker films using spin coating were explored and compared. In chapter 6 the effect of changing the surface pattern on the coercivity reduction phenomenon was studied and magnetic force microscopy measurements used to explore the origin of the coercivity reduction. Chapter 7 reports on a theoretical study of coercivity reduction in thick and thin films. The results were calculated and compared to the experimental data to explain the observed domain structure in the patterned films.

The main findings are briefly summarized in the following points:
• Previously developed 2-MOE solvent based NiFe$_2$O$_4$ sol-gel solution preparation procedure was simplified without a loss of quality. The solution was made in air and a final purification step was added.

• A direct nanoimprint lithography technique was used to imprint NiFe$_2$O$_4$ thin films prior to crystallization, eliminating additional steps associated with post imprint etching. In addition, this method removes some of the constraints associated with an etching procedure.

• Surface patterning equaled state-of-the-art reports in the literature with complete pattern transfer over large scale without noticeable defects or grain growth disruption.

• Highly textured surface patterned NiFe$_2$O$_4$ films were grown. The patterning was shown not to affect the degree of texture in the films.

• Coercivity reduction in the surface patterned films, as compared to the unpatterned films, was observed.

• Probable causes for coercivity reduction have been investigated and surface patterning has been shown to be the direct cause of the coercivity reduction phenomena.

• Coercivity reduction has been shown to translate to thicker films.

• To grow thicker films, layer-by-layer and bulk manufacturing methods have been used. A layer-by-layer method, in which individual layers are fully crystallized before a new layer is deposited, has been shown to give better texture than a bulk method. The bulk manufacturing method, in which individual layers are all deposited before a final annealing, has exhibited a larger reduction in coercivity.
• The effect of changing the surface pattern on the topography, crystallography and magnetic properties was investigated and different trends were observed for the measurements done with the magnetic field parallel and perpendicular to the film surface. Coercivity reduction was shown to increase with increasing feature size in the case of magnetic field oriented perpendicular to the film surface. For the field parallel to the film surface the opposite was observed. In all cases, the coercivity was reduced relative to the unpatterned film and relative to the base layer onto which the patterned film was deposited. All films showed a similar magnetic response as indicated by similarities in the curve shape.

• Crystallography measurements showed the imprint process did not affect the grain growth and orientation regardless of the surface feature size as indicated by all films having virtually identical diffraction patterns.

• The lower limit of surface patterning here was shown to be around 500 nm. Below 750 nm, the pattern quality degraded and the feature height reduced.

• The domain configurations of the plain and patterned films were investigated. Deviation from the expected domain configuration was found in the patterned films. The domain configuration of patterned films was similar regardless of the magnetic history of the sample.

• A theoretical study investigated the change in the demagnetization factor with surface patterning. Changes in the demagnetization factor were eliminated as a source of the observed coercivity reduction.
Micromagnetism and domain theory were used to investigate the energetics of different film configurations. Changing the domain sizes within values used in this study has been shown to have a very small effect on the energy of the system. Combining the theoretical prediction with the experimental measurements, the origin of the observed domain structure and coercivity reduction has been shown to be the surface topography induced change in the minimum energy configuration of the sample. This results in the minimization of the total sample magnetization through formation of stripe domains.

8.2. Suggestions for future work

Future directions can focus on further pursuing the fundamental science or advancing the technology. Some of recommended topics are:

- Investigate the effect of surface patterning on coupling in multilayered thin films. The investigation can be conducted on mechanical and magnetic coupling.
- Study the effect of different patterns on the multilayer coupling and the coercivity reduction.
- Expand the study of the effect to different materials and material types.
- Investigation on the high frequency behavior of surface patterned magnetic films.
- Explore the upper scaling limits of the coercivity reduction with regards to feature and the film size.