DEPOSITION, MICROSTRUCTURE AND MAGNETIC ANISOTROPY OF COBALT FERRITE THIN FILMS

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Summary

The potential applications of Co-ferrite films require achieving films with excellent crystallographic texture, perpendicular magnetic anisotropy ($K_u$) and high coercivity on inexpensive substrates at a low temperature.

This thesis mainly focused on fabricating Co-ferrite films using pulsed laser deposition (PLD) with different heating processes, investigating mechanisms for thin film growth and magnetic anisotropy, and tuning crystallographic orientation and magnetic properties of Co-ferrite films.

Firstly, polycrystalline Co-ferrite films were prepared by PLD at room temperature followed by post-annealing. The films showed an isotropic crystallographic orientation and isotropic magnetic properties. The study of magnetic properties of these films indicates that controlling grain size close to single domain size of Co-ferrite materials is critical to obtain high coercivity.

Secondly, Thin film growth mechanisms for both epitaxial and polycrystalline Co-ferrite films with in-situ heating were summarized. When using oxide substrates (single crystal (0001)-Al$_2$O$_3$, (002)-MgO) with the corresponding small lattice mismatch with CoFe$_2$O$_4$, (001)-epitaxial films on (002)-MgO and (111)-epitaxial films on (111)-Al$_2$O$_3$ formed even at a low temperature. With using amorphous oxide layers (Al$_2$O$_3$, MgO, and SiO$_2$) or single crystal SiO$_2$ with different planes, which have no corresponding lattice matching with any plane of CoFe$_2$O$_4$, polycrystalline Co-ferrite films formed. The texture evolution of the polycrystalline films is attributed to the competition between surface or interfacial energy and strain energy density. When film thickness is small or substrate temperature is high, the texture tends to be (111)-texture. Whereas, when thickness is thick or substrate temperature is low, the
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Thirdly, the mechanisms for magnetic anisotropy of both epitaxial and polycrystalline Co-ferrite films with in-situ heating were investigated. Thickness-dependent magnetic anisotropy of both (111) and (001)-epitaxial films illustrates that strain-induced stress anisotropy is critical to be considered for the interpretation of thickness-dependent reorientation of magnetic anisotropy. The calculated values for $K_u$ are well consistent with the measured ones. Furthermore, the evolution of magnetic anisotropy of polycrystalline films can also be well explained with stress anisotropy induced by residual strain. $K_u$ is found to be proportional to out-of-plane strain in polycrystalline films. Therefore, both residual strain and (111)-texture are prerequisite to achieve polycrystalline films with high coercivity and large $K_u$.

Fourthly, based on the previous predictions, a (0001)-ZnO layer was demonstrated as an effective underlayer to obtain Co-ferrite films with excellent (111)-texture, high coercivity (over 10.7 kOe), and large $K_u$ ($2.3 \times 10^6$ ergs/cm$^3$). Especially, these films with nanocrystalline grain size of 20 nm were successfully deposited on inexpensive glass at a low temperature of 300 °C.
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Chapter I Introduction

This chapter gives the background information about this research work. Section 1.1 gives a brief introduction to structure and physical properties of \( \text{CoFe}_2\text{O}_4 \) Co-ferrite materials. Section 1.2 introduces magnetic anisotropy of magnetic thin films. Section 1.3 shows a brief review of film growth mechanisms and strain formation in thin films. Section 1.4 gives a brief literature review of fabricating Co-ferrite films. Section 1.5 describes the motivation and objectives of this research.

1.1 Spinel structure and physical properties of \( \text{CoFe}_2\text{O}_4 \)

Magnetic materials are widely used in many magnetic devices, which play a critical role in almost all electronic apparatus or systems. For a magnet, the most important magnetic parameters can be obtained from a hysteresis loop (magnetization \( M \) versus applied magnetic field \( H \)), as shown in Fig. 1.1.

![Hysteresis Loop](image)

Fig. 1.1. Typical hysteresis loops of a ferromagnetic material.
Among various magnetic materials, magnetic oxides – ferrites have been attracted a lot of research efforts [1,2,3]. The unique electric and magnetic properties of ferrite materials enable them to have a wide range of applications, such as high-frequency devices, microwave components [4,5], magnetic fluids [6,7,8] and magnetic data storage [9] as well as potential biomedical applications (e.g. drug delivery) [10,11].

In terms of crystal structure, ferrites can be classified into three groups, namely, spinel, garnet and magnetoplumbite [12]. The details of these three types of ferrites are shown in Table 1.1.

<table>
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<th>Type</th>
<th>Crystal structure</th>
<th>General Formula</th>
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</tr>
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<tr>
<td>Spinel</td>
<td>Cubic</td>
<td>$M^{II}_{\text{III}}\text{Fe}_2\text{O}_4$</td>
<td>$M^{II}=$Fe, Cd, Co, Mg, Ni, and Zn</td>
</tr>
<tr>
<td>Garnet</td>
<td>Cubic</td>
<td>$M^{III}_{\text{III}}\text{Fe}<em>2\text{O}</em>{12}$</td>
<td>$M^{III}=$Y, Sm, Eu, Gd, Tb, and Lu</td>
</tr>
<tr>
<td>Magnetoplumbite</td>
<td>Hexagonal</td>
<td>$M^{II}<em>{\text{III}}\text{Fe}</em>{12}\text{O}_{19}$</td>
<td>$M^{II}=$Ba, Sr</td>
</tr>
</tbody>
</table>

As an important member in the family of spinel ferrites, Co-ferrite (CoFe$_2$O$_4$) materials have been accepted as the promising candidates for a wide variety of applications, such as magnetic recording and magneto-optic devices. Co-ferrite (CoFe$_2$O$_4$) is chosen as the research subject of this thesis. In the following sections, a review of the crystal structure and the ferrimagnetism in Co-ferrite materials will be presented.
1.1.1 Spinel structure of CoFe$_2$O$_4$

CoFe$_2$O$_4$ belongs to the family of spinels. The spinel family is a group of compounds with a general formula of AB$_2$O$_4$ (A and B are cation; X is an anion). This spinel structure is named after the mineral spinel (MgAl$_2$O$_4$), which is the parent compound of this group. The unit cell of the spinel structure is illustrated in Fig. 1.2. There are eight formula units per cubic unit cell, each of which consists of 32 anions and 24 cations with a total of 56 atoms. As a consequence, the spinel’s lattice parameters are large, for CoFe$_2$O$_4$, $a = 8.38$ Å.

Fig. 1.2. Schematic diagram of the spinel structure, showing octahedral and tetrahedral sites occupied by A and B cations.

The 32 anions, i.e., O$^{2-}$, are arranged in a face-centered cubic (f.c.c.) lattice. There are 64 tetrahedral interstices (A sites) that exist between the anions, 8 of them are occupied by cations. There are 32 octahedral interstices (B sites) between the anions, 16 cations occupy half of the sites. Full occupation of the tetrahedral (8a) sites with a divalent transition metal produces a normal spinel structure, while occupation of the octahedral (16d) sites with divalent transition metal ions yields an inverse
spinel structure. Table 1.2 shows the site occupancy in the normal and inverse spinels. If divalent transition-metal ions are present in both A and B sublattices, the structure is mixed or disordered.

Normally, CoFe$_2$O$_4$ has an inverse spinel structure, with 8 Co$^{2+}$ occupying half of the octahedral sites, 8 Fe$^{3+}$ occupying the rest of octahedral, and the 8 Fe$^{3+}$ in tetrahedral sites. Many factors have influences on the distribution of the cations on A and B sites, including the radii of the metal ions, electrostatic energies of the lattice, and the matching of the electronic configuration of the metal ions to the surrounding oxygen ions. Sometimes, CoFe$_2$O$_4$ can be a partial normal spinel, while the tetrahedral sides are partially occupied by Co$^{2+}$.

Table 1.2. Site occupancy in normal and inverse spinel CoFe$_2$O$_4$.

<table>
<thead>
<tr>
<th>Site type</th>
<th>Interstices (per unit cell)</th>
<th>Number of interstices occupied (per unit cell)</th>
<th>Normal spinel cation occupation</th>
<th>Inverse spinel cation occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedral (A)</td>
<td>64</td>
<td>8</td>
<td>8 Co$^{2+}$</td>
<td>8 Fe$^{3+}$</td>
</tr>
<tr>
<td>Octahedral (B)</td>
<td>32</td>
<td>16</td>
<td>16 Fe$^{3+}$</td>
<td>8 Co$^{2+}$, 8 Fe$^{3+}$</td>
</tr>
</tbody>
</table>

1.1.2 Ferrimagnetism of CoFe$_2$O$_4$

Ferrimagnetism was proposed by Néel to describe the magnetization behaviours of ferrite materials in which the magnetic ions occupy two different crystallographic positions and with antiferromagnetic arrangement. He made the assumption that the exchange force acting between an ion on A site and an ion on B site was negative [13,14]. Thus the lattice of A ions spontaneously magnetized in one
direction and the lattice of B ions spontaneously magnetized in an opposite direction, namely antiparallel to each other as shown in Fig. 1.3(a). However, the difference in the magnitude of magnetization of A site and B site leads to a net spontaneous magnetization without an external field. Therefore, just as ferromagnetic materials, ferrimagnetic materials exhibit substantial spontaneous magnetization at room temperature which makes them industrially important. With temperature increasing, the arrangement of the spins is disturbed by thermal agitation which is accompanied by a decrease of spontaneous magnetization. At a certain temperature, called the Curie point ($T_c$), the thermal agitation leads to the random arrangement of the spins and the spontaneous magnetization vanishes, as shown in Fig.1.3(b). Above the Curie point ($T_c$), the substance exhibits paramagnetism, and the susceptibility ($\chi$) decreases with increasing temperature (Fig.1.3(b)).

![Fig. 1.3. The schematic drawing for ferrimagnetism: (a) spin configuration in two sublattices; (b) the variation of magnetization ($\sigma_s$) with the temperature.]

Based on the Néel ferrimagnetism, the saturation magnetization of Co-ferrite materials at 0 K can be calculated using the ionic moments of Co$^{2+}$ and Fe$^{3+}$ in both A and B sites. Table 1.3 shows the calculated net magnetic moment per formula of CoFe$_2$O$_4$ for Co-ferrite with fully inverse and partially inverse structure. Using 3 $\mu$B per Co$^{2+}$ and 5 $\mu$B per Fe$^{3+}$, the calculated saturation magnetization of the complete
inversed $\text{CoFe}_2\text{O}_4$ is $3 \mu B$ per formula. However, $\text{CoFe}_2\text{O}_4$ usually has a partially inversed structure. In this case, if the inversion extent is $\delta$, the calculated saturation magnetization is $(7-4\delta)$ per formula of $[\text{Co}_{1-\delta}\text{Fe}_\delta]_A[\text{Co}_\delta\text{Fe}_{2-\delta}]_B\text{O}_4$.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Structure</th>
<th>A sites</th>
<th>B sites</th>
<th>Net moment per formula ($\mu B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CoFe}_2\text{O}_4$</td>
<td>Fully inverse $[\text{Co}]_A[\text{Fe}_2]_B\text{O}_4$</td>
<td>$\text{Fe}^{3+}(5\downarrow)$</td>
<td>$\text{Fe}^{3+}(5\uparrow)$, $\text{Co}^{2+}(3\uparrow)$</td>
<td>3</td>
</tr>
<tr>
<td>$\text{CoFe}_2\text{O}_4$</td>
<td>Partially inverse $[\text{Co}<em>{1-\delta}\text{Fe}</em>\delta]<em>A[\text{Co}</em>\delta\text{Fe}_{2-\delta}]_B\text{O}_4$</td>
<td>$\text{Fe}^{3+}(5\downarrow)$</td>
<td>$\text{Fe}^{3+}(5\uparrow)$, $\text{Co}^{2+}(3\downarrow)$, $\text{Co}^{2+}(3\uparrow)$</td>
<td>$7-4\delta$</td>
</tr>
</tbody>
</table>

Additionally, Table 1.4 gives a short summary of some physical properties of $\text{CoFe}_2\text{O}_4$ bulk materials.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter $a$ (Å)</td>
<td>8.38</td>
</tr>
<tr>
<td>Space group</td>
<td>$Fd3m$ (227)</td>
</tr>
<tr>
<td>Curie temperature ($^\circ$C)</td>
<td>520</td>
</tr>
<tr>
<td>Magnetocrystalline anisotropy constant</td>
<td>$2 \times 10^6$ ergs/cm$^3$</td>
</tr>
<tr>
<td>Magnetostriction constants $\lambda$</td>
<td></td>
</tr>
<tr>
<td>$\lambda_{111}$</td>
<td>$-200 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\lambda_{100}$</td>
<td>$120 \times 10^{-6}$</td>
</tr>
<tr>
<td>Stiffness constants $(10^{12}$ dynes/cm$^2)$</td>
<td></td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>2.73</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>1.06</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>0.97</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>5.29</td>
</tr>
</tbody>
</table>
With the advance of miniaturization of devices and the maturity of integrated chip (IC) fabrication processes, thin films of Co-ferrite are of great interest due to their potential applications in high density data storage, magneto-electronic devices and microelectromechanical system devices (MEMS) [15, 16]. Scientifically, they also provide a great opportunity to study magnetism at small length scales. In next sections, basic magnetic anisotropy and growth mechanism of thin films are reviewed, which provides the background to understand this work.

1.2 Magnetic anisotropy and coercivity of thin films

1.2.1 Magnetic anisotropy of films

Magnetic anisotropy is the coupling of the magnetization of a material to particular directions, either at a local or a macroscopic level. It means that the measured magnetic properties depend on the direction, in which the magnetic field is applied. Without an applied field, the magnetization will lie along preferred direction(s). Magnetic anisotropy is responsible for coercivity and remanent magnetization that are needed for permanent magnets or magnetic recording media. For these technologies, high anisotropy is generally advantageous, as it causes the moment to remain fixed in the desired direction. Especially, as for magneto-optic recording and perpendicular recording media, thin films are required to have perpendicular anisotropy. A higher magnetic anisotropy allows greater thermal stability of magnetic bits, and hence can lead in a reduction of the bit size. At the same time, minimizing magnetic anisotropy is equally important for technologies that require high susceptibility, such as transformers and magnetic inductors. Understanding of anisotropy mechanisms is thus crucial to the technological use of nearly all the magnetic materials, especially for magnetic films.
There are many sources of magnetic anisotropy in solids. All sources of anisotropy are fundamentally linked to the structure of the material. One of the most important sources of anisotropy is the magneto-crystalline anisotropy that is associated with the symmetry of that structure. In the case of thin films, beside of the magneto-crystalline anisotropy, interface and strain stresses may cause additional magnetic anisotropy. Experimentally, it is not always easy to separate these contributions. For films with uniaxial magnetic anisotropy, the overall magnetic anisotropy $K_u$ is usually written as a sum of the various contributions [14].

$$K_u = K_{sh} + K_{ui} + K_{u\sigma}$$  \hspace{1cm} \text{Eq. 1.1}

Where $K_{sh}$ is the shape anisotropy; $K_{u\sigma}$ is the stress-induced anisotropy; $K_{ui}$ is the intrinsic magnetocrystalline anisotropy.

The source of shape anisotropy lies in the difference in demagnetization factors in the directions parallel and perpendicular to the film plane; this energy is fundamentally a summation of the magnetic dipole-dipole coupling of all the magnetic moments in the film. For a film whose thickness is much less than its other dimensions, shape anisotropy gives an easy axis in the film plane, which is equivalent to a hard perpendicular axis:

$$K_{sh} = -2\pi M_s^2$$  \hspace{1cm} \text{Eq. 1.2}

Where $M_s$ is the saturation magnetization of magnetic thin films.

The microscopic origin of magnetocrystalline anisotropy is related to the spin state of the magnetic moments and by the symmetry of their arrangement in the crystal lattice that involves spin-lattice coupling. It occurs in all crystalline ferro- and ferrimagnetic materials. The anisotropy can be described phenomenologically in terms of the direction cosines of the magnetization with respect to rectangular coordinate axes or in terms of spherical harmonics. Any perpendicular magnetization
will realistically occur in an effectively uniaxial system. The magnetocrystalline anisotropy gives, for Co-ferrite (CoFe₂O₄) with a simple cubic symmetry:

\[ K_m = K_i (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2 + \ldots \]  

Eq. 1.3

in terms of the anisotropy constant \( K_i \) and the cosine angles \( \alpha_1, \alpha_2, \alpha_3 \) between the magnetization and the \( a, b, c \)-axes of crystal lattice.

For Co-ferrite (CoFe₂O₄), \( K_i \) at room temperature is \( 2.0 \times 10^6 \) ergs/cm³ [13]. The large magnetocrystalline anisotropy results mainly from the contribution of Co²⁺ ions in the spinel lattice. To explain the origins of the large magnetocrystalline anisotropy of CoFe₂O₄, based on one-ion model, J. C. Slonczeweski [17] proposed that the large magnetocrystalline anisotropy could be ascribed to the incompletely quenched orbital moment of Co²⁺ ions in the octahedral sites (B sites) of the spinel lattice. The residual orbital moment of Co²⁺ is constrained by the crystal electric field to lie parallel to the axis of trigonal symmetry. Spin-orbit energy couples the spins to this axis, accounting for the large anisotropy energy of CoFe₂O₄. Accordingly, the magnetocrystalline anisotropy of CoFe₂O₄ materials is closely related to the distribution of magnetic ions in the sublattices, i.e. tetrahedral (A) sites and octahedral (B) sites. Therefore, any changes in the site occupation of Co²⁺ ions may result in the change of magnetocrystalline anisotropy, and then coercivities.

Stress anisotropy comes from stresses produced in the films during the deposition process, or by thermal expansion differences or lattice parameter differences between substrates and magnetic films [18]. The magnetoelastic energy produced by a stress \( \sigma \) is essentially the product of this stress and the resulting value of magnetic strain or magnetostriction \( \lambda \). Assuming a uniaxial system, the volume magnetoelastic energy is given by

\[ F_{me} = -3\sigma \lambda \cos^2 \theta / 2 \]  

Eq. 1.4
where $\lambda_s$ is an isotropic magnetostriction coefficient and $\theta$ is the angle between the magnetization $M$ and $\sigma$. Stress can therefore create uniaxial anisotropy with a relevant stress-induced anisotropy constant given by

$$K_{a\sigma} = 3\sigma\lambda_s / 2$$

Eq. 1.5

As shown in Table 1.4, for Co-ferrite (CoFe$_2$O$_4$), it has a very large magnetostriction $\lambda_s$. $\sigma$ is given as

$$\sigma = C \cdot \varepsilon$$

Eq. 1.6

in which $\varepsilon$ is the strain tensor and $C$ is the matrix of stiffness constants, which are also listed in Table 1.4.

### 1.2.2 Size effects on magnetic properties

The coercivity of fine particles has striking dependence on their size. As the particle size is reduced, the coercivity increases, goes through the maximum and then tends toward zero. It can be best explained on the basis of the following figure.

Fig. 1.4. Variation of coercivity $H_c$ with particle size $D$.
This figure shows the dependence of coercivity on particle size. The maximum of coercivity usually appears in the range of single-domain particle size. The formation of single domain and multi-domain depends on the minimization of the total energy, i.e. sum of magnetostatic energy and domain wall energy [19].

In small particles, particularly in the single domain region, magnetization reversal is dominated by the coherent rotation. In coherent rotation mode, a high magnetic anisotropy can result in a large resistance against rotation, therefore in a high coercivity. Although, in single domain region the coercivity ($H_c$) also decreases with decreasing particle size ($D$) below $D_s$ (single domain size) due to randomizing effect of thermal energy according to the relation [20],

$$H_c = [1 - (\frac{D}{D_s})^{0.77}] (0.96K_a/M_s)$$

where $K_a$ is magnetic anisotropy constant and $M_s$ is saturation magnetization. When the particle size approaches to $D_p$ (superparamagnetic size), the thermal energy becomes comparable to magnetocrystalline anisotropy energy. Coercivity becomes zero due to thermal fluctuation.

In relatively large particle multi-domain exists, where coercivity varies inversely with the size of the particle in accordance to the equation, $H_c = a + \frac{b}{D}$, where $a$ and $b$ are constants for a given material [14]. In this case, coercivity is determined by nucleation and domain wall motion. Since the nucleation process is caused by inhomogeneities, and the probability of large inhomogeneities is high at surface of the particle. The inhomogeneities much larger than Bloch wall width reduce the coercivity due to local reduction in magnetic anisotropy constant. Therefore, the large particle, due to large surface area per particle has more large inhomogeneities, and magnetization reversal is governed by nucleation controlled
mechanism. Also, domain wall motion becomes easy due to nucleation. Hence, the coercivity of large particle is low.

### 1.3 Growth, texture evolution and strain formation in thin films

This section gives a brief background to understand growth mechanisms of Co-ferrite films described in the latter chapters. Fig. 1.5 outlines the fundamental processes through which the grain structure of polycrystalline thin films develop during film formation. These processes include nucleation, growth, coalescence and thickening [21].

Fig. 1.5. Overview of grain structure evolution of thin films [21].

#### 1.3.1 Nucleation and growth
There is no clear demarcation between the end of nucleation and the onset of nucleus growth. In equilibrium phase diagrams, when the critical lines separating stable phase field are crossed, a new phase appears. Solidification or solid state phase transformation from the unstable melts or solid matrices may be triggered at this point. When such a transformation occurs, a new phase of generally different structure and composition emerges from the prior parent phase or phases. The process known as nucleation occurs at the very early state of phase change. Film formation occurs when atoms or molecules attach themselves to the substrate and aggregate; they tend either to grow in size or disintegrate into smaller entities through the process of dissociation.

![Diagram of nucleation process](image)

**Fig. 1.6. Schematic diagram of nucleation process on substrate surface during deposition [22].**

Fig. 1.6 shows the normal cap-shaped nucleus in deposition. The radius of the cap-shape nuclei is \( r \). The curved surface area between the nuclei top surface and the free space \( (a_1r^2) \), the surface area between the substrate and the condensed phase \( (a_2r^2) \), and the volume of film nucleus \( (a_3r^3) \) are involved in the deposition; the respective geometric constants are

\[
a_1 = 2\pi(1 - \cos \theta) \quad \text{Eq. 1.7}
\]
\[
a_2 = \pi \sin^2 \theta \quad \text{Eq. 1.8}
\]
\[ a_3 = \pi \left( 2 - 3 \cos \theta + \cos^3 \theta \right) / 3 \]  
Eq. 1.9

The free-energy change \((\Delta G)\) accompanying the formation of an aggregate of mean dimension \(r\) is given by:

\[ \Delta G = -a_3 r^3 \Delta G_v + a_1 r^2 \gamma_{vf} + a_2 r^2 \gamma_{fs} - a_1 r^2 \gamma_{sv} \]  
Eq. 1.10

Here, \(\gamma_{vf}\) refers to the surface energy between the surfaces of film and the surrounding medium; \(\gamma_{fs}\) refers to the interface energy between the surfaces of the substrate and film; and \(\gamma_{sv}\) refers to the surface energy between the surfaces of the substrate and the surrounding medium. The change of chemical free energy per unit volume, \(\Delta G_v\), drives the condensation reaction. When a new interface appears, there is an increase in surface free energy, here the positive sign for the first two surface terms. Similarly, the loss of interface under the cap implies a reduction in system energy and negative contribution to \(\Delta G\).

The dependence of Gibbs energy of nucleation on nuclei radius is shown schematically in Fig. 1.7, which demonstrates that there are a critical radius, \(r^*\), and a critical free-energy barrier for nucleation \(\Delta G^*\).

**Fig. 1.7.** Free energy \((\Delta G)\) as a function of cluster \((r<r^*)\) or stable nucleus \((r>r^*)\) size.
If a solid-like cluster of atoms momentarily forms by some thermodynamic fluctuation, but with radius less than \( r^* \), the cluster is unstable and will shrink by losing atoms. Clusters larger than \( r^* \) have surmounted the nucleation energy barrier and are stable. They tend to grow larger while lowering the energy of the system.

When critical cluster sizes are sufficiently large that the crystallography of the nucleating phase is defined, specific nuclei crystallographic orientations will minimize surface and interface energies [23], with nucleation rates higher for nuclei with energy minimizing orientations. In this case, nucleation is orientation selective, and the nucleation process can play an important role in determining the distribution of orientations in the resulting films.

After nucleation, the average island size with a system of isolated islands can increase through a coarsening process. This can occur through detachment of atoms from islands and diffusion of atoms on the substrate surface to attach to other islands, resulting in the shrinkage and even disappearance of some islands and the growth of other islands, so that the average island size increases. Such a coarsening process would be driven by differences in the average energy per atom for islands of different sizes. For islands with the same surface and interface energies, the energy per atom will scale with the island surface to volume ratio, so that the atoms in small islands will have high energies relative to those in larger islands. In the more general case, the free energy per atom in an island will be a function of the island size and of the total surface and interface energies of the island.

Because the surface and interface energy are a function of the crystallographic orientation of the lattice of the island relative to the orientations of the substrate lattice and interface plane, the energy differences driving coarsening processes include
contributions that depend on the crystallographic orientation of an island as well as its size relative to that of its neighbors.

1.3.2 Coalescence

With the islands further growing up, they will make contact together. There is an energetic driving force for formation of a grain boundary that eliminate the energies of the free surfaces of the two contacting islands, in exchange of the low energy of the newly formed grain boundary. This process is called coalescence.

Considering a fully coalesced polycrystalline films, grain coarsening can occur through motion of grain boundary resulting in the shrinkage and elimination of small grains which, in turn, result in an increase in the average size of the remaining grains. This is a well-known phenomenon called grain growth.

1.3.3 Texture evolution

With the grain growth in films, the thickness of films becomes thicker and textured through the preferential growth of grains with crystallographic orientations. One aspect of energetics of texture formation is minimization of surface and interface energy; another important aspect of the energetics of grain growth in thin films is that they are often under high intrinsic or extrinsic stresses. In continuous films, these strains are largely biaxial, thus the associated strain energy density in different grains is given by

$$E_s = \varepsilon^2 M_{hkl}$$

Eq. 1.11

and depends on the magnitude of the strain $\varepsilon$ and the effective biaxial modulus $M_{hkl}$. $M_{hkl}$ depends on the crystallographic direction $(hkl)$, which is normal to the plane of
the film and therefore normal to the plane of the strain. The biaxial modulus for grains with arbitrary \((hkl)\) texture can be calculated using equations given in ref. [24].

In terms of energy minimization, surface and interface energy minimization and strain energy minimization compete in defining the texture during grain growth. The average driving force arising from surface and interface energy minimization is

\[
\overline{E}_{s/i} = \frac{\Delta \gamma_s + \Delta \gamma_i}{h}
\]  
Eq. 1.12

where \(\Delta \gamma_s\) is the difference in the average surface energy of the film and the minimum surface energy, \(\Delta \gamma_i\) is similarly defined for the interfacial energy, and \(h\) is the film thickness. It is thought that for polycrystalline films on amorphous substrates, interface energy minimization does not favor growth of grain with specific in-plane orientation. However, for polycrystalline films on single-crystal substrates or textured underlayers, \(\Delta \gamma_i\) depends on the in-plane orientation of the grain, and grain growth is expected for films composed of grain with three-dimensionally constrained or epitaxial orientations.

The average driving force arising from strain energy density minimization is

\[
\overline{E}_e = \varepsilon^2 \Delta \overline{M}
\]  
Eq. 1.13

where \(\Delta \overline{M}\) is the difference in the average biaxial modulus of the film and the minimum modulus. A transition in dominant texture will occur when \(\overline{E}_{s/i} = \overline{E}_e\), with surface and interface energy minimization dominating when \(\overline{E}_{s/i} > \overline{E}_e\), i.e. in films with low \(h\) and \(\varepsilon\), and strain energy minimization dominating when \(\overline{E}_{s/i} < \overline{E}_e\), i.e. in thicker films with higher elastically accommodated strains. One way in which \(\varepsilon\) can be varied at the temperature at which grain growth occurs is to vary the deposition temperature, \(T_{dep}\), so that strain energy minimizing textures are expected to be favored.
during grain growth of films which are deposited at low temperatures. In sufficiently thin films surface and interface energy minimizing textures are favored, regardless of their strain or thermal history.

1.3.4 Strain formation in thin films

Strain $\varepsilon$ in thin films can be introduced during and after fabrication of thin films. These are established when the constraint of the substrate forces the atoms in the film to maintain a spacing different from their equilibrium positions under the ambient conditions [25].

Of the strains that occur during processing, the simplest conceptually are epitaxial strains arising during heteroepitaxial growth. The elastic accommodation strain is

$$
\varepsilon = \frac{\Delta a}{a} = \frac{a_s - a_f}{a_s}
$$

Eq.1.14

where $a_s$ and $a_f$ are the lattice parameters of the film and substrate.

Another strain called thermal strain results from a thermal coefficient mismatch between substrates and films. The strain needed to fit the film to the substrate is

$$
\varepsilon = -(\alpha_f - \alpha_s)(T - T_0) = -\Delta\alpha\Delta T
$$

Eq.1.15

where $\alpha_s$ and $\alpha_f$ are the thermal expansion coefficient of the film and substrate, respectively. $T$ is the current temperature, and $T_0$ is the initiate temperature at which both film and substrate are in a strain-free state.

Other strains arising during processing are sometimes referred to as growth strains. Among the mechanisms that can introduce growth strain are grain growth, the introduction of defects and dopants, and the sintering and drying of powder compacts [26,27]. Another source for the growth strains in thin films can result from the
deposition process itself. The temperature for film deposition is often far below the melting temperature of the material. The deposition then occurs under highly nonequilibrium conditions; the atoms are insufficient mobile to attain minimum energy positions during depositions. The sign of the strain depends on the nature of the deposition. Sputtering typically produces films in compression, since newly arriving atoms are forced into places where they do not belong. Films produced by chemical vapor deposition (CVD), on the other hand are frequently initially in tension, as a result of the departure of by-products, such as water, of the deposition reaction. Plasma enhanced chemical vapor deposition (PECVD) may produce films in compression, due to ion implantation from the plasma.

1.4 Fabrication of Co-ferrite thin films

Because Co-ferrite films have their unique physical properties, such as high Curie temperature, large magnetic anisotropy, moderate magnetization, excellent chemical stability, large Kerr and Faraday rotations, and low cost [28,29,30,31,32], they have attracted much attention in recent years as one of the candidates for high density magnetic recording, magneto-optical recording media, hard permanent magnet and microelectromechanical system (MEMS) devices. Recent studies also demonstrated that Co-ferrite films could also act as a pinning layer to enhance room-temperature spin filtering in a magnetic tunnel junction (MTJ) [33]. Furthermore, epitaxial CoFe2O4 films were also achieved to be utilized in multiferroic devices due to their large magnetostriction [34,35]. The application of magnetic recording thin film media requires small grain size, excellent out-of-plane texture, smooth surface roughness (<2 nm for 500 Gb/in²), large perpendicular anisotropy and high coercivity [36]. Likewise, the application of hard magnetic thin films as the pinning layer in
spintronics devices also requires uniaxial magnetic anisotropy, large coercivity and small surface roughness (<1 nm) to reduce surface scattering for spin current transport [37]. Basically, for all these applications as described above, magnetic anisotropy ($K_u$) and coercivity (over 6 kOe) are key parameters, which need to be studied. Accordingly, various methods have been used to fabricate Co-ferrite films with different heat treatment processes to tune their microstructure and magnetic properties.

Firstly, chemical methods were used to prepare Co-ferrite films since they are relatively inexpensive and do not need high vacuum. Among these methods, chemical vapor deposition (CVD) was utilized to synthesize Co-ferrite films by Dhara [38]. However, the films possessed a low coercivity ($H_c$) of less than 1.0 kOe after post-annealing at 450 ºC, and the films were inhomogeneous with rough surface as well as lacking of preferential orientation. On the other hand, Sol-gel was another chemical method for deposition of Co-ferrite films [39,40]. Although this method can enhance $H_c$ to 2.5 kOe, it required high heat-treatment temperature over 900 ºC. After such a heat treatment, grain size was over 60 nm, which was too large for high density magnetic recording. At the same time, Kitamoto [41] reported a new chemical method, spin spray ferrite plating. This method was able to deposit films with perpendicular anisotropy after deposition at 90 ºC, which was a great progress in achieving Co-ferrite films at a low temperature. However, the disadvantage of this method was that the $H_c$ was still low, less than 3 kOe.

Since the coercivity of Co-ferrite films prepared using chemical methods is still not large enough for potential applications, many research groups have experimented with physical methods to obtain high coercivity Co-ferrite films. RF sputtering is one of these methods which are applied broadly in modern
microelectronics technology for the fabrication of ceramics films. Ding’s group has prepared Co-ferrite films with the grain size of 60-70 nm and $H_c$ over 7.4 kOe but with no magnetic texture and preferential crystallographic texture [42]. In their work, the films were post-annealed with the temperature over 700 °C. Recently, Lee also prepared Co-ferrite films using sputtering with both substrate heating and post-annealing processes [43]. Their films also showed a relatively high coercivity but without magnetic anisotropy or crystallographic orientation. Even worse, these films possessed a large grain size and broad size distribution. Up to this point, although Co-ferrite films using RF sputtering could achieve high $H_c$, the relationship between microstructure (grain size, orientation, effects of temperature, substrate and thickness) and magnetic properties was still unknown. To study this relationship more clearly, Wang [44] systematically investigated magnetic properties of Co-ferrite films using sputtering and found it to be highly dependent on annealing temperature, film thickness, and annealing duration. All the films under his works presented isotropic crystallographic orientation. The film with the $H_c$ of approximately 9.3 kOe was successfully obtained. Based on thickness-dependent coercivity and the fitting of X-ray diffraction data to extract strain data, it was assumed that high coercivity may be associated with the large residual strain in the films. So far, no quantitative model has been proposed to explain the coercivity mechanism and to predict magnetic properties of Co-ferrite films. Moreover, Gu [45] have prepared nanocrystalline Co-ferrite films on quartz with RF sputtering with post-annealing process recently. Although the films exhibited (311) and (220) preferred orientations, they possessed no magnetic texture with $H_c = 3.0$ kOe.

Besides the growth of polycrystalline Co-ferrite films, single crystal CoFe$_2$O$_4$ films were also reported previously. Suzuki [46] have fabricated single crystal (001)-
Co-ferrite films on CoCr$_2$O$_4$ buffered SrTiO$_3$ using pulsed laser deposition (PLD). The films showed perpendicular magnetic anisotropy, which was dependent on film thickness. This was explained with the dominant role of strain induced magnetic anisotropy. After that, single crystal (001)-CoFe$_2$O$_4$ films on single crystal (002)-MgO using oxygen-plasma-assisted molecule beam epitaxy (OPA-MBE) also exhibited thickness-dependent magnetic anisotropy [47]. However, it still needs more works to quantitatively study the strain induced magnetic anisotropy.

1.5 Motivation and objectives

As various methods including both chemical and physical ones are utilized to fabricate Co-ferrite films, different crystallographic structures (isotropic, textured and epitaxial) have been reported and various magnetic anisotropies (in-plane, out-of-plane and isotropic) have been observed. There are still several problems, which I will cover in this thesis. The first one is how to fabricate Co-ferrite films with small grain size, high coercivity, and large perpendicular $K_u$ at a low deposition or post-annealing temperature. The second is how to clarify the relationship between microstructure and magnetic properties of Co-ferrite films, in order to understand the mechanisms for thin film growth, high coercivity, and large magnetic anisotropy. The third one is how to optimize crystallographic orientation and magnetic anisotropy of Co-ferrite films based on the understandings.

In order to overcome the problems described above, the purposes of this study can be listed as the following:

1. To explore the feasibility of depositing of high-coercivity polycrystalline Co-ferrite films using PLD with post-annealing processes and to investigate the
relationship between microstructure (e.g. grain size, texture) and magnetic properties of the resultant films. (Chapter 3).

2. To explore the feasibility of achieving epitaxial Co-ferrite films with different orientations and thicknesses using PLD. With the epitaxial films as the samples, to quantitatively model the magnetic anisotropy of these films related to different contributing factors such as shape anisotropy, magnetocrystalline anisotropy and stress anisotropy and to determine the main contributing factors (Chapter 4).

3. To explore the feasibility of the deposition of high-coercivity polycrystalline Co-ferrite films using PLD with in-situ heating process and to investigate the effects of experimental parameters such as thickness, temperature, substrate on the magnetic properties of the resultant films. With the experimental results, to propose the physical mechanisms of film growth, texture evolution, strain formation and sources of magnetic anisotropy for polycrystalline thin films. (Chapter 5 & 6)

4. Based on the understandings of physical mechanisms for film growth and magnetic anisotropy of Co-ferrite films, to develop an experimental method to obtain Co-ferrite films with high coercivity, large perpendicular anisotropy, small grain size, and excellent texture on inexpensive substrates at low temperatures. (Chapter 7)

1.6 References


2 Chapter II Thin film deposition and characterization

The experimental details including thin film deposition using pulsed laser deposition (setup, mechanisms, and features), structural characterization, and magnetic property characterization are given in this chapter.

2.1 Pulsed laser deposition system

Pulsed laser deposition (PLD) is now a well-established technique for growing high-quality thin films such as insulator, semiconductor and superconductors. This technique was introduced in 1960’s and kept on developing with the step of high energy laser technology [1]. In 1984 and 1985, the excimer laser was used to get shorter pulse duration and high pulse energy, which were found to be favorable for better film quality and higher deposition rate. In 1987, PLD was first successfully applied in the fabrication of high $T_c$ superconducting (HTS) thin films.

2.1.1 Setup of PLD system

The deposition system consists of an excimer laser, guiding optics, vacuum chamber, and vacuum pumps. The most commonly used laser is a pulsed excimer laser with a wavelength in the UV range. Fig. 2.1 shows the schematic diagram of the PLD system used in this study.

A KrF excimer laser (Lamda Physik Compex 205), operating at a wavelength of 248 nm, with a repetition rate from 1 Hz to 50 Hz and pulsed duration of about 23 ns, was used in our lab.

The laser beam was guided through a focusing lens ($f = 50$ cm). After passing through a UV SiO$_2$ window located on the wall of the vacuum chamber, the laser
beam was focused on the targets at an incident angle of 45°. The target was mounted on the rotating target holder. A small DC motor was used to rotate the target. By mounting six targets on the holder, a number of materials could be deposited without breaking the vacuum, permitting the multilayer structures.

Fig. 2.1. Schematic diagram of the pulsed laser deposition system.

The load lock system was adapted to transfer the substrate without opening the main chamber (18"). The substrates were mounted on a spring-loaded susceptor plate,
which was fixed on a heating block. The heating block could be heated up to 1000 °C. A type K thermocouple was used to monitor the temperature.

The main chamber was pumped with a turbo-pump (UMU520H) and a MD4 membrane pump (oil-free roughing). The optimal base pressure could reach $5 \times 10^{-8}$ Torr. A convectron (10 mTorr ~ 1 atm.) and a cold cathode vacuum gauging ($1 \times 10^{-10}$ torr ~ 10 mTorr) were used the gas pressure inside the chamber. One fine and coarse valve attached to a flowmeter were used to adjust flow rate. The working gas pressure during thin film deposition was adjusted through changing the flow rate and the pumping speed of turbo-pump.

### 2.1.2 Mechanisms of PLD

PLD is one kind of physical vapor deposition, in which films are formed by atoms directly transported from source to substrate through gas phase. There are three major physical processes involved in the deposition.

1. **Laser beam and target surface interaction**
   
   A pulsed laser beam is focused onto the surface of a metallic or ceramic target by an optical focus lens. The surface layer material of the target is evaporated when the laser energy density (energy per unit area at the target surface) is above a threshold value, forming a plasma plume with high energetic species.

2. **Dynamic of the ablation materials**
   
   The material evaporated from the target is highly energized and consists of exited and ionized species forming the plasma. The plasma expands away from the target with a strongly forward-directed trajectory toward a heated substrate placed directly in the line of the plume.

3. **Film condensation**
The dissociated energetic species impinge onto the substrate surface and the mechanism of the interaction is illustrated in Fig. 2.2. Equilibrium is established between the incoming and re-evaporating species depending on the rate of the particles and substrate temperature, which in turn determines the film growth rate.

![Schematic diagram of nucleation and growth of films on a substrate.](image)

**Fig. 2.2. Schematic diagram of nucleation and growth of films on a substrate.**

Each stage in PLD is critical to the formation of high quality thin film in terms of epitaxy, stoichiometry, and surface roughness. Several parameters need to be optimized for specific material growth, such as substrate temperature, laser energy density and frequency, background pressure, and target to substrate distance.

The crystalline film growth depends on the surface diffusion of the atoms. Normally, the atoms will diffuse through several atomic distances before sticking to a stable position within the newly formed film. High temperature gives atoms high mobility which results in rapid and defect free crystal growth, whereas a crystal growth at low temperatures or large super-saturations may be dominated by the energetic particle impingement, resulting in disordered or even amorphous structures. To achieve an epitaxial growth, the substrate temperature should be optimized, which
is different for different materials. The energy density of the laser beam has significant affects the uniformity of the film. Target-to-substrate distance is a parameter that governs the angular spread of the ablated materials. The oxygen partial pressure is also a very important parameter in the growth of oxide films.

2.1.3 Features of PLD

Compared with other thin film deposition methods, PLD shows several advantages such as:

1. The ability to transfer the target stoichiometry accurately and effectively to the film, so it was widely used to manufacture the high temperature superconducting and other complex oxide thin films. The laser intensity is on the order of $10^8$ and $10^9$ W/cm$^2$, which results in extremely high heating rates of the target (100 K/s). The target elements evaporate simultaneously regardless of different evaporating points. The very short duration time of the laser pulse ensures negligible evaporation loss of the target, so that every component of the target phase has a similar deposition rate thus yielding thin films which replicate the target composition. Actually, among film deposition techniques, PLD has the best control of the stoichiometry of films with respect to the target materials and is applicable in the wide range of ambient reactive gas pressure, typically from $10^{-9}$ to $10^{-2}$ Torr [2];

2. High deposition rate (>12 Å/sec) and relatively low deposition temperature. It is due to that the dissociated target species are highly energetic. Consequently, even substrate materials with low melting point can be used;

3. Simple and versatile. The decoupling of the vacuum hardware and evaporation power source make this method so flexible that it is adaptable to different operation modes. All kind of materials can be grown by PLD as long as the laser energy density is high enough to dissociate the target surface material. Furthermore,
film growth can be carried out in a reactive environment containing any kind of gas with or without plasma excitation. These advantages enable PLD for fabrication of a long list of different materials. Until now, nearly two hundred kind of materials have been fabricated into thin films by PLD, including metals, various oxides, semiconductor, borides, nitrides, fluorides, silicides, sulfides, polymer, diamond-like carbon, etc [3].

There are, however, certain drawbacks associated with PLD. The intrinsic “splashing” associated with laser ablation results in the incorporation of micron to submicron size particles on the film surface. However, a number of techniques can eliminate the particles, which include using a high quality target, velocity filter and shadow mask, etc. Scaling up is another concern for PLD. The highly directional plume makes the film uniform only over a relatively small area. Up to date, PLD is mainly used in research purposes. Nevertheless, with the demand for improved electronics based on metal-oxide, or other multicomponent thin films, the commercial development of PLD systems is undertaken. It has been reported that some PLD systems can deposit thin films on 8-inch wafers with the deposition rates of more than $1\times10^{-6}$ cm/s [4].

### 2.2 Target and film preparation

#### 2.2.1 Mechanical alloying

In this project, mechanical milling and subsequent sintering are used in the fabrication of targets for PLD processes. Mechanical alloying has been widely used as one of the most efficient synthesis techniques for obtaining large quantities of nanoparticles or nanocrystalline powders. Mechanical alloying is also called mechanical activation or high-energy ball milling. During mechanical alloying, a
solid-state reaction takes place. The fresh powder surfaces of the reactant materials are subjected to high-energy collision by the balls. The repeated cold-welding and fracturing [5] of the powder mixture are the two most important processes involved in mechanical alloying.

SPEX shaker mills, planetary mills [6] and horizontal ball mills are three types of mills commonly used for mechanical alloying. The basic principle of operation is the same for all the above mills. The structure and properties of milled powders are related to a number of parameters, such as: the size of the balls, the energy intensity, weight ratio of powders to balls, the number of balls, the milling temperature, the milling atmosphere, and milling time.

In our work, a planetary mill (Frisch GmbH) was used to obtain nano-sized Co-ferrite powders as the starting materials for preparing Co-ferrite target. Cobalt powders (99.9 % purity) and $\alpha$-Fe$_2$O$_3$ powders (99.9 % purity) with the molar ratio of 1:1 were mechanically milled. The mixed powders of ~20 g and stainless steel balls (10 mm in diameter) with a weight ratio of 1:10 were loaded in a hardened stainless steel container. The planetary mill was operated at a rotation disk speed of 300 rpm. Milling cycles consisting of alternative ½ hour milling and ½ hour pause was carried out in air for 60 hours (excluding pause time).

### 2.2.2 Target preparation

The fine mixed powders were obtained with mechanical milling, and then liquid polyvinyl alcohol was added to the powders to increasing stickiness between particles. The powders were grinded till they reached nearly identical particle size and then pressed into a disc with a diameter of 25 mm and thickness of 5 mm. This disc was sintered in the furnace. The thermal process consisted of three stages, at 100 °C for 4 hours; at 500 °C for 4 hours; at 1300 °C for 6 hours with a temperature ramping
rate below 3 °C/min. After that, the target was cooled slowly down to room temperature with a cooling rate of 3 °C/min. The target density was calculated to be 4.92 g/cm³, which is compared favorably with the bulk density of 5.27 g/cm³.

### 2.2.3 Thin film preparation using post-annealing

In this project, some Co-ferrite films were deposited at room temperature and crystallized through post-annealing. The substrates were single crystal quartz (SiO₂) with different planes, (001)-Si, (0001)-Al₂O₃, and amorphous SiO₂. The typical size of substrates was 10 mm × 10 mm × 1 mm. The substrates were firstly cleaned using ultrasonic cleaning in acetone, ethanol, rinsed with deionized water, and then dried with highly pure N₂ gas. Whereas, in order to remove thermal native SiO₂ on (001)-Si, it was firstly dip into dilute HF solution (1HF: 5H₂O) for 2 minutes before cleaning. Prior to each deposition, the vacuum chamber was pumped down to the base pressure (2×10⁻⁷ Torr). The beam of KrF excimer laser (150 mJ, 248 nm wavelength, and 23 ns pulse width) was focused with a lens on the rotated Co-ferrite target, where its energy density was estimated to be 3.5 Jcm⁻². Additionally, the laser repetition rate and the distance between target and substrate were fixed to be 10 Hz and 55 mm, respectively. Deposition rate was calibrated using a surface profilometer. For post-annealing process, films obtained with a thickness between 20 and 500 nm were annealed under air atmosphere at various temperatures from 500 to 1100 °C with a temperature increasing rate at 5 °C/min and then cooled down to room temperature through the furnace cooling.

### 2.2.4 Thin film preparation using in-situ heating

The substrates used for in-situ heating included single crystal quartz (SiO₂) with different planes, (002)-MgO, (0001)-Al₂O₃, and amorphous SiO₂ as well different
oxide or metal layers. The substrates were also cleaned with the same procedures with that for post-annealing. The substrates were heated following a predetermined temperature profile. The substrate temperature was selected from room temperature (27 °C) to 900 °C. When the temperature of the substrate reached the desired temperature, the working gas oxygen was introduced through the nozzle into chamber by tuning the needle valve and the rotation frequency of the turbomolecular pump. In this work, the oxygen partial pressure was varied from $2 \times 10^{-5}$ to $2 \times 10^{-2}$ Torr. The laser fluence was varied from 1.2 to 15.5 Jcm$^{-2}$. At the same time, the laser repetition rate and the distance between target and substrate were also fixed to be 10 Hz and 55 mm, respectively. Immediately after the deposition, the films were cooled down to room temperature gradually within 90 min in the same working oxygen partial pressure. The substrate was removed from the chamber when the temperature dropped below 60 °C.

2.3 Structural characterization

2.3.1 X-ray diffraction

The phase composition and phase transformation of the samples were examined by means of X-ray diffraction. The instrumentation for X-ray diffraction involves an X-ray source, which provides the incident beam on the sample, and a X-ray detector, which measures the intensity of the diffracted beam emanating from the sample at a certain angle. Diffraction patterns showing peaks and intensity of various crystallographic textures can then be obtained and analyzed.

The simplest and most useful description of crystal diffraction is the Bragg’ law (Eq. 2.1) [7]:

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

Eq. 2.1

where \( n \) is the integer representing the order of diffraction, \( \lambda \) is the wavelength, \( d \) is the interplanar spacing of the reflecting (diffracting) plane, and \( \theta \) is the angle of the incidence and of the diffraction of the radiation relative to the reflecting plane.

For a polycrystalline powdered material, if the individual crystal is less than 100 nm in size, the crystallite size can be estimated using the Scherrer equation [8]:

\[ L = \frac{\kappa \lambda}{B \cos \theta} \]  

Eq. 2.2

where \( B \) is peak width measured at half intensity (radians), \( \lambda \) is the wavelength (Å), \( \kappa \) is particle shape factor (for spherical particles, \( \kappa =0.9 \)), and \( L \) is diameter of the crystallites (Å).

The texture fraction of the \( \{hhh\} \) planes is estimated from the XRD patterns using the Lotgering method [9]. The Lotgering factor \( f \) is defined as the fraction of the area textured with the crystallographic plane of interest using
\[ f = \frac{(P - P_0)}{(1 - P_0)} \]  

Eq. 2.3

Where \( P = \sum I(hkl) / \sum I(\theta) \) and \( P_0 = \sum I^0(hkl) / \sum I^0(\theta) \), with \( I(hkl) \) and \( I^0(hkl) \) being the intensities of \((hkl)\) peaks for the textured and randomly oriented films, respectively.

In addition, the standard \( \sin^2 \psi \) technique is applied to determine the strain in thin films [10]. This technique is based upon the measurement of the strain \( \varepsilon_{hkl} \) corresponding to a specific \{hkl\} plane in films. This strain can be experimentally determined by measuring the change in interplanar spacing of this plane.

\[ \varepsilon_{hkl} = \frac{(d - d_0)}{d_0} \]  

Eq. 2.4

with \( d_0 \) being the interplanar spacing in the unstressed material and \( d \) being the interplanar spacing in the material under stress. The relation between this specific strain and the strain tensor components with respect to the film coordinate system in the measured film is [10,11]

\[ \varepsilon_{hkl} = (\varepsilon_{xx} \cos^2 \varphi + \varepsilon_{yy} \sin 2 \varphi + \varepsilon_{zz} \sin^2 \varphi - \varepsilon_{zx}) \sin^2 \psi + \]  

(\varepsilon_{xx} \cos \varphi + \varepsilon_{yx} \sin \varphi) \sin 2\psi + \varepsilon_{zz} \]  

Eq. 2.5

where \( \psi \) is the angle between the film normal and the normal of the diffracting plane \{hkl\} and \( \varphi \) is the angle in the plane of the film. \( \varepsilon_{xx} \) and \( \varepsilon_{zz} \) are the in-plane and out-of-plane strain. In this work, Eq. 2.5 can be simplified to a linear relation between \( \varepsilon_{hkl} \) (or \( d \)) and \( \sin^2 \psi \) by assuming an equal biaxial strain in the film plane

\[ \varepsilon_{hkl} = (\varepsilon_{xx} - \varepsilon_{zz}) \sin^2 \psi + \varepsilon_{zz} \]  

Eq. 2.6

or,

\[ d = d_0 (\varepsilon_{xx} - \varepsilon_{zz}) \sin^2 \psi + d_0 (\varepsilon_{zz} + 1) \]  

Eq. 2.7

In this study, the scan with glancing angle configuration (GAXRD) was used to perform the standard \( \sin^2 \psi \) technique. A Lorentz fit was used to determine the
precise positions of the diffraction peaks. The measured interplanar spacings ($d$) were calculated and plotted versus $\sin^2 \psi$. According to Eq. 2.7, $\varepsilon_{xx}$ and $\varepsilon_{zz}$ can be calculated in terms of the slope and intercept of this plot if the value of $d_0$ is known.

In this study, Bruker D8 (ADVANCE) with monochromatic and Ni filtered Cu $K_a$ radiation ($\lambda = 1.54056$ Å) was used for the phase characterization and grain size analysis of thin films, while high resolution X-ray diffraction (PANalytical X'pert Pro HR-XRD) with the minimum step size of 0.0001° was used to conduct analysis including texture, strain, rocking curves, and $\varphi$ scans for highly textured and epitaxial films in this dissertation.

### 2.3.2 Extended X-ray absorption fine structure

Absorption of X-ray radiation is a useful tool in materials science due to its ability to give information on the local atomic environmental of selected atoms in complicated system. This technique opens the possibility of structural determinations that are not possible by diffraction technique [12].

The absorption of X-ray by atoms is smoothly varying with X-ray energy except at some discrete energy levels where abrupt increases occur, called absorption edges. As shown in Fig. 2.4, it is typical X-ray absorption spectrum.

These edges correspond to the X-ray photon attaining enough energy to excite additional occupied electron levels in the atom. When atoms are present in condensed matter, the absorption of X-rays on the high-energy side of absorption edges has a complicated behavior that extends past the edge by an amount typically of the order of 1 keV. Isolated atoms do not show this fine structure. This non-monotonic variation caused by the presence of surrounding atoms is named extended absorption fine structure (EXAFS). The oscillatory structures are due to changes in the final state wavefunction as a consequence of the interference between the outgoing
photoelectron waves ejected in the absorption process with the backscattered waves from neighboring atoms. By tuning the X-ray photon energy to that of a particular absorption edge, the local arrangement about each type of atoms can be determined separately. It is also important to note that EXAFS can measure short-range order and thus aperiodic systems can be studied with the same ease as crystals. In principle, the kinds of surrounding atoms can be distinguished by energy dependence of their contribution to the EXAFS.

![EXAFS Spectrum](image)

**Fig. 2.4.** A typical EXAFS spectrum including the absorption edge and oscillation part.

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Preliminary EXAFS data were obtained at the SINS beamline of the Singapore Synchrotron Light Source (SSLS). In this study, the EXAFS data was mainly used to calculate the cation distribution of Co$^{2+}$ and Fe$^{3+}$ in the spinel structure of CoFe$_2$O$_4$ thin films.

### 2.3.3 Atomic force microscopy

Atomic force microscopy (AFM) is one of the most powerful tools for determining the surface topography of specimens at sub-nanometer resolution [13]. It reproduces the image of the sample surface using a sharp tip as a probe which is commonly made from silicon or silicon nitride which is attached to a flexible cantilever with a specific spring constant. The cantilever detects in the Z-direction due to the surface topography during tip scanning. A laser reflecting off the cantilever is tracked by a 4 segment photodiode. The computer processes the electrical differential signal of the photodiode obtained from each point of the surface and generate a
feedback signal for a piezo-scanner to maintain a constant force on the tip. This information is then processed into a topographical image.

Three basic measuring modes: contact mode, tapping mode and non-contact mode are used for the surface analysis. In the tapping mode AFM, as shown in Fig. 2.5 [14], the cantilever is oscillated typically with a frequency of 50 to 500 Hz. When the tip nears the surface, it “taps” the surface which leads to a reduction in oscillation amplitude. This reduction is used to identify and measure surface topographic features. The average cantilever deflections are used as an input signal into the feedback loop to maintain a constant applied force on the surface.

Fig. 2.5. Schematic illustration of an AFM system.
2.3.4 Transmission electron microscopy

In order to investigate the structure and microstructure of the films, transmission electron microscopy (TEM) observations were performed using a JOEL 3010 electron microscope at an accelerating voltage of 300 kV.

![Schematic diagram for TEM image and diffraction.](image)

Fig. 2.6. Schematic diagram for TEM image and diffraction.

Fig. 2.6 shows the basic principle of electron microscopy imaging and diffraction [15]. A parallel beam of electrons accelerated by a voltage $V_0$ is transmitted through a specimen (thin foil) and is diffracted in a number of directions by the crystal. The diffracted electron beams are brought into focus in the back focal plane of the objective lens, forming a diffraction pattern that can be magnified and
studied if subsequent lenses in the microscope are arranged to focus on the back focal plane of the objective. The diffraction pattern consists of a two dimensional array of spots corresponding to a particular set of reflecting planes.

From the diffraction pattern one can approximately derive the inter planar spacing $d$ by means of the Eq. 2.8

$$d = \frac{L\lambda}{d}$$

which is derived by Bragg’s law. Here $L$ is distance between specimen and focal plane, $\lambda$ is the wavelength of the electron beam that depends on the acceleration voltage, and $r$ is the distance of a diffracted spot and the center spot on the back focal plane. $L\lambda$ is called the apparatus constant. The objective lens also forms an image of the lower surface of the specimen in the image plane. This image can be magnified subsequently by other lenses of the instrument and is finally projected onto the fluorescent screen. Since a set of planes participating in the diffraction is perpendicular to the direction from the diffracted spot to the central spot, one may also find some special crystallographic directions in image.

In the bright field (BF) mode of the TEM, an aperture is placed in the back focal plane of the objective lens that allows only the direct beam to pass. In this case, mass-thickness and diffraction contrast contribute to image formation: thick areas, areas in which heavy atoms are enriched, and crystalline areas appear with dark contrast. In spite of the useful information obtainable from BF images, it should be mentioned that the interpretation of contrast is often impeded since these phenomena occur simultaneously.

In dark field (DF) images, one or more diffracted beams are allowed to pass the objective aperture. The direct beam is blocked by the aperture. In contrast to the direct beam, the diffracted beam has interacted strongly with the specimen, and often
very useful information is present in DF images, e.g., about planar defects, stacking faults or particle size.

To obtain lattice images, a larger objective aperture has to be selected that allows many beams including the direct beam to pass. The image is formed by the interference of the diffracted beams with the direct beam (phase contrast). If the point resolution of the microscope is sufficiently high and a suitable sample oriented along a zone axis, then high-resolution TEM (HRTEM) images are obtained. In many cases, the atomic structure of the specimen can directly be investigated by HRTEM.

Electron diffraction (ED) is a collective elastic scattering phenomenon with electrons being scattered by atoms in a regular array (crystal). The incoming plane electron wave interact with the atoms, and secondary waves are generated which interfere with each other. This occurs either constructively (reinforcement at certain scattering angles generating diffracted beams) or destructively (extinguishing of beams). As in XRD, the scattering event can be described as a reflection of the beams at planes of atoms (lattice planes). The Bragg law gives the relation between interplanar distance $d$ and diffraction angle $\theta$.

Since the wavelength $\lambda$ of the electrons is known, interplanar distances can be calculated from electron diffraction patterns. Furthermore, information about crystal symmetry can be obtained. Consequently, electron diffraction represents a valuable tool in crystallography.

### 2.3.5 X-ray photoelectron spectroscopy

Surface analysis by x-ray photoelectron spectroscopy (XPS) involves irradiating a solid in a vacuum with monoenergetic soft x-rays and analyzing the emitted electrons [16]. These photons have limited penetrating power into a solid on
the order of 1~10 nm. The photons interact with atoms in the surface region. The kinetic energy of the electron can be measured as:

\[ KE = h\nu - BE - \phi_s \]

where \( h\nu \) is the energy of the photo, \( BE \) is the binding energy of the atomic orbital from which the electron originates, and \( \phi_s \) is the spectrometer work function.

**Fig. 2.7. Schematic diagram for a XPS system.**

As shown in Fig. 2.7, The XPS system includes a source of fixed-energy radiation, and an electron energy analyzer (which can disperse the emitted electrons according to their kinetic energy, and thereby measure the flux of emitted electrons of a particular energy) as well as a high vacuum environment, which enable the emitted photoelectrons to be analyzed without interference from gas phase collisions.
The spectrum is obtained as a plot of the number of detected electrons per energy interval versus their kinetic energy. Each element has a unique spectrum. The spectrum of a mixture of elements is approximately the sum of the peaks of the individual constituents. Identification of chemical states often can be made from exact measurement of peak position and separations, as well as from certain spectral features. In the XPS, the composition of the film can be measured by utilizing peak area and peak height sensitivity factors. In practice, many samples exhibit compositional changes with depth, and acknowledge of the concentration depth profiles of the elements present within the surface region is therefore desirable. To obtain the depth profile, the sample is bombarded with a flux of ions generated by means of a discharge in an ion gun fed with an inert gas, usually argon. The impacting ions remove clusters of atoms from the surface, eroding (sputtering) the sample layer by layer. X-ray photoelectron spectra are recorded at intervals to monitor the changing surface composition and relate this to the composition profile in the sample.

In this investigation, surface analysis by XPS (PHI Quartera SXM) with an Al $K\alpha$ (1486.6 eV) X-ray source was performed by irradiating thin films with monoenergetic soft x-ray and analyzing the energy of the detected electrons.

2.4 Magnetic property measurement

Normally, magnetic properties of magnetic thin films can be described using hysteresis loops, and hysteresis loops and the shape of magnetization curves are mainly characterized with $H_c$, $M_r$, $M_s$ and $K_u$. Thus, the discussion on magnetic properties in this thesis mainly focuses on these four parameters.

2.4.1 Vibration sample magnetometer
A Vibrating Sample Magnetometer (VSM) is used to measure the magnetic properties of the films [17]. The principle of this measurement is very simple. When a sample is placed in a homogenous magnetic field, a magnetic moment is induced in the sample. If this sample is made to undergo sinusoidal motion (i.e. mechanically vibrated), the vibration induces a magnetic flux change. This in turn induces a voltage in the pick-up coils. The magnetic moment determined by the VSM is related to the magnetization of the sample and its susceptibility.

![Scheme of VSM](image)

**Fig. 2.8. Schematic diagram of a VSM system.**

Fig. 2.8 shows a typical VSM set up. The sample is suspended from a vibrating drive head by a non-magnetic rod and placed between two electromagnets which produce a magnetic field. The vibrator generates a vertical sinusoidal vibration with a frequency of 82 Hz. Therefore, the sample experiences sinusoidal motion, which
induces an electrical signal in the coils mounted on the pole faces of the electromagnets. The signal picked up by the coils is proportional to the frequency and amplitude of the sinusoidal motion, and the total magnetic moment of the sample at the applied magnetic field. The frequency and amplitude of the sinusoidal motion are maintained constant by a capacitor (reference signal generator). By feeding the signals from the pick-up coils and the reference signal into a demodulator, the magnetic moment of the sample is extracted.

In this study, magnetic properties (hysteresis loops) were measured using the vibrating sample magnetometer (Lakeshore 7400) with the applied field maximum 21 kOe at room temperature. Before the VSM measurement, a standard Ni foil or Ni sphere was used to calibrate the magnetic moment of the equipment. A sufficient magnetic field was applied on the sample until the sample was saturated. By switching the magnetic field, a hysteresis loop was obtained. The applied field can be applied in two configurations, parallel (||) and perpendicular (⊥) to the film plane.

For the magnetization measurement, samples were carefully cut in a size of 5×5 mm by a diamond cutter. The thicknesses of the thin films were measured by a surface profilometer. Hence the total volume to the film can be obtained by the formula:

\[ V = a \times b \times t_f \]  \hspace{1cm} \text{Eq. 2.10}

\(a\) is the length, \(b\) is the width and \(t_f\) is the film thickness. The magnetization is obtained by \(M = m / V\), where \(M\) is the magnetization and \(m\) is the measured moment of the film. \(V\) is the volume of the film.

### 2.4.2 Alternating gradient force magnetometer
The alternating gradient force magnetometer (AGM) has a high sensitivity. The AGM has a noise floor of $10^{-8}$ emu compared to $10^{-6}$ emu for the VSM [18,19]. As shown in Fig. 2.9 [18], the sample is mounted on an extension rod attached to a piezoelectric element. An alternating gradient field produces a periodic force on a sample placed in a DC field of an electromagnet. The alternating field gradient exerts an alternating force on the sample proportional to the magnitude of the gradient field, the magnetic moment of the sample and the intensity of the applied field. The resulting deflection of the extension is transmitted to the piezoelectric sensing element. The output signal from the piezoelectric element is synchronously detected at the operating frequency of the gradient field. The signal developed by the piezoelectric element is greatly enhanced by operating at or near the mechanical resonant frequency of the assembly. A built-in software function automatically determines mechanical resonance and sets the appropriate operating frequency for the sample under study.

Fig. 2.9. Schematic diagram of an AGFM system.
In this work, the AGFM system (Micromag-2900, Princeton Measurements Co.) with the maximum field of 21 kOe was used.

2.5 Summary

In this chapter, the sample preparation using the PLD system was introduced. A variety of techniques including XRD, EXAFS, TEM, AFM, and XPS were employed to investigate composition, morphology and microstructure of thin films. Magnetic properties were examined by VSM and AGFM.

2.6 References


3 Chapter III Growth and magnetic properties of CoFe$_2$O$_4$ films with post-annealing

In this chapter, CoFe$_2$O$_4$ (Co-ferrite) films were prepared by PLD followed by post-annealing heat treatment. Effects of annealing temperature, substrate, and thickness on film growth, microstructure and magnetic properties of these films were investigated. As described in Chapter 2, CoFe$_2$O$_4$ films were mainly deposited on single crystal (0001)-SiO$_2$. As a comparison study, other substrates ((001)-Si, (0001)-Al$_2$O$_3$ and amorphous SiO$_2$ were used as the substrates for film deposition.

3.1 Film growth of Co-ferrite films with post-annealing

![Graph showing film growth with time.](image)

**Fig. 3.1.** The thickness of films deposited at room temperature with different times.

The thicknesses of a series of films with varied deposition times between 7 to 60 minutes were measured using a surface profilometer to calibrate deposition rate.
The films were deposited at room temperature. Fig. 3.1 shows a fitted deposition rate to be 6.8 nm/min.

Fig. 3.2 showed the XRD patterns with the glancing angle configuration (GAXRD) of Co-ferrite films with a thickness of 100 nm prepared using PLD and subsequently annealed at different temperatures (500 – 1100 °C). No crystalline peaks were found in the XRD pattern of the as-deposited film, indicating an amorphous structure. With increasing annealing temperature, the crystalline structure was formed at 500 °C or higher. The phase transformation can be explained with the classic phase formation theory. Since the atoms have a high mobility when annealed at a high temperature, the driving force to minimize thermodynamic Gibbs free energy makes nucleation and growth of the grains with the ordered crystalline structure from as-deposited amorphous phase [1]. All the main diffraction peaks of the films after annealed over 500 °C were clearly indexed with the peaks of the Co-ferrite target with a spinel structure. The peaks’ positions and intensity ratios matched well with the standard JDPDS No. 22-1086 [2], suggesting that the grains possessed random orientation without texture for all the films annealed at different temperatures. Based on Fig. 3.2, the XRD patterns revealed that the increase of the annealing temperature yielded the sharpness of the major peaks, indicating an increase in grain size. The grain size was calculated using Scherer equation and listed in Table 3.1. It should be noted that there was no value for the as-deposited film due to very poor crystallinity. The film after annealed at 500 °C possessed an average grain size of 22.3 nm. With increasing annealing temperature, the grain sizes were 35.9, 37.0, 75.2, and 262.1 nm for the films annealed at 700 °C, 800 °C, 900 °C, and 1100 °C, respectively. This trend clearly revealed grain growth with increasing temperature. The lattice parameter was calculated based on the XRD patterns and indicated that all the films annealed at
different temperatures showed a similar value of approximate 8.381 Å, which was very close to that of the Co-ferrite target (8.380 Å). Moreover, no peak shift was observed for all these films. The unchangeable lattice parameter revealed that there was no detectable lattice distortion in the films annealed at different temperatures. Accordingly, the heat treatment using post-annealing at such a high temperature makes Co-ferrite films in a thermo-equilibrium state without lattice distortion and intrinsic strain.

The AFM images of films prepared by PLD and then annealed at different temperatures are shown in Fig. 3.3, indicating a clear relationship between grain growth and annealing temperature. The root-mean-squared (rms) values of these films
Fig. 3.3. The AFM images (1×1 um) of Co-ferrite films prepared on (0001)-SiO₂ using PLD and subsequently annealed at different temperature: as-deposited (a), 500 °C (b), 700 °C (c), 800 °C (d), 900 °C (e) and 1100 °C (f).

are also listed in Table 3.1. The as-deposited film had a very uniform and flat surface with a rms value of 0.6 nm, which was associated with the disorder structure with
poor crystallinity. When the annealing temperature increased to 500 and 700 °C, the
time value increased to be 1.2 and 1.7 nm, respectively. After annealing at 800 °C, the
film possessed a uniform microstructure, as the diameters of all the particles were
found to be approximate 40 nm, which agreed well with the grain size (47 nm)
calculated using XRD data (Table 1.1). However, when annealed at above 800 °C, the
average particle size using AFM examination became bigger and a few large particles
were observed. Furthermore, the surface was fully covered with large particles and the
size distribution was not uniform when the annealing temperature reached 1100 °C.
The similar trend about AFM images related to annealing temperature were also
obtained in the films prepared using RF sputtering and subsequently annealed at
different temperatures in our previous works [3].

Table 3.1. Lattice parameter, grain size, and surface roughness for as-deposited Co-
fe-rich films and subsequently annealed at different temperatures.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lattice parameter (Å)</th>
<th>Grain size (nm)</th>
<th>Surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 nm as-deposited</td>
<td>----</td>
<td>----</td>
<td>0.6</td>
</tr>
<tr>
<td>100 nm A500 °C</td>
<td>8.389</td>
<td>26.4</td>
<td>1.2</td>
</tr>
<tr>
<td>100 nm A700 °C</td>
<td>8.385</td>
<td>35.9</td>
<td>1.7</td>
</tr>
<tr>
<td>100 nm A800 °C</td>
<td>8.385</td>
<td>37.0</td>
<td>2.3</td>
</tr>
<tr>
<td>100 nm A900 °C</td>
<td>8.383</td>
<td>75.1</td>
<td>3.6</td>
</tr>
<tr>
<td>100 nm A1100 °C</td>
<td>8.381</td>
<td>262.1</td>
<td>8.4</td>
</tr>
<tr>
<td>CoFe2O4 target</td>
<td>8.381</td>
<td>432.1</td>
<td>----</td>
</tr>
</tbody>
</table>
In this study, the effects of film thickness on film growth of Co-ferrite films using post-annealing were studied. Fig. 3.4 shows the XRD patterns of Co-ferrite films with different thicknesses (25-400 nm) after annealed at 700 °C. All these films exhibited an isotropic crystallographic orientation without preferential texture. The peak intensity became sharper with increasing thickness from 25 nm to 100 nm, indicating grain size increased in the thicker films. When film thickness was too small (25 nm), the film was partially continuous. With increasing thickness, islands made contact together. The film became gradually fully continuous and grain grew through grain boundary diffusion. The grain size calculated for the films with different thicknesses using Scherer equation are summarized in Table 3.2. The grain size was 19.4 nm for the film (25 nm). When increasing thickness to 50 nm, the grain size reached around 26.4 nm for films. When the thickness was over 100 nm, the grain...
size showed no obvious change with a value of ~35 nm. In addition, no peak shift was observed in the XRD patterns of all these films. The calculated lattice parameters as shown in Table 3.2 were very close to that of the Co-ferrite target.

**Table 3.2. Lattice parameter, grain size, and surface roughness for Co-ferrite films with different thicknesses (25 – 400 nm) after subsequently annealed at 700 °C.**

<table>
<thead>
<tr>
<th>Samples with various thicknesses</th>
<th>Lattice parameter (Å)</th>
<th>Grain size (nm)</th>
<th>Surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 nm</td>
<td>8.387</td>
<td>19.4</td>
<td>0.9</td>
</tr>
<tr>
<td>50 nm</td>
<td>8.385</td>
<td>26.4</td>
<td>1.5</td>
</tr>
<tr>
<td>100 nm</td>
<td>8.383</td>
<td>33.7</td>
<td>1.6</td>
</tr>
<tr>
<td>200 nm</td>
<td>8.381</td>
<td>37.5</td>
<td>1.8</td>
</tr>
<tr>
<td>400 nm</td>
<td>8.381</td>
<td>40.1</td>
<td>1.8</td>
</tr>
</tbody>
</table>

In this work, AFM images of Co-ferrite films using post-annealing with variable thicknesses are shown in Fig. 3.5. With a thickness of 25 nm, the particle size was less than 20 nm, due to the thickness-suppressed grain growth [4], while at the thickness of over 50 nm, the particles showed an identical size of 35 nm and a rms value of 1.6 nm. When the film’s thickness was over 100 nm, the particle size showed no obvious change with a value of around 40 nm. The particle size was consistent with the grain size listed in Table 3.2. The growth morphology can be explained with normal grain growth mechanisms, which is mainly resulted from the capillarity driving force. Thus, for the films using post-annealing, the grain growth is more dependent on annealing temperature and less dependent on film thickness.
Fig. 3.5. The AFM images (1×1 um) of Co-ferrite films prepared on (0001)-SiO₂ using PLD and subsequently annealed at 700°C with different thicknesses: 25 nm (a), 50 nm (b), 100 nm (c), 200 nm (d), 400 nm (e).
In this work, effects of substrates on film growth of Co-ferrite with post-annealing were also studied. Co-ferrite films were prepared on single crystal substrates including (0001)-Al₂O₃ and (001)-Si substrates as well as amorphous glass (SiO₂). The deposition and post-annealing procedures for the films on (0001)-Al₂O₃ and amorphous SiO₂ were the same as that for film deposition on (0001)-SiO₂ substrate. However, the cleaning procedure for (001)-Si was different. The Si-wafers were cut into small pieces (1×1 cm²). Before deposition, the pieces were dip into dilute HF solution (1HF: 5H₂O) for 2 minutes to remove surface contaminant and native oxide. These pieces were taken out of the solution and dried by blowing N₂. Then the Si substrates without native oxide were loaded into the deposition chamber as well as other substrates (SiO₂ and Si).

![XRD patterns](image)

**Fig. 3.6.** The XRD patterns of the 100 nm Co-ferrite films deposited using PLD and annealed at 700 °C on (001)-Si, (0001)-Al₂O₃, and amorphous SiO₂.
Fig. 3.6 shows the XRD patterns of the 100 nm Co-ferrite films, which were prepared on (001)-Si, (0001)-Al₂O₃, and amorphous SiO₂ and subsequently annealed at 700 °C. All the films on different substrates showed a purely spinel Co-ferrite phase with isotropic orientation but without peak shift. The grain size for all these films showed negligible changes, suggesting no obvious effects of substrates on film growth of Co-ferrite films with post-annealing.

### 3.2 Magnetic properties of Co-ferrite films with post-annealing

Table 3.3 shows the magnetic properties of the 100 nm Co-ferrite films using post-annealing at different temperatures. The perpendicular coercivity ($H_{c\perp}$) of the films firstly increased with increasing annealing temperature, reached the maximum value of around 5.9 kOe at 800 °C, and then decreases with further increasing of annealing temperature above 800 °C. The parallel coercivity ($H_{c\parallel}$) followed the same trend as $H_{c\perp}$ and was almost comparable to the values of $H_{c\perp}$, indicating that these films possessed almost isotropic magnetic anisotropy in both directions-perpendicular and parallel directions. The slight difference between $H_{c\parallel}$ and $H_{c\perp}$ maybe result from imperfect microstructure, such as incompletely circular grain shape or imperfect isotropic texture. The monotone increasing of $M_s$ with annealing temperature was due to improved phase crystallinity of spinel Co-ferrite phase and grain growth [5].

Fig. 3.7 shows hysteresis loops of the 100 nm Co-ferrite films after annealed at 700 and 1100 °C, respectively. These two films exhibited obviously no magnetic texture with comparable magnetic remanence ratio ($M_r/M_s$) in both perpendicular and parallel directions. The $M_r/M_s$ ratio value the film at 700 °C was around 60 %, while that of the film at 1100 °C was around 65 %.
As shown in AFM images (Fig. 3.3), the trend of the relationship between coercivity and annealing temperature is consistent with the variation of particle size with annealing temperature, indicating that grain size plays a critical role in tuning the coercivity of Co-ferrite thin films. It has been reported that the coercivity of Co-ferrite materials increases with increasing grain size and reaches a maximum value for the grain size of about 40 nm, which is the single domain size for CoFe₂O₄ materials [6, 7, 8]. Grains more than 40 nm divide into domains and domain-wall movements result in a reduced coercivity with further increasing grain size. As observed in the Co-ferrite films using post-annealing in this work, the films after annealed at around 700–800 °C had an average grain size close to single domain size of Co-ferrite. Accordingly, the films annealed at this range of temperatures showed the optimal coercivity.

Table 3.3. Magnetic properties of Co-ferrite films with a thickness of 100 nm after annealed at various temperatures [Coercivity $H_c$ and the remanence ratio $(M_r/M_s)$ measured in both in-plane and out-of plane directions].

| Annealing Temperature | $H_{c||}$ (kOe) | $(M_r/M_s)_{||}$ (%) | $H_{c\perp}$ (kOe) | $(M_r/M_s)_{\perp}$ (%) | $M_s$ (emu/cm³) |
|-----------------------|-----------------|----------------------|--------------------|-------------------------|----------------|
| As deposited          | 1.1             | 23.7                 | 1.4                | 26.1                    | 48             |
| 500 °C                | 2.4             | 44.0                 | 3.4                | 45.8                    | 154            |
| 700 °C                | 4.9             | 63.7                 | 5.4                | 55.4                    | 205            |
| 800 °C                | 5.5             | 69.0                 | 5.9                | 61.3                    | 257            |
| 900 °C                | 4.4             | 70.5                 | 5.5                | 66.4                    | 342            |
| 1100 °C               | 2.5             | 73.3                 | 3.1                | 67.6                    | 380            |
Fig. 3.7. The hysteresis loops of Co-ferrite films with a thickness of 100 nm prepared by PLD and subsequently annealed at 700 °C, and 1100 °C, respectively.

Table 3.4 gives magnetic properties ($H_c$ and $M_s$ in two directions) of Co-ferrite films with different thicknesses. All these films exhibited an isotropic magnetic orientation, and the films with the thickness of over 100 nm possessed similar $H_c$ and $M_s/M_s$ ratio. The similar magnetic properties of the films with thicknesses over 100 nm are due to the identical grain size and film morphology as shown in AFM Images.
(Fig. 3.5), which further illustrated that grain size is a critical parameter to tune magnetic properties of Co-ferrite films using post-annealing process.

### Table 3.4. Magnetic properties of the Co-ferrite films annealed at 700°C with different thicknesses [Coercivity $H_c$ and the remanence ratio ($M_r/M_s$) measured in both in-plane and out-of-plane directions].

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$H_c$(_\parallel) (kOe)</th>
<th>($M_r/M_s$)(_\parallel) (%)</th>
<th>$H_c$(_\perp) (kOe)</th>
<th>($M_r/M_s$)(_\perp) (%)</th>
<th>$M_s$ (emu/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.0</td>
<td>42.3</td>
<td>2.3</td>
<td>55.5</td>
<td>162</td>
</tr>
<tr>
<td>50</td>
<td>3.4</td>
<td>59.5</td>
<td>4.1</td>
<td>63.9</td>
<td>179</td>
</tr>
<tr>
<td>100</td>
<td>4.9</td>
<td>63.7</td>
<td>5.3</td>
<td>55.4</td>
<td>205</td>
</tr>
<tr>
<td>200</td>
<td>4.7</td>
<td>63.6</td>
<td>5.4</td>
<td>55.9</td>
<td>225</td>
</tr>
<tr>
<td>400</td>
<td>4.9</td>
<td>62.7</td>
<td>5.5</td>
<td>56.8</td>
<td>231</td>
</tr>
</tbody>
</table>

Table 3.5 shows the magnetic properties of the 100 nm Co-ferrite films on different substrates. The film on (001)-Si possessed $H_c$\(_\perp\)$ and $H_c$\(_\parallel\)$ of 5.1 and 4.4 kOe, respectively, and the $M_r/M_s$ ratio in perpendicular and parallel directions were 69.5 % and 59.9 % while the film on (0001)-Al\(_2\)O\(_3\) exhibited $H_c$\(_\perp\)$ and $H_c$\(_\parallel\)$ of 5.2 and 4.5 kOe. In addition, the film on amorphous SiO\(_2\) exhibited $H_c$\(_\perp\)$ and $H_c$\(_\parallel\)$ of 5.4 and 4.9 kOe. As the results illustrated, all the hysteresis loops of films on different substrates including single crystal (0001)-Al\(_2\)O\(_3\), (001)-Si and amorphous SiO\(_2\) were similar to that of the film on single crystal (0001)-SiO\(_2\). The results revealed that various substrates have no obvious effects on magnetic properties (coercivity, magnetic anisotropy) of Co-ferrite films using post-annealing, as well as that no substrate effects on film growth of Co-ferrite films using post-annealing.
Table 3.5. Magnetic properties of the Co-ferrite films (100 nm) on different substrates annealed at 700 °C [Coercivity $H_c$ and the remanence ratio $(M_r/M_s)$ measured in both in-plane and out-of plane directions].

| Substrate       | $H_c ||$ (kOe) | $(M_r/M_s) ||$ (%) | $H_c \perp$ (kOe) | $(M_r/M_s) \perp$ (%) | $M_s$ (emu/cm$^3$) |
|-----------------|---------------|-------------------|-------------------|----------------------|------------------|
| (0001)-SiO$_2$  | 4.9           | 63.7              | 5.3               | 55.4                 | 205              |
| (001)-Si        | 4.4           | 69.5              | 5.1               | 59.9                 | 199              |
| (0001)-Al$_2$O$_3$ | 4.5           | 64.7              | 5.2               | 57.4                 | 215              |
| Amorphous SiO$_2$ | 4.9           | 63.6              | 5.4               | 59.7                 | 206              |

3.3 Summary

To summarize this Chapter, Co-ferrite films were prepared with post-annealing heat treatment. Microstructure and magnetic properties of the films with different thicknesses (20-400 nm), under annealing at different temperature (500-1100 °C) and on different substrates (sapphire, Si, quartz and glass) were investigated. Whether the films were annealed at various temperatures or the films were deposited with various thicknesses, the films showed an isotropic crystallographic orientation with no intrinsic strain. The films also exhibited isotropic magnetic anisotropy without magnetic texture. Moreover, film growth and magnetic properties of films in function of annealing temperature, thickness, and substrate revealed that (1) controlling grain size close to single domain size of spinel Co-ferrite is critical to obtain high coercivity; (2) using post-annealing heat treatment is difficult to achieve Co-ferrite films with large perpendicular anisotropy; (3) thin film growth using post-annealing is highly related to isotropic growth without texture development; (4) substrate has no obvious effects on film growth and magnetic properties of films.
Accordingly, in this case, PLD with post-annealing may not be a practical method to obtain textured Co-ferrite films with large perpendicular anisotropy. Accordingly, In-situ heating may be a possible method to control texture and magnetic anisotropy of Co-ferrite films. In Chapter 4, we will discuss epitaxial growth and magnetic anisotropy of Co-ferrite films on single crystal substrates with in-situ heating.

### 3.4 References

4 Chapter IV Growth and magnetic anisotropy of epitaxial Co-ferrite thin films

In this chapter, epitaxial Co-ferrite (CoFe$_2$O$_4$) films were deposited with in-situ heating. Both (111) and (001) epitaxial structure were achieved on single crystal (0001)-Al$_2$O$_3$ and (002)-MgO substrates. Epitaxial growth and magnetic properties of the films were characterized. Furthermore, a theoretical analysis on magnetic anisotropy of these epitaxial films was also conducted.

4.1 Growth of (111)-epitaxial CoFe$_2$O$_4$ films on (0001)-Al$_2$O$_3$

4.1.1 Effects of oxygen pressure on stoichiometric compositions

In order to achieve Co-ferrite films with the same chemical compositions as the CoFe$_2$O$_4$ target, effects of oxygen working pressure during deposition on the stoichiometric compositions of Co-ferrite films were investigated. A series of films with a thickness of 40 nm were deposited on (0001)-Al$_2$O$_3$ (sapphire) at 500 °C under oxygen pressures between $2 \times 10^{-5}$ and $2 \times 10^{-2}$ Torr.

As shown in Fig. 4.1, typical XPS spectra of Co-ferrite films prepared under 2 mTorr oxygen pressures were clearly indexed with the peaks only from Co, Fe, and O elements. The narrow XPS scans for these films are shown in Fig. 4.2. A quantitative fitting was performed on the XPS data. The results indicated the stoichiometric compositions were Co$_{1.05}$Fe$_{1.95}$O$_4$, Co$_{1.0}$Fe$_{2.0}$O$_4$, Co$_{0.96}$Fe$_{2.04}$O$_4$, and Co$_{0.9}$Fe$_{2.1}$O$_4$ for the films deposited under $2 \times 10^{-2}$, $2 \times 10^{-3}$, $2 \times 10^{-4}$, and $2 \times 10^{-5}$ Torr, respectively. The compositions of all the films deposited under different oxygen pressures are very close to that of the CoFe$_2$O$_4$ target, especially for the films deposited under 2 mTorr.
Moreover, effects of deposition temperature on Co-ferrite films’ stoichiometric compositions were also investigated. Films with a thickness of 40 nm were deposited on (0001)-Al₂O₃ under 2 mTorr at different temperatures including 27 °C, 550 °C, and 800 °C. All these films showed the similar chemical compositions close to the CoFe₂O₄ target, suggesting negligible effects of substrate temperature on films’ stoichiometric compositions. The results revealed the PLD process in this work can obtain thin films with very close stoichiometric composition to the target. Accordingly, if not specially stated, Co-ferrite films were prepared under 2 mtorr in this work.
Fig. 4.2. The XPS spectra of the 40 nm Co-ferrite films deposited under different oxygen pressures.

4.1.2 Effects of substrate temperature

In this part, effects of substrate temperature on growth of Co-ferrite films were studied. Fig. 4.3(a) shows the XRD patterns using the $\theta$-2$\theta$ configuration of the Co-ferrite films with the same thickness of 40 nm prepared on (0001)-Al$_2$O$_3$ at different substrate temperatures. The 2$\theta$ range from 40-44° was removed from the curves because the intensity of the (0003) peak from single crystal sapphire was too strong compared to the film peaks of CoFe$_2$O$_4$ films. When deposited at room temperature, the film only exhibited the same peaks as the sapphire substrate, indicating an amorphous film structure. While deposited at 150 °C, the film exhibited a series of reflections from the {111} planes of a crystalline phase, which were identified as the spinel structure. It is of great significance to grow (111)-textured Co-ferrite films on sapphire at such a low temperature below 200 °C. An increasing of substrate
temperature resulted in a similar pattern but with strong diffraction intensity. Moreover, it was observed that there was an obvious peak shift with increasing deposition temperature by taking the constant positions of the substrates’ (0003) peak as the reference. The (333) peak’s position of the film at 150 °C was 36.23° while the one for the film at 800 °C was 36.63°. The similar results about peak shift occurred to epitaxial films at different substrate temperatures were also reported previously [1].

Fig. 4.3. The XRD patterns of the 40 nm Co-ferrite films prepared on (0001)-Al₂O₃ using PLD at different substrate temperature (a), phi scan (b) and rocking curve for the (222) peaks of Co-ferrite films at 550 °C (c).

In order to observe the in-plane orientation of Co-ferrite film on sapphire, the phi scan was taken from the (400) reflection of the film at 550 °C (Fig. 4.3(b)). The phi scan exhibited six peaks every 60°, suggesting a double domain structure. Fig. 4.3(c) shows the linewidth of the rocking curve for the (222) reflection of this film.
The FWHM was around 0.045°, indicating an excellent (111)-textured structure. Furthermore, based on the comparison of phi scans for both the film and sapphire substrate, it was found that the (111)-epitaxial Co-ferrite film was grown on (0001)-sapphire with in-plane alignment of [110]-CoFe$_2$O$_4$ parallel to [1100]-Al$_2$O$_3$. The in-plane orientation relationship between the film and the substrate is displayed in Fig. 4.4. The oxygen to oxygen distance along the [110] of bulk CoFe$_2$O$_4$ with the spinel structure was calculated from the lattice parameter of 0.838 nm. The calculated value is 0.296 nm, 2.8 % larger than that (0.288 nm) along the [1100] of Al$_2$O$_3$. The excellent epitaxial structure is certainly related to the small lattice mismatch between substrate and film.

![Schematic representation of the oxygen alignment of the (111)-CoFe$_2$O$_4$ layer on the (0001)-Al$_2$O$_3$.](image)

Fig. 4.4. Schematic representation of the oxygen alignment of the (111)-CoFe$_2$O$_4$ layer on the (0001)-Al$_2$O$_3$.  

[10-1]  
[1-10]  
[0-110]  
[1100]  

○ Oxygen in the (111) plane of CoFe$_2$O$_4$  
● Oxygen in the (0001) plane of sapphire
The AFM examination of the (111)-epitaxial Co-ferrite film (40 nm) deposited at 550 °C and 800 °C on (0001)-Al\(_2\)O\(_3\) is shown in Fig. 4.5, indicating a typical surface morphology for epitaxial films with very excellent film smoothness. The rms for both films was below 0.4 nm [2,3].
The XPS depth profile of this film as shown in Fig. 4.6 indicated a sharp interface between film and substrate, suggesting that there is a negligible interfacial diffusion. It indicated that the deposition temperature of 550 °C was suitable for epitaxial growth of Co-ferrite films on (0001)-Al₂O₃ without substrate damage.

### 4.1.3 Effects of thickness

In this part, effects of film thickness on epitaxial growth of Co-ferrite films on (0001)-Al₂O₃ were examined. CoFe₂O₄ films with a thickness between 40 and 700 nm were deposited at 550 °C in this work.

![XRD patterns](image)

**Fig. 4.7.** The XRD patterns using θ~2θ symmetric scan for CoFe₂O₄ films deposited at 550 °C with different thicknesses on (0001)-Al₂O₃.

As shown in the XRD patterns (Fig. 4.7) using the symmetric θ~2θ scan, only {111} diffraction peaks appeared for all these films. In-plane phi-scan and rocking curve measurement using HRXRD indicated the formation of excellent (111)-
epitaxial structure for all the films with various thicknesses. Especially, the epitaxial structure can be maintained even with a thickness up to 700 nm. The shift of (333) peaks for the films with various thicknesses was observed, which is shown in Fig. 4.8(a). Compared to the target, the shift was dependent on film thickness. For the film with a thickness of 40 nm, there was a relatively large shift (the (333) peak at $2\theta = 56.29^\circ$, compared to $56.96^\circ$ for the target), indicating a lattice distortion with an expanded $d$-space for the (111) plane. The shift decreased with increasing film thickness. For the film with a thickness of 700 nm, the peak position (56.95$^\circ$) was almost the same as that of the target.

![XRD patterns](image)

**Fig. 4.8.** The XRD patterns of the (333) peaks using $\theta$--$2\theta$ symmetric scan (a) and the (400) peaks using asymmetric scan (b) for CoFe$_2$O$_4$ films deposited at 550 °C with different thicknesses on (0001)-Al$_2$O$_3$.

In order to further study the lattice distortion, XRD with the asymmetric configuration was used in this work. Because of the excellent epitaxial structure, only
the series of peaks from epitaxial planes appeared in XRD patterns. Thus, narrow scan using HRXRD was performed with focusing on one of these peaks to study $d$-spacing. Fig. 4.8(b) shows thickness dependence of the (400) peaks of epitaxial films with various thicknesses. Compared to the (400) peak position ($2\theta = 43.07^\circ$) of the CoFe$_2$O$_4$ target, the peak position was $43.34^\circ$ for the film with a thickness of 40 nm. When the film thickness was 700 nm, the peak position decreased to $43.09^\circ$. The positive peak shift indicated a shrinking $d$-space for the (400) plane. Combined with the XRD results using both symmetric and asymmetric configurations, the 40 nm possessed an in-plane compressive strain and an out-of-plane tensile strain. The reduced peak shift of the (400) peaks with increasing thickness and then no shift for the film (700 nm) are a good indication of the relaxation of lattice distortion. The in-plane compressive strain can be relaxed by defects of dislocations or stack fault in the thick films. The relaxation of strain with increasing thickness was also reported previously in epitaxial films due to the insertion of defects during epitaxial growth [4].

### 4.1.4 Cation distribution in (111)-epitaxial films on (0001)-Al$_2$O$_3$

In this part, cation (Co$^{2+}$) distribution in the (111)-epitaxial CoFe$_2$O$_4$ films with different thicknesses was examined in this work. EXAFS has generally reported to examine cation occupation in spinel ferrite, including Co-ferrite [5,6]. As discussed previously, spinel CoFe$_2$O$_4$ unit cell has the $f\bar{d}3m$ space group and is based on a close-packed oxygen lattice where metal cations (Co, Fe) reside on 8 of the 64 tetrahedral sites (A sites) and 16 of the 32 octahedral sites (B sites). The A-site cations have 4 O neighbors at a distance of 1.96 Å, while the B-site cations have 6 O neighbors at a distance of 2.12 Å.
Because of the limit of equipment sensitivity, only the films with a thickness of \( \geq 100 \) nm were examined. The collected EXAFS spectra data (Fig. 4.9) were normalized and converted the photoelectron wave vector space \((k)\). After that, the data were then Fourier transformed to radial coordinates. In this study, the EXAFS investigation focused only on the local environmental of \( \text{Co}^{2+} \) ions. As a reference, \( \text{CoFe}_2\text{O}_4 \) powders after annealed at a high temperature (over 1300 °C) followed by a slow cooling with a rate of 1 °C/min were assumed to possess fully inverse spinel structure [7]. Additionally, other oxide powders including \( \text{CoO} \) (\( \text{Co}^{2+} \) in B sites), \( \text{CoAl}_2\text{O}_4 \) (\( \text{Co}^{2+} \) in A sites), and \( \text{Co}_3\text{O}_4 \) (\( \text{Co}^{2+} \) and \( \text{Co}^{3+} \) in both A and B sites) were used as standard reference samples for the calibration of absorption data for Co ions from different sites (octahedral and tetrahedral).

After calibration, the occupancy of Co cation in different sites can be calculated by the fitting experimental data from \( \text{CoFe}_2\text{O}_4 \) films with the referential standard data with non-linear least squares. The fitting results revealed that the Co ion’s valence was +2. For the 100 nm film, the coordination number of \( \text{Co}^{2+} \) was close to 6, suggesting a fully inverse spinel structure, i.e. all the \( \text{Co}^{2+} \) ions occupy octahedral sites. Furthermore, the EXAFS-derived Co-O distance (2.11 Å) was almost the same as that predicted for octahedrally coordinated \( \text{Co}^{2+} \) in spinel \( \text{CoFe}_2\text{O}_4 \). With increasing thickness to 200 nm, the occupation of \( \text{Co}^{2+} \) in B sites decreased and the occupation of \( \text{Co}^{2+} \) in A sites increased as the coordination number decreased from 6 to 5.7. The Co-O distance was 2.08 Å. The shorter observed Co-O distance could be also interpreted with a small amount of tetrahedral \( \text{Co}^{2+} \), which was predicted to have a Co-O distance of 1.96 Å. Furthermore, the coordination number of \( \text{Co}^{2+} \) in the film with a thickness of 700 nm was 5.6 and the Co-O distance was 2.06 Å, indicating
more Co$^{2+}$ ions moved from B sites to A sites. Thus, the cation occupation of Co$^{2+}$ in B sites had slightly difference for the CoFe$_2$O$_4$ films with different thicknesses.

![FT EXAFS data from (111)-epitaxial films with different thicknesses and reference powders.](image)

**Fig. 4.9.** The Fourier transformation of Co $K$ EXAFS data from (111)-epitaxial films with different thicknesses and reference powders.

The Co $K$-edge XANES spectrum can be used to determine the dominant oxidation state of Co in the epitaxial films. As shown in Fig. 4.10, the inflection point
in the main absorption edge of epitaxial films, as indicated by the first derivative, matched well with that of spinel Co-ferrite or CoO reference powders, and significantly less than that of Co$_3$O$_4$ reference powders. The comparison clearly indicates that Co is dominantly in the +2 oxidation state in the epitaxial films with different thicknesses.

![Graph showing the absorption edge of Co K-shell XAS for different thicknesses and reference powders.](image)

**Fig. 4.10.** Co K-shell XAS for the (111)-epitaxial Co-ferrite films on (0001)-Al$_2$O$_3$ with different thickness and reference powders.

### 4.2 Magnetic properties of (111)-epitaxial CoFe$_2$O$_4$ films on (0001)-Al$_2$O$_3$

Fig. 4.11 shows hysteresis loops of CoFe$_2$O$_4$ films on (0001)-Al$_2$O$_3$ with thicknesses of 40 and 700 nm deposited at 550 °C. For the 40 nm film, the $H_{c\perp}$ reached 8.8 kOe while the $H_{c\parallel}$ was much lower (1.0 kOe), indicating a high perpendicular anisotropy. If the film’s thickness was 100 nm, the $H_{c\perp}$ decreased to 7.1
kOe while the $H_{||}$ increased to 1.9 kOe, suggesting degraded perpendicular anisotropy. A further increasing of thickness to 200 nm, the film possessed $H_{\perp}$ and $H_{||}$ of 4.5 and 3.0 kOe, respectively. When film thickness was 700 nm, the film possessed slight in-plane magnetic anisotropy with $H_{\perp}$ and $H_{||}$ of 4.4 and 4.7 kOe, respectively. The magnetic properties of the films with various thicknesses between 40 and 700 nm are also summarized in Table 4.1. Based on the table, $H_{\perp}$ considerably decreased with increasing film thickness, whereas the $H_{||}$ showed a substantial increase. A transition from perpendicular anisotropy to parallel anisotropy occurs to the film with a critical thickness between 400 to 500 nm from a rough estimation from the plot using the data in Table 4.1.

![Hysteresis loops](image)

**Fig. 4.11.** The hysteresis loops of the (111)-epitaxial CoFe$_2$O$_4$ films on (0001)-Al$_2$O$_3$ with the thickness of (a) 40 nm, (b) 100 nm, (c) 200 nm, and (d) 700 nm.
Moreover, perpendicular magnetic anisotropy constant $K_u$ can be directly estimated from the following difference between the magnetization curves along the perpendicular and parallel directions:

$$K_u = \int_{0}^{M_s} (H^\perp - H^\parallel) \, dM$$  

Eq. 4.1

Where $H^\perp$ and $H^\parallel$ are the applied magnetic fields in the perpendicular and parallel directions, respectively [8]. Based on Eq. 4.1, measured magnetic anisotropy $K_u$ of CoFe$_2$O$_4$ films on (0001)-Al$_2$O$_3$ with different thicknesses (40-700 nm) were estimated and listed in Table 4.1. The $K_u$ for the 40 nm film was $2.5 \times 10^6 \text{ erg/cm}^3$ whereas the $K_u$ for the 700 nm film was $-0.7 \times 10^6 \text{ erg/cm}^3$. The orientation of the easy axis is highly dependent on film thickness and presents a clear evidence of the reorientation transition from out-of-plane to in-plane anisotropy with varying film thickness.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$H_{c\parallel}$ (kOe)</th>
<th>$H_{c\perp}$ (kOe)</th>
<th>In-plane Strain (%)</th>
<th>Out-of-plane Strain (%)</th>
<th>Measured $K_u$ ($10^6 \text{ ergs/cm}^3$)</th>
<th>Calculated $K_u$ ($10^6 \text{ ergs/cm}^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>4.7</td>
<td>4.4</td>
<td>-0.083</td>
<td>0.055</td>
<td>-0.7</td>
<td>-0.3</td>
</tr>
<tr>
<td>200</td>
<td>3.0</td>
<td>4.5</td>
<td>-0.299</td>
<td>0.199</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>100</td>
<td>1.9</td>
<td>7.1</td>
<td>-0.681</td>
<td>0.454</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>40</td>
<td>1.0</td>
<td>8.8</td>
<td>-1.163</td>
<td>0.775</td>
<td>2.5</td>
<td>2.6</td>
</tr>
</tbody>
</table>

In addition, the calculation using Eq. 4.1 for these films with a thickness of 40 nm at different temperatures was also done and listed in Table 4.2. The $K_u$ was
1.5×10^6 ergs/cm^3 for the film at 150 °C. The $K_u$ increased to 2.5×10^6 ergs/cm^3 at 550 °C, and then decreases to 1.1×10^6 ergs/cm^3 at 800 °C. It is to be noted that the optimized $K_u$ was obtained at the temperature of 550 °C. Therefore, if not specially stated, the deposition temperature was fixed on of 550 °C for the deposition of (001)-epitaxial films on (002)-MgO in this work, which will be discussed later.

Table 4.2. Coercivity $H_c$, strain $\varepsilon$, measured $K_u$ and calculated $K_u$ of CoFe$_2$O$_4$ films with a thicknesses of 40 nm deposited on (0001)-Al$_2$O$_3$ at different temperatures.

| Temperature (°C) | $H_{c||}$ (kOe) | $H_{c\perp}$ (kOe) | In-plane Strain (%) | Out-of-plane Strain (%) | Measured $K_u$ (10^6 ergs/cm^3) | Calculated $K_u$ (10^6 ergs/cm^3) |
|------------------|------------------|---------------------|---------------------|-------------------------|-------------------------------|-------------------------------|
| 800              | 0.7              | 6.4                 | -0.740              | 0.493                   | 1.2                           | 0.9                           |
| 500              | 1.0              | 8.8                 | -1.163              | 0.775                   | 2.5                           | 2.6                           |
| 300              | 1.3              | 7.4                 | -1.213              | 0.809                   | 2.3                           | 2.7                           |
| 150              | 3.0              | 6.3                 | -1.266              | 0.844                   | 1.5                           | 2.9                           |

4.3 Magnetic anisotropy of epitaxial Co-ferrite films

The analysis on magnetic anisotropy for (111)-epitaxial CoFe$_2$O$_4$ films with different thicknesses on (0001)-Al$_2$O$_3$ was studied in this work.

For magnetic thin films, the magnetic anisotropy $K_u$ is usually written as a sum of various contributions [9]:

$$K_u = K_{ui} + K_{u\sigma} + K_{sh}$$  \hspace{1cm} \text{Eq. 4.2}$$

Where $K_{sh}$ is the shape anisotropy, $K_{u\sigma}$ is the stress-induced anisotropy; $K_{ui}$ is the intrinsic magnetocrystalline anisotropy.

For the magnetocrystalline anisotropy $K_{ui}$ of CoFe$_2$O$_4$ materials, it is highly attributed to cation (Co$^{2+}$) distribution in spinel structure. As it is well known, the
perfect CoFe$_2$O$_4$ is a fully inverse spinel structure, in which one iron ions (Fe$^{3+}$) occupies the tetrahedral site (denoted as A site) while the other one Fe$^{3+}$ and one Co$^{2+}$ ions occupy the two octahedral sites (denoted as B site). According to single-ion model [7,10], the $K_{ui}$ of CoFe$_2$O$_4$ materials is highly associated with the occupation rate of Co$^{2+}$ in B sites.

Based on previously described EXAFS analysis, the cation occupation of Co$^{2+}$ in B sites decreased slightly for (111)-epitaxial films with increasing thickness. Accordingly, $K_{ui}$ intends to become degraded due to slight reduction of cation occupation of Co$^{2+}$ in B sites with increasing thicknesses. However, the slightly decreased $K_{ui}$ value cannot cause the thickness-dependent coercivity and reorientation of magnetic anisotropy of (111)-epitaxial CoFe$_2$O$_4$ films on (0001)-Al$_2$O$_3$. There must have other mechanisms to explain them.

It has also been reported that large strain in magnetic films can lead to strong stress anisotropy in CoFe$_2$O$_4$ films [11,12,13,14,15]. The decrease in coercivity and re-orientation of magnetic anisotropy with increasing thicknesses might be attributed to degradation of stress anisotropy due to strain relaxation. In terms of magnetoelastic theory, the strain may induce an additional uniaxial magnetic anisotropy (stress anisotropy) $K_{us}$ which is given by $K_u = -3\lambda \sigma / 2$ ($\lambda$ is the magnetostriction constant and $\sigma$ is the stress).

For epitaxial cubic films, a phenomenological model can be used to calculate the total energy that controls magnetic anisotropy of magnetization for thin films. The total energy can be written as [16]
\[
E = K_i (\alpha_1^2 \alpha_2 + \alpha_2^2 \alpha_3 + \alpha_3^2 \alpha_1) - \frac{3}{2} \lambda_{100} (C_{11} - C_{12}) (\epsilon_\alpha \alpha_1^2 + \epsilon_\beta \alpha_2^2 + \epsilon_\gamma \alpha_3^2) - \frac{3}{2} \lambda_{111} C_{44} (\epsilon_\alpha \alpha_1 \alpha_2 + \epsilon_\beta \alpha_2 \alpha_3 + \epsilon_\gamma \alpha_3 \alpha_1) + 2 \pi M_s^2 \]
\]
Eq. 4.3

Where the first term accounts for the magnetocrystalline anisotropy \( K_{\alpha i} \), the second and third terms are for the magneto-elastic energy \( K_{\mu \sigma} \), and the last for the magnetostatic energy \( (K_{sh}) \) of a thin film. Here, the magnetization directions is given by \( \alpha_i \) and the film strains are denotes \( \epsilon_i \), where the contracted Voigt-notion has been applied to contract the two-suffix symmetric strain tensor \( \epsilon_{ij} \) to \( \epsilon_k \) [17]. Both directions cosines \( \alpha_i \) and strain \( \epsilon_i \) are given in a cubic crystal system, which does not coincide with the film coordinate system in general. This requires approximate tensor transformations for orientation other than (001)-cubic films. \( f \) is the demagnetization coefficients. For magnetic thin films, we can assume \( f=1 \) for perpendicular and \( f=0 \) for parallel direction. In this work, the measured value of the saturation magnetization of all the CoFe\(_2\)O\(_4\) films in this works was around \( M_s = 200 \text{ emu/cm}^3 \).

Thus, perpendicular anisotropy \( K_u \) for epitaxial (111)-CoFe\(_2\)O\(_4\) films on (0001)-Al\(_2\)O\(_3\) can be calculated as the energy difference between two directions (in-plane and out-of-plane), which is written as

\[
K_u = E_{[1\overline{1}0]} - E_{[\overline{1}1\overline{1}]} \quad \text{Eq. 4.4}
\]

Where \( E_{[1\overline{1}1]} = K_i / 3 + 2 \pi M_s^2 \), and \( E_{[1\overline{1}0]} = K_i / 4 - \frac{3}{2} \lambda_{[\overline{1}10]} \sigma_{[\overline{1}10]} \) while

\[
\sigma_{[\overline{1}10]} = M_{[\overline{1}1\overline{1}]} \epsilon_{[\overline{1}10]} \quad \text{Eq. 4.5}
\]

In which, \( M_{[1\overline{1}1]} \) is the appropriate biaxial modulus. The general formula for cubic materials can be determined as a function of the grain orientation \( (hkl) \) and the stiffness constants \( (C_{11}, C_{12}, C_{44}) \) as [18]
\[ M_{hkl} = C_{11} + C_{12} + K - \frac{2(C_{12} - K)^2}{C_{11} + 2K} \]  
Eq. 4.6

Where

\[ K = (2C_{44} - C_{11} + C_{12})(h^2k^2 + k^2l^2 + h^2l^2)/(h^2 + k^2 + l^2)^2 \]  
Eq. 4.7

Furthermore, \( \varepsilon_{[110]} \) is in-plane strain, which can be calculated by combining XRD scans (symmetric and asymmetric). The \( \varepsilon_{[hkl]} \) can be estimated by measuring the accurate \( d \)-space of the \( (hkl) \) plane using high resolution XRD and calculated using the following equation [19]

\[ \varepsilon_{[hkl]} = \frac{d_{[hkl] \text{films}} - d_{[hkl] \text{arg et}}}{d_{[hkl] \text{arg et}}} \]  
Eq. 4.8

Based on the above equations, both the in-plane strain \( \varepsilon_{[110]} \) and the out-of-plane strain \( \varepsilon_{[111]} \) are calculated for the (111)-epitaxial films and listed in Table 4.1. For the film with a thickness of 40 nm, the in-plane strain was -1.163 % (compressive strain) while the out-of-plane strain was 0.775 % (tensile strain). With increasing thicknesses, the strains in both directions decreased. The in-plane and out-of-plane strain for the epitaxial film (700 nm) were -0.083 % (compressive strain) and 0.055 % (tensile strain), respectively. The strain was almost negligible with almost completely relaxation.

Given the calculated in-plane strain \( \varepsilon_{[110]} \) described above, the magnetostriction constant of bulk CoFe\(_2\)O\(_4\) materials is \( \lambda_{t \rightarrow 0} \approx 60 \times 10^{-6} \), and bulk magnetocrystalline anisotropy is \( K_1=2 \times 10^6 \) ergs/cm\(^3\). The estimated \( K_u \) for all the (111)-epitaxial films on (0001)-Al\(_2\)O\(_3\) with different thicknesses using Eq. 4.4 is also shown in Table 4.1. The (111)-epitaxial films with in-plane compressive strain and out-of-plane tensile strain possessed perpendicular anisotropy. The calculated \( K_u \) for the film (40 nm) was
2.6×10^6 ergs/cm³. The value is very close to the measured value (2.5×10^6 ergs/cm³) extracted from the measured hysteresis loops. Furthermore, the calculated values of \( K_u \) for other thicknesses (100-700 nm) are also well consistent with these experimentally measured values.

With the same method, as shown in Table 4.2, the calculated \( K_u \) for (111)-epitaxial CoFe₂O₄ films with a thickness of 40 nm at different temperatures was also comparable with the measured values except the film deposited at 150 °C. The non-matching \( K_u \) for the film (40 nm) at 150 °C may be due to degraded (111)-epitaxial degree, as its large FWHM for this film indicated. Thus, all the results directly revealed that taking strain induced stress anisotropy in accounting can give a reasonable explanation for thickness-dependent re-orientation of magnetic anisotropy and high coercivity. At the critical thickness, the stress anisotropy is comparable with the shape anisotropy and results in isotopic magnetic anisotropy. Moreover, due to strain relaxation in the films with a large thickness, the drastic reduction in stress anisotropy allows the shape anisotropy to dominate, leading to in-plane magnetic anisotropy.

### 4.4 Growth and magnetic anisotropy of (001)-epitaxial CoFe₂O₄ films on (002)-MgO

In this work, (001)-epitaxial Co-ferrite films with different thicknesses (40-700 nm) were also prepared on single crystal (002)-MgO substrates. The films were deposited at the constant deposition temperature of 550 °C. The excellent (001)-epitaxial structure was characterized with both HRXRD and cross-section HRTEM images. As shown in the Fig. 4.12, an obvious thickness-dependent shift of the (008) peaks indicated strain relaxation with increasing thickness. After measuring positions of the (008) peaks, the out-of-plane \( d \)-space for the 40 nm film was 8.328 Å while that
of the 700 nm film was 8.379 Å, which was close to the bulk value of 8.380 Å for the CoFe$_2$O$_4$ target. Shrinking out-of-plane $d$-space for the (001)-plane illustrated a distorted cubic lattice with out-of-plane compressive strain. The distorted lattice recovered to cubic lattice with increasing thickness. Additionally, epitaxial growth of (001)-CoFe$_2$O$_4$ films on (002)-MgO were also previously reported using both MBE and PLD. Strain relaxation in those films was also observed to be thickness-dependent [3, 11,20].

![Graph showing XRD patterns](image)

**Fig. 4.12.** The XRD patterns of (001)-epitaxial Co-ferrite films prepared with different thicknesses on (002)-MgO substrate PLD at 550 °C.

The excellent (002)-epitaxial structure on MgO was also directly identified with the HRTEM image, which is shown in Fig. 4.13. The inset of SAED patterns clearly indicated the epitaxial structure with [100](001)-CoFe$_2$O$_4$ || [100](001)-MgO.
Fig. 4.13. The HRTEM images of the (001)-epitaxial 40 nm CoFe$_2$O$_4$ film on (002)-MgO.

The excellent of (001)-epitaxial CoFe$_2$O$_4$ films on MgO substrate obtained using PLD is definitely related to small lattice mismatch between these two materials. As shown in Fig. 4.14, both MgO and CoFe$_2$O$_4$ are cubic *f.c.c* structure, and the lattice mismatch is calculated to be only 0.47 %. Additionally, XPS measurement revealed a constant chemical composition CoFe$_2$O$_4$ for the films with different thicknesses. The depth profile (Fig. 4.15) was also illustrated a clear sharp interface between the MgO and CoFe$_2$O$_4$ films, which indicated the deposition temperature of 550 °C was not high to cause serious interdiffusion and damage epitaxial growth of films on single crystal substrate.
Fig. 4.14. The (001) planes of f.c.c NaCl-type MgO (a) and spinel type CoFe$_2$O$_4$ (b).

Fig. 4.15. The XPS depth profile of the (001)-epitaxial CoFe$_2$O$_4$ film (40 nm) on (002)-MgO at 550 °C.
Fig. 4.16 shows hysteresis loops of (001)-epitaxial CoFe\(_2\)O\(_4\) films on (002)-MgO with the thicknesses between 40 and 700 nm. The films’ magnetic anisotropy was highly dependent on film thickness. The 40 nm film obviously exhibited perpendicular anisotropy with \(H_{c\perp}\) of 9.1 kOe but \(H_{c\parallel}\) of less than 2.0 kOe. Whereas, the film (700 nm) possessed in-plane anisotropy. The \(H_{c\perp}\) was only 2.3 kOe but \(H_{c\parallel}\) was over 6.0 kOe. The results are consistent with the same thickness-dependent re-
orientation of magnetic anisotropy reported previously for the similar (001)-epitaxial
CoFe$_2$O$_4$ films on (002)-MgO [3,13,14].

Based on Eq. 4.1, the $K_u$ values for all the (001)-epitaxial films on (002)-MgO
with different thicknesses are listed in Table 4.3. The estimated $K_u$ values were 1.1,
0.9, 0.4, and -0.2×$10^6$ ergs/cm$^3$ for the films with 40, 100, 200 and 700 nm,
respectively. A transition from perpendicular anisotropy to parallel anisotropy occurs
for the film with a critical thickness between 200 and 700 nm. With the same method
used for calculating magnetic anisotropy with that used for (111)-epitaxial films on
(0001)-Al$_2$O$_3$, magnetic anisotropy of (001)-epitaxial CoFe$_2$O$_4$ films on (002)-MgO
with different thicknesses can also be estimated. The in-plane and out-of-plane strains
have been calculated and are shown in Table 4.3. For the film (40 nm), the in-plane
strain was tensile (+0.322 %) and the out-of-plane strain is compressive (-0.609 %).
Likewise, for (001)-epitaxial CoFe$_2$O$_4$ films, $K_u$ can be calculated with

$$K_u = -\frac{3}{2}\lambda_{[100]}\sigma_{[100]} - 2\pi M_s^2$$

Eq. 4.9

While $\sigma_{[100]} = M_{[001]}\varepsilon_{[100]}$ and $M_{[001]} = C_{11} + C_{12} - 2C_{12}^2 / C_{11}$. With $\lambda_{[100]} \sim -200 \times 10^6$,
(001)-epitaxial CoFe$_2$O$_4$ films with in-plane tensile strain and out-of-plane
compressive strain exhibited perpendicular anisotropy. The calculated $K_u$ of the film
(40 nm) was $1.8\times10^6$ ergs/cm$^3$, which was comparable to the measured value ($1.1\times10^6$
ergs/cm$^3$). When film thickness increased to be 700 nm, the calculated $K_u$ ($-0.4\times10^6$
ergs/cm$^3$) also matched well with that measured one ($-0.8\times10^6$ ergs/cm$^3$). The
consistent results directly present strong evidences for the critical role of strain-
induced stress anisotropy which plays in tuning the thickness-oriented magnetic
anisotropy for epitaxial CoFe$_2$O$_4$ films.
Table 4.3. Coercivity $H_c$, strain $\varepsilon$, measured $K_u$ and calculated $K_u$ of (001)-CoFe$_2$O$_4$ films with different thicknesses deposited on (002)-MgO.

| Thickness (nm) | $H_{c||}$ (kOe) | $H_{c\perp}$ (kOe) | In-plane Strain (%) | Out-of-plane Strain (%) | Measured $K_u$ $(10^6$ ergs/cm$^3$) | Calculated $K_u$ $(10^6$ ergs/cm$^3$) |
|---------------|-----------------|------------------|---------------------|------------------------|-------------------------------|---------------------------------|
| 700           | 6.1             | 2.3              | 0.006               | -0.012                 | -0.8                          | -0.4                            |
| 200           | 4.6             | 5.8              | 0.082               | -0.155                 | 0.3                           | 0.1                             |
| 100           | 3.8             | 7.1              | 0.221               | -0.418                 | 0.9                           | 1.1                             |
| 40            | 1.9             | 9.1              | 0.322               | -0.609                 | 1.1                           | 1.8                             |

4.5 Summary

Epitaxial Co-ferrite films with different thicknesses (40-700 nm) were prepared on (0001)-Al$_2$O$_3$ and (002)-MgO substrate. It was observed that the films on (0001)-Al$_2$O$_3$ exhibited (111)-epitaxial structure while the films on (002)-MgO showed (001)-epitaxial structure. These epitaxial films acted as strong evidence to identify the thickness-dependent magnetic anisotropy related to strain induced stress anisotropy. The calculated $K_u$ for the epitaxial films based on the phenomenological model matched very well with the measured value.

Based the understanding, in order to achieve nanocrystalline polycrystalline Co-ferrite films with large perpendicular anisotropy, it requires to fabricate polycrystalline Co-ferrite thin films with a certain crystallographic texture. According to the fabrication of epitaxial Co-ferrite films on single crystal substrate with in-situ heating, in-situ heating may be possible to fabricate textured polycrystalline Co-ferrite films with high coercivity and perpendicular anisotropy. Therefore, polycrystalline Co-ferrite films will be fabricated with in-situ heating in Chapter 5.
4.6 References


5 Chapter V Growth and magnetic properties of polycrystalline CoFe$_2$O$_4$ films on SiO$_2$ with in-situ heating

In this chapter, textured polycrystalline Co-ferrite (CoFe$_2$O$_4$) films were deposited on SiO$_2$ substrates with PLD using in-situ heating. Effects of different experimental conditions including substrate temperature, thickness, and various substrates including single crystal and amorphous SiO$_2$ on film growth, microstructure and magnetic properties were studied. Moreover, the mechanisms for texture evolution and residual strain formation were also investigated.

5.1 Film growth and magnetic properties of Co-ferrite films on (0001)-SiO$_2$

5.1.1 Film growth of Co-ferrite films on (0001)-SiO$_2$

Fig. 5.1(a) shows the XRD patterns with $\theta$-$2\theta$ scans of the films with a thickness of 100 nm deposited at different substrate temperatures. The results indicated that the crystallized structure could be obtained using PLD at a low deposition temperature. Compared to the XRD patterns of the Co-ferrite target, the films prepared at 150 °C and below showed an (220)-textured structure, while the films prepared at 300 °C and above exhibited a strong (111) crystallographic texture as indicated by the high Lotgering factor $f$ for the series of {111} peaks. The $f$ for the film deposited at 550 °C reached a value of 0.62, whereas it was almost 0 for the polycrystalline target with an isotropic structure (Fig. 5.1(b)). Moreover, the film at 900 °C exhibited only {111} peaks without other diffraction peaks, suggesting a pure (111)-texture with the $f$ of 1. The (111)-texture obviously enhanced with increasing temperature. Fig. 5.1(c) revealed an obvious peak shift as the positions of the (333)
peak shifted back to that of the Co-ferrite target with increasing substrate temperature. The (333) peak’s position for the film at 550 °C was 56.50° while it increased to 56.86° for the film at 900 °C, more close to 57.06° for the target.

![XRD patterns](image)

**Fig. 5.1.** The XRD patterns of (a) the 100 nm CoFe$_2$O$_4$ films deposited at different substrate temperatures, (b) Co-ferrite target, and (c) the magnified (333) diffraction peaks.

The surface morphologies of these Co-ferrite films deposited at different temperatures were examined with AFM (Fig. 5.2). At room temperature, the film presented a poor crystallinity without obvious crystalline grain formation. With increasing temperature, the grain nucleation formed and the particle size was around 20 nm at 550 °C. With further increasing temperature, the images indicated the beginning of island coalescence. Film growth and agglomeration resulted in large particle size at 900 °C. On the other side, the films also exhibited excellent surface smoothness with the rms less than 1 nm for the films deposited at a substrate
Fig. 5.2. The AFM (1×1 μm) images of 100 nm Co-ferrite films prepared at 2 mTorr with in-situ-heating at: 27 °C (a), 300 °C (b), 550 °C (c), 600 °C (d), 800 °C (e), and 900 °C (f).
temperature below 700 °C. The extraordinary smooth surface is probably attributed to small grain size at a low deposition temperature during the PLD deposition process.

XPS depth profiles for these films were also examined in this work. As shown in Fig. 5.3, there was no obvious difference between the film deposited at 550 °C and 900 °C. Both two films presented sharp interface without obvious interdiffusion at the interface between Co-ferrite films and SiO₂ substrate.

![XPS profiles of the Co-ferrite films with a thickness of 100 nm on (0001)-SiO₂ at 550 °C and 900 °C.](image)

Fig. 5.3. The XPS profiles of the Co-ferrite films with a thickness of 100 nm on (0001)-SiO₂ at 550 °C and 900 °C.

Fig. 5.4 shows the XRD patterns of the Co-ferrite films on (0001)-SiO₂ with different thicknesses deposited at 550 °C. When the thickness was around 17 nm, the film showed a pure (111)-texture without other diffraction peaks from the crystalline phase of CoFe₂O₄. The 33 nm film also possessed a (111)-texture but small other peaks such as (311) peak appeared. The (311) peak’s intensity became stronger and
comparable with that of the (222) peak for the film with a thickness of 54 nm. When the thickness increasing to 130 nm, the (111) texture became further weaker, which was identified with the reduced Lotgering factor $f$. It decreased from 0.78 at 54 nm to 0.55 at 130 nm. While the thickness was 228 nm, the (111) texture almost disappeared and the pattern appeared to be (220) and/or (311)-texture. Moreover, with the thickness increasing to 350 nm, the pattern became (311)-texture. The thickness-related texture evolution will be discussed in more details later.

![XRD patterns of Co-ferrite films on (0001)-SiO$_2$ deposited at 550 °C with different thicknesses.](image)

**Fig. 5.4.** The XRD patterns of the Co-ferrite films on (0001)-SiO$_2$ deposited at 550 °C with different thicknesses.

The dark field (DF) TEM image of the 33 nm Co-ferrite film deposited on (0001)-SiO$_2$ at 550 °C is shown in Fig. 5.5(c). It indicated the grain size in the range of 10-20 nm, suggesting an excellent nanocrystalline structure. The grains in this
figure were isolated from each others. The selected area electron diffraction pattern (SAED) as shown in Fig. 5.5(a) provided another strong evidence for the textured structure with some ranges of the diffraction rings showing abnormally strong diffraction intensities. As shown in the cross section TEM image Fig. 5.5 (b), the surface of the film obviously exhibited an excellent smoothness. Additionally, Fig. 5.5(b) also indicated a sharp contrast between the film and the substrate, revealing that the interdiffusion between the film and single crystal SiO₂ substrate was not serious, consistent with the indication from the XPS depth profile [1].

![Fig. 5.5.](image)

**5.1.2 Magnetic properties of Co-ferrite films on (0001)-SiO₂**

Table 5.1 gives the magnetic properties (coercivity and remanence measured in both in-plane and out-of-plane directions) of the films on (0001)-SiO₂ with a thickness of approximate 100 nm deposited at different substrate temperatures. It was
found that all the films possessed relatively high values of coercivity, which are much higher than that of the bulk Co-ferrite materials (~1.0 kOe) [2]. The films deposited at 150 °C and below exhibited an in-plane magnetic anisotropy with a $K_u$ of $-0.3 \times 10^6$ ergs/cm$^3$, while perpendicular anisotropy was observed for the films deposited at 300 °C and higher. The $H_{c,\perp}$ reached a maximum of 10.5 kOe for the film deposited at 550 °C, and then decreased to 6.1 kOe with increasing temperature to 900 °C. Likewise, both the $K_u$ and $H_{c,||}$ of these films showed the similar trend with $H_{c,\perp}$ related to substrate temperature. The $H_{c,||}$ presented the values in the range between 1.0 to 6.0 kOe. The reduced coercivity for the films deposited at high temperature can be partially explained with large grains formed at high temperatures, which was identified with the AFM observation.

**Table 5.1. Magnetic properties of Co-ferrite films on (0001)-SiO$_2$ with a thickness of 100 nm deposited at different substrate temperatures [Coercivity $H_c$, the remanence ratio ($M_r/M_s$), and $K_u$].**

| Substrate temperature(°C) | $H_{c,||}$ (kOe) | ($M_r/M_s$)$_{||}$ (%) | $H_{c,\perp}$ (kOe) | ($M_r/M_s$)$_{\perp}$ (%) | $K_u$ ($10^6$ ergs/cm$^3$) |
|---------------------------|------------------|------------------------|--------------------|--------------------------|---------------------------|
| 27                        | 4.2              | 53.3                   | 3.4                | 45.0                     | -0.4                      |
| 150                       | 6.3              | 68.9                   | 6.9                | 74.0                     | -0.3                      |
| 300                       | 4.9              | 51.5                   | 7.7                | 70.0                     | 0.8                       |
| 400                       | 5.0              | 53.1                   | 8.8                | 77.4                     | 1.0                       |
| 550                       | 5.8              | 58.2                   | 10.5               | 81.6                     | 1.2                       |
| 650                       | 5.4              | 56.0                   | 8.7                | 68.1                     | 1.1                       |
| 800                       | 2.9              | 50.5                   | 7.8                | 67.6                     | 0.9                       |
| 900                       | 1.7              | 40.4                   | 6.1                | 59.8                     | 0.7                       |
The results about the relationship between coercivity and temperature for the film deposited using in-situ heating is consistent with that for the films using post-annealing, indicating that grain size is one of the critical parameters to obtain optimal coercivity for Co-ferrite films. The grain size can be tuned by substrate temperature. The other reasons for reduced coercivity for the films at high temperatures may be due to residual strain relaxation inside the films at high temperatures, which was also identified with the recovery of peaks’ position. The mechanisms will be discussed later.

As the relationship between coercivity and substrate temperature indicated that the optimized substrate temperature for films with high coercivity using in-situ heating is 550 °C. Moreover, the optimized $K_u$ for the film on (0001)-SiO$_2$ with a thickness of 100 nm at 550 °C was $1.2 \times 10^6$ ergs/cm$^3$.

| Thickness (nm) | $H_{c||}$ (kOe) | $(M_r/M_s)_{||}$ (%) | $H_{c\perp}$ (kOe) | $(M_r/M_s)_{\perp}$ (%) | $K_u$ (10$^6$ ergs/cm$^3$) |
|---------------|-----------------|---------------------|------------------|---------------------|-----------------|
| 350.0         | 4.7             | 35.8                | 5.5              | 42.5                | 0.2             |
| 228.4         | 6.8             | 62.4                | 7.9              | 64.9                | 0.6             |
| 129.2         | 5.8             | 58.2                | 10.5             | 81.6                | 1.2             |
| 53.7          | 5.7             | 62.8                | 11.8             | 95.7                | 1.5             |
| 33.5          | 4.2             | 53.7                | 12.5             | 97.4                | 1.7             |
| 17.5          | 0.9             | 43.8                | 8.0              | 77.2                | 1.3             |

The effects of film thickness on magnetic properties were also investigated in this work. As shown in Table 5.2, all the Co-ferrite films were deposited at the optimized substrate temperature of 550 °C. The film with a thickness of ~17 nm
exhibited a high $H_{c,\perp}$ of 8.0 kOe as well as a very low $H_{c,||}$ of 0.9 kOe. Moreover, the film with a thickness of ~33 nm possessed a high $H_{c,\perp}$ of 12.5 kOe, which is a very promising coercivity value at room temperature for Co-ferrite materials. As the thickness further increased to 230 nm, the $H_{c,\perp}$ and $H_{c,||}$ decreased to 7.9 kOe, 6.8 kOe respectively. The film with a thickness of 350 nm presented almost isotropic magnetic texture with both $H_{c,\perp}$ and $H_{c,||}$ of 5.0 kOe. Moreover, $K_u$ of the films decreased with increasing thicknesses. The optimal $K_u$ was achieved for the film with the thickness of 33.5 nm. Moreover, it decreased to $0.2 \times 10^6$ ergs/cm$^3$ for the film (350 nm), indicating thickness-dependent magnetic anisotropy.

![Graph](image)

**Fig. 5.6.** The coercivity $H_c$ of (a) Co-ferrite films on (0001)-SiO$_2$ with different thicknesses with post-annealing at 700 °C and (b) Co-ferrite films with different thicknesses on (0001)-SiO$_2$ with in-situ heating at 550 °C.
The trends about coercivity of films with different thicknesses prepared using both post-annealing and in-situ heating are summarized in Fig. 5.6. The thickness-dependent coercivity of films using in-situ heating is much different from that for the films using post-annealing (Table 3.4), suggesting additional coercivity mechanisms for the films with in-situ heating, which will be discussed.

Except for the high $H_{c⊥}$ of 12.5 kOe, the 33 nm Co-ferrite film also possessed a high remanence ratio of approximate 95 % in the perpendicular direction, which is shown in Fig. 5.7. The calculated $K_u$ was $1.7 \times 10^6 \text{erg/cm}^3$. This $K_u$ is relative large for spinel cubic ferrite films. Theoretically, the magnetocrystalline anisotropy of cubic CoFe$_2$O$_4$ films with (111)-texture is around $0.2 \times 10^6 \text{erg/cm}^3$ along the [111] direction [3]. There definitely are other mechanisms accounting for the high coercivity and large perpendicular anisotropy except for the intrinsic magnetocrystalline anisotropy.

![Fig. 5.7. The hysteresis loops of the 33 nm Co-ferrite film on (0001)-SiO$_2$ deposited at 550 °C.](image-url)
5.2 Film growth and magnetic properties of Co-ferrite films on amorphous SiO$_2$

Like the films on single crystal (0001)-SiO$_2$, Co-ferrite films were also deposited on amorphous SiO$_2$ (glass) in this work.

![XRD patterns](image)

**Fig. 5.8.** The XRD patterns of (a) the CoFe$_2$O$_4$ films with a thickness of 40 nm at different temperatures and (b) the CoFe$_2$O$_4$ films with different thicknesses at 550 °C on amorphous SiO$_2$.

Fig. 5.8(a) showed the XRD patterns of the 40 nm Co-ferrite films on glass at different temperatures. At the temperature of 150 °C, the film possessed a (220)-texture. Whereas, at the temperature of 550 °C, the film obviously exhibited a (111)-
textured structure as well as other diffraction peaks. Moreover, at the high temperature of 800 °C, the film’s (111) texture enhanced and appeared to be pure without additional diffraction peaks. Additionally, a temperature-dependent peak shift was also observed. The trend about the effects of substrate temperature on texture evolution for the films on amorphous SiO\textsubscript{2} is similar to that of films deposited on single crystal (0001)-SiO\textsubscript{2}. The thickness-dependent XRD patterns of Co-ferrite films deposited on glass at 550 °C are shown in Fig. 5.8(b). They were also consistent with the films on (0001)-SiO\textsubscript{2} with various thicknesses. With the thickness of 40 nm, the films was (111) texture, while increasing the thickness to 350 nm, the texture turned to be (311)-texture. Thus, both amorphous glass and single crystal quartz show no different substrate effects on texture formation of Co-ferrite films with in-situ heating.

Table 5.3. Magnetic properties of Co-ferrite films deposited on amorphous SiO\textsubscript{2} with varied experimental conditions [Coercivity $H_c$, the remanence ratio $(M_r/M_s)$, and $K_u$].

| Samples             | $H_c||$ (kOe) | $(M_r/M_s)||$ (%) | $H_c\perp$ (kOe) | $(M_r/M_s)\perp$ (%) | $K_u$ (10$^6$ ergs/cm$^3$) |
|---------------------|---------------|-------------------|------------------|---------------------|-----------------------------|
| 40 nm at 150 °C     | 4.9           | 60.3              | 3.4              | 41.7                | -0.4                        |
| 40 nm at 550 °C     | 4.0           | 58.6              | 8.4              | 73.4                | 0.9                         |
| 40 nm at 800 °C     | 2.0           | 28.6              | 7.2              | 68.7                | 0.6                         |
| 100 nm at 550 °C    | 4.6           | 60.3              | 7.4              | 70.4                | 0.7                         |
| 350 nm at 550 °C    | 5.0           | 45.6              | 5.8              | 53.2                | 0.2                         |

Magnetic properties of the Co-ferrite films on amorphous glass are listed in Table 5.3. The film with a thickness of 40 nm deposited at 150 °C possessed an in-
plane magnetic anisotropy with the $K_u$ of $-0.4 \times 10^6$ ergs/cm$^3$ while the film with the same thickness deposited at 550 °C turned to be perpendicular anisotropy with the $K_u$ of $0.9 \times 10^6$ ergs/cm$^3$. However, the $K_u$ further decreased to $0.6 \times 10^6$ ergs/cm$^3$ at the temperature of 800 °C. Meanwhile, the thickness-dependent magnetic anisotropy of Co-ferrite films on glass indicated the same trend as that of films on single crystal (0001)-SiO$_2$. With the thickness up to 350 nm, the $K_u$ degraded to $0.2 \times 10^6$ ergs/cm$^3$.

### 5.3 Film growth and magnetic properties of Co-ferrite films on (1000)-SiO$_2$ and (11-20)-SiO$_2$

Except for using single crystal (0001)-SiO$_2$ as the substrates, Co-ferrite films were also prepared on single crystal SiO$_2$ with other planes such as (1000) and (11-20)-SiO$_2$.

![XRD patterns of Co-ferrite films on different substrates](image_url)

**Fig. 5.9.** The XRD patterns of the Co-ferrite films with a thickness of 40 nm on different substrates including (1000)-SiO$_2$, (11-20)-SiO$_2$, and (0001)-SiO$_2$ at 550 °C.
All the films’ thickness was kept at 40 nm and deposited temperature was set at 550 °C. As shown in Fig. 5.9, the XRD patterns of all the films exhibited (111)-
texture and obvious (333) peak shift compared to that of the Co-ferrite target. Magnetic properties of these films (Table 5.4) revealed negligible difference. The $K_u$
was around $1.5 \sim 1.6 \times 10^6$ ergs/cm$^3$. All these results suggested negligible effects of
different planes of single crystal SiO$_2$ on texture formation and magnetic properties of polycrystalline Co-ferrite films using in-situ heating.

Table 5.4. Magnetic properties of Co-ferrite films with a thickness of 40 nm deposited at 550 °C on single crystal SiO$_2$ with different planes [Coercivity $H_c$, the remanence ratio $(M_r/M_s)$, and $K_u$].

| Substrate     | $H_{c||}$ (kOe) | $(M_r/M_s)_{||}$ (%) | $H_{c\perp}$ (kOe) | $(M_r/M_s)_{\perp}$ (%) | $K_u$ ($10^6$ ergs/cm$^3$) |
|---------------|-----------------|----------------------|--------------------|-------------------------|-----------------------------|
| (11-20)-SiO$_2$ | 4.3             | 49.3                 | 10.1               | 84.6                    | 1.5                         |
| (1000)-SiO$_2$    | 4.0             | 52.1                 | 10.3               | 87.6                    | 1.5                         |
| (0001)-SiO$_2$     | 3.7             | 48.2                 | 10.8               | 89.6                    | 1.6                         |

5.4 Texture evolution of Co-ferrite films with in-situ heating

In general, the crystallographic change in polycrystalline or epitaxial thin films is driven by a reduction in the system total anisotropy energy, which can be described as [4],

$$E_{total} = \frac{\gamma_s + \gamma_i}{h} + M_{hkl} \varepsilon^2$$

Eq. 5.1

Where $\gamma_s$ is surface energy; $\gamma_i$ is interfacial energy; $h$ is film thickness. The last term $M_{hkl} \varepsilon^2$ is elastic strain energy density, $\varepsilon$ is intrinsic residual strain, and $M_{hkl}$ is the
biaxial modulus, which is closely related to crystallographic direction. Based on Eq. 5.1, texture evolution of polycrystalline films is mainly due to minimization of total system energy by changing the surface energy of oriented crystal planes and interfacial energy between film and substrate or by changing the elastic strain energy density, which is related to different textured orientation.

In Chapter 4, when using substrates (single crystal Al₂O₃, MgO) with small lattice mismatch with CoFe₂O₄, \( \gamma \) has a dominant contribution to minimize the total anisotropy energy. Thus, the (001)-epitaxial films on (002)-MgO and the (111) epitaxial films on (111)-Al₂O₃ formed even at a low temperature or with a thickness up to 700 nm. However, when using amorphous or single crystal SiO₂, whose planes showing no corresponding lattice matching with any planes of CoFe₂O₄, \( \gamma \) has negligible contribution to the total anisotropy energy and then can be neglected.

The surface energies for particular crystallographic planes of spinel CoFe₂O₄ phase can be calculated using a phenomenological model, in which the surface energy of different surfaces can be calculated with Eq. 5.2

\[
\gamma_{\{hkl\}} = \frac{E_{\{hkl\}} q_{\{hkl\}}^2}{\pi^2 d_{\{hkl\}}} \quad \text{Eq. 5.2}
\]

Where \( E \) is the elastic modulus normal to the \((hkl)\) plane, \( d \) is the d-space of \((hkl)\) plane, and \( q \) is the smallest possible interlayer spacing for the \((hkl)\) plane. The value of \( E \) can be calculated from the stiffness constants \((C_{11}, C_{12}, \text{and } C_{44})\). Taking the (111) plane as an example, \( E_{111} = (C_{11} + 2C_{12} + 4C_{44})/3 \), \( d_{111} = a/\sqrt{3} \), and \( h_{111} = a\sqrt{3}/24 \), in which \( a \) is lattice parameter. With the stiffness constant of bulk CoFe₂O₄ \((C_{11}=2.73 \times 10^{12} \text{ dynes/cm}^2, C_{12}=1.06 \times 10^{12} \text{ dynes/cm}^2, C_{44}=0.97 \times 10^{12} \text{ dynes/cm}^2)\) and Eq. 5.2 [6], the surface energies for different planes of CoFe₂O₄ are anisotropic: \( \gamma_{\{111\}} (208 \text{ ergs/cm}^2) < \gamma_{\{400\}} (1486 \text{ ergs/cm}^2) < \gamma_{\{220\}} (1916 \text{ ergs/cm}^2) < \)}
Thus, CoFe$_2$O$_4$ films intend to be (111) preferred orientation since it is more energetically favorable than other orientations such as (400), (220) or (311).

In addition to surface energy minimizing effect, there is a competing factor (strain energy density) which also influences the total energy and the film texture. The strain energy density depends on the crystallographic orientations ($hkl$), and the effective biaxial modulus of the grains. Generally, the strain energy density is given by

$$E_s = M_{hkl} \varepsilon^2$$

Eq. 5.3

Where $M_{hkl}$ is the appropriate biaxial modulus, which for cubic materials can be determined as a function of the grain orientation ($hkl$) and the stiffness constants ($C_{11}$, $C_{12}$, $C_{44}$) as [8]

$$M_{hkl} = C_{11} + C_{12} + K - \frac{2(C_{12} - K)^2}{C_{11} + 2K}$$

Eq. 5.4

Where

$$K = (2C_{44} - C_{11} + C_{12})(h^2k^2 + k^2l^2 + h^2l^2) / (h^2 + k^2 + l^2)^2$$

Eq. 5.5

With the stiffness constants of bulk CoFe$_2$O$_4$ and Eq. 5.4, the $M_{hkl}$ can be obtained as follows:

$$M_{111}(3.68 \times 10^{12} \text{ dynes/cm}^2) > M_{220}(3.17 \times 10^{12} \text{ dynes/cm}^2) > M_{311}(3.09 \times 10^{12} \text{ dynes/cm}^2)$$

Eq. 5.6

Based on the above results, strain energy density minimization leads to the formation of (311) or (220) texture, rather than (111) texture because the formation of (111) texture films possesses larger strain energy density than the formation of other textures.
According to the driving force described in Eq. 5.1, the texture map of polycrystalline CoFe$_2$O$_4$ films on amorphous or single crystal SiO$_2$ has been developed, which is shown in Fig. 5.10. When film thickness is small ($h$ is small) or substrate temperature is high (over 550 °C) with small $\varepsilon$, the texture is dominated by the first item in Eq. 5.1, i.e. the minimization of surface energy. The films tend to have (111)-texture. With increasing film thickness ($h$ is large) or decreasing substrate temperature to below 150 °C with large $\varepsilon$, the texture is determined by the second item, i.e. the minimization of strain energy density, which leads to form (311) and/or (220) or (311) texture.
(220) texture. The critical parameters for the transition from surface energy determination to strain energy density determination can be (1) thickness, (2) residual strain $\varepsilon$, which is highly related to atomic diffusion. The formation mechanisms of residual strain will be discussed in the next section.

## 5.5 Formation mechanisms of residual strain

Generally, residual strain in thin film may result from a difference in thermal expansion coefficient (CTE) between substrate and film, which can be estimated with

$$
\varepsilon_{\text{thermal}} = (\alpha_{\text{film}} - \alpha_{\text{substrate}}) \cdot (T_{\text{dep}} - T_0).
$$

In the equation, $\alpha$ is CTE, $T_{\text{dep}}$ is deposition temperature, and $T_0$ is room temperature. Accordingly, normally, high deposition temperature causes large residual strain inside films at room temperature. However, as we have observed that there was larger residual strain in the film deposited at a relatively low temperature (550 °C) than the film deposited at a higher temperature (900 °C) (Fig. 5.1). This result cannot be explained with the residual strain due to the CTE difference. There are still other formation mechanisms of the large residual strain in films deposited in this work.

To investigate the formation mechanisms of strain in films, CoFe$_2$O$_4$ films (40 nm) on single crystal (0001)-SiO$_2$ at the temperature of 550 °C were prepared with varying laser fluences in this work. The out-of-plane strain was calculated with the same method described in Chapter 4. The texture evolution of these films is shown in Fig. 5.11, and magnetic properties of these films are listed in Table 5.5. The optimal laser fluence of was 3.5 J/cm$^2$ to obtain the optimal coercivity and magnetic anisotropy. With this laser fluence, the deposition rate was 3.7 nm/min and the out-of-plane tensile strain was +0.551 %. However, with decreasing laser fluence to 1.2 J/cm$^2$, the deposition rate reduced to 0.9 nm/min, and the film possessed an enhanced
(111)-texture but a relaxed out-of-plane strain (+0.188 %). On the other hand, with increasing laser fluence to 10.5 J/cm$^2$, the deposition rate reached 8.6 nm/min. The film exhibited a degraded (111)-texture and but possessed an enhanced residual strain (+0.641 %). As the laser fluence further increased to 15.5 J/cm$^2$, the film texture turned to be (311)-texture as well as the out-of-plane strain of (+0.704 %).

![XRD patterns of the Co-ferrite films with a thickness of 40 nm on (0001)-SiO$_2$ deposited with different laser fluences.](image)

**Fig. 5.11.** The XRD patterns of the Co-ferrite films with a thickness of 40 nm on (0001)-SiO$_2$ deposited with different laser fluences.

The laser-fluence-dependent residual strain and its effects on texture evolution indicate that the formation of strain in films is from the deposition process itself. Normally, the temperature during deposition is often far below the melting temperature of Co-ferrite materials. The film deposition then occurs under highly nonequilibrium conditions. The atoms are insufficient mobile to reach positions with minimal thermodynamic energy during deposition and thus the films possess strong
intrinsic residual strain. As reported previously, large out-of-plane tensile strain and in-plane compressive strain was also observed in films prepared using PLD. The strain in films is believed to be caused by shot-peening effects generated by the impingement of energetic particles on the already grown film, which results in out-of-plane tensile strain and then in-plane compressive strain [9]. Accordingly, laser-fluence-dependent strain formation observed in this work can be well explained with the shot-peening effects. Due to increasing laser fluence, the kinetic energy of particles (atoms, ions, clusters, et al.) increased during laser ablation. With increasing kinetic energy, the particles can easily impinge into the already grown films and then cause strong in-plane compressive strain and out-of-plane tensile strain. As a result, with the formation of enhanced residual strain, the minimization of strain energy density makes films to form (311) texture, which is well consistent with the prediction as shown in Fig. 5.10.

Table 5.5. Texture, magnetic anisotropy $K_u$, and strain state of the CoFe$_2$O$_4$ films (40 nm) on (0001)-SiO$_2$ prepared with different laser fluences.

<table>
<thead>
<tr>
<th>Laser Fluence (J/cm$^2$)</th>
<th>Deposition rate (nm/min)</th>
<th>$H_{c\parallel}$ (kOe)</th>
<th>$H_{c\perp}$ (kOe)</th>
<th>$K_u$ (10$^6$ ergs/cm$^3$)</th>
<th>Out-of-plane Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>0.9</td>
<td>6.3</td>
<td>7.5</td>
<td>0.5</td>
<td>0.188</td>
</tr>
<tr>
<td>3.5</td>
<td>3.7</td>
<td>3.7</td>
<td>10.8</td>
<td>1.6</td>
<td>0.551</td>
</tr>
<tr>
<td>10.5</td>
<td>8.6</td>
<td>5.7</td>
<td>9.1</td>
<td>1.0</td>
<td>0.641</td>
</tr>
<tr>
<td>15.5</td>
<td>11.4</td>
<td>7.4</td>
<td>7.9</td>
<td>0.2</td>
<td>0.704</td>
</tr>
</tbody>
</table>

Moreover, the observation of temperature-dependent strain formation in polycrystalline films on both single crystal and amorphous SiO$_2$ can also be explained
with the shot-peening effect. As we have observed, the XPS depth profiles of CoFe$_2$O$_4$ films (40 nm) deposited on (0001)-SiO$_2$ at both 900 °C and 550 °C (Fig. 5.3) also showed as a sharp interface, indicating negligible interdiffusion between substrate and films. Thus, when deposited at a high temperature, it may be due to grain growth through grain boundary diffusion that can relax the residual strain. Moreover, weak mobility of atoms at low temperatures such as 150 °C leads to the formation of large residual strain inside films. As a result of it, (220)-textured films form due to the minimization of strain energy density.

![XRD patterns](image)

**Fig. 5.12.** The XRD patterns of (a) the CoFe$_2$O$_4$ film with a thickness of 40 nm deposited at 550 °C, and (b) the same sample after post-annealing at 900 °C.

In addition, for the 40 nm film deposited at 550 °C, we have also performed a post-annealing for it at 900 °C. As shown in Fig. 5.12, the shift of the (333) peak positions from 56.44° to 56.87° was observed after post-annealing, indicating residual strain relaxation. This result further revealed that the residual strain formation is due
to nonequilibrium growth process, and the strain can be relaxed through grain growth during high temperature annealing in this work.

Magnetic properties of the sample after post-annealing were also studied. As shown in Fig. 5.13, it clearly indicated that $H_{c\perp}$ decreased from 10.8 to 6.1 kOe after post-annealing and the $K_u$ reduced from 1.7 to $0.6 \times 10^6$ ergs/cm$^3$, suggesting a degraded perpendicular anisotropy after post-annealing at a high temperature. The

![Hysteresis Loops](image_url)
weakening of perpendicular anisotropy is possibly related to strain relaxation during high temperature annealing. The detailed study of magnetic anisotropy related to residual strain in polycrystalline Co-ferrite films will be discussed in next chapter later.

5.6 Summary

Co-ferrite films were prepared on amorphous and single crystal SiO₂ using PLD with in-situ heating. Texture formation is highly dependent on film thickness, substrate temperature and laser fluence. The texture evolution mechanisms can be attributed to the competition between strain energy density and surface (interfacial) energy. The texture formation map was developed based on this understanding. Moreover, magnetic properties of these films indicated that magnetic anisotropy was closely associated with substrate temperature, deposition rate, and thickness. The \( H_{c,\perp} \) over 12.5 kOe was obtained in the ~33 nm Co-ferrite film deposited on (0001)-SiO₂ at 550 °C. The high coercivity and large perpendicular anisotropy may be attributed to the formation of excellent (111)-textured orientation and large residual strain which induce strong stress anisotropy. Furthermore, the likely formation mechanisms for the large residual strain were found to be the shot-peening effect. In Chapter 6, Co-ferrite films were prepared on other substrates or underlayers to further investigate the mechanisms for thin film growth and magnetic anisotropy.

5.7 References


6 Chapter VI Texture and magnetic anisotropy of polycrystalline CoFe$_2$O$_4$ films on different substrates

In this chapter, besides the deposition of Co-ferrite films on SiO$_2$, polycrystalline Co-ferrite films were also fabricated on other substrates including amorphous oxide layer (Al$_2$O$_3$, and MgO), textured MgO and polycrystalline isotropic metal layers with in-situ heating. The mechanisms for texture evolution and strain-induced magnetic anisotropy of polycrystalline films on various substrates were also studied.

6.1 Co-ferrite films on amorphous Al$_2$O$_3$

In order to further clarify film growth mechanisms, polycrystalline Co-ferrite films on amorphous Al$_2$O$_3$ underlayers were also prepared in this work. The amorphous Al$_2$O$_3$ underlayer with a thickness of 50 nm was deposited on (0001)-SiO$_2$ substrate at room temperature. Its XRD patterns (Fig. 6.1(a) showed no crystalline peaks and the XPS spectra showed the film composition of Al$_2$O$_3$. On the amorphous underlayer, the Co-ferrite film with a thickness of 40 nm was deposited at 550 °C. Other experimental conditions followed the preparation procedures of polycrystalline films on single crystal (0001)-SiO$_2$. The XRD patterns indicated an obvious (111)-texture as well as a peak shift, suggesting large residual strain inside the film. The estimated out-of-plane tensile strain was 0.597 %.
Fig. 6.1. The XRD patterns of (a) the amorphous Al₂O₃ layer on (0001)-SiO₂ and (b) the Co-ferrite film (40 nm) on (0001)-SiO₂ with an amorphous Al₂O₃ underlayer.

Fig. 6.2. The hysteresis loops of the 40 nm Co-ferrite film on an amorphous Al₂O₃ underlayer.
The hysteresis loops of the film are shown in Fig. 6.2. The film possessed $H_{c\perp}$ and $H_{c\parallel}$ of 9.7 and 3.3 kOe, respectively, obviously suggesting perpendicular anisotropy with the calculated $K_u$ of $K_u = 1.5 \times 10^6 \text{ergs/cm}^3$. The XPS depth profile measurement of the film (Fig. 6.3) revealed a clear layer structure with negligible interfacial diffusion between films and amorphous layers.

![Fig. 6.3. The XPS depth profile of the 40 nm Co-ferrite film on amorphous Al$_2$O$_3$ underlayer.](image)

### 6.2 Co-ferrite films on amorphous MgO underlayer

In this work, Co-ferrite films were also deposited on MgO underlayers. MgO underlayers on (001)-Si were prepared at room temperature using PLD from a polycrystalline MgO target (Fig. 6.4(a)). The XPS and XRD examination (Fig. 6.4(c)) revealed that the MgO film prepared at room temperature was amorphous but with the stoichiometric compositions of 1:1. On the amorphous MgO, the Co-ferrite
film (40 nm) exhibited (111)-texture with the out-of-plane residual strain of 0.621 % compared to the isotropic CoFe$_2$O$_4$ target with a negligible residual strain.

![XRD patterns of MgO target, amorphous MgO/Si, CoFe$_2$O$_4$ film on amorphous MgO, and CoFe$_2$O$_4$ target.](image)

**Fig. 6.4.** The XRD patterns of (a) the sintered MgO target, (b) the MgO film on (001)-Si substrates at 25 °C, (c) the 40 nm Co-ferrite film on amorphous MgO at 550 °C, and (d) the CoFe$_2$O$_4$ target.

Magnetic properties (Fig. 6.5) of the film on amorphous MgO showed perpendicular anisotropy with a $K_u$ of $1.6 \times 10^6$ ergs/cm$^3$. The $H_{c\perp}$ and $H_{c\parallel}$ were 8.9 and 2.1 kOe, respectively. The XPS depth profile (Fig. 6.6) examination showed a
sharp interface without serious interfacial diffusion for the film on the amorphous MgO.

![Hysteresis Loop](image)

**Fig. 6.5.** The hysteresis loops of the 40 nm Co-ferrite film on an amorphous MgO underlayer.

![XPS Depth Profile](image)

**Fig. 6.6.** The XPS depth profile of the 40 nm Co-ferrite film on an amorphous MgO underlayer.
6.3 Co-ferrite films on (002)-textured MgO underlayer

![XRD patterns](image)

Fig. 6.7. The XRD patterns of (a) the sintered MgO target, (b) (002)-textured MgO films on (001)-Si substrates at 800 °C, (c) the 40 nm Co-ferrite film on (002)-textured MgO underlayer at 550 °C, and (d) the CoFe$_2$O$_4$ target.

(002)-textured MgO films were successfully prepared on (001)-Si at 800 °C. The XRD patterns (Fig. 6.7(b)) indicated that only the (002) peak was observed in the XRD patterns compared with that of the MgO target. After achieving textured MgO
films on (001)-Si, the Co-ferrite film with a thickness of 40 nm was deposited at 550 °C. The XRD patterns of the films are shown in Fig. 6.7(c), which presented a (001)-textured orientation. However, no peak shift was observed for this film. The (004) position for the film was 43.07º, which was the same of that (43.07º) of the Co-ferrite target. The results revealed negligible residual strain formed in the film on the (002)-textured MgO.

![Hysteresis loops of the 40 nm Co-ferrite film on a (002)-textured MgO underlayer.](image)

**Fig. 6.8. The hysteresis loops of the 40 nm Co-ferrite film on a (002)-textured MgO underlayer.**

The hysteresis loops of the film are shown in Fig. 6.8. It possessed almost isotropic magnetic texture. The $H_c$ in both directions was identical with the values of around 3 kOe. The low coercivity and lack of perpendicular anisotropy of the film on (002)-textured MgO was different from that of the film on amorphous MgO. It is highly related to the negligible strain inside the film on textured MgO. The XPS depth profile of the film on textured MgO (Fig. 6.9) revealed serious interfacial diffusion. The Co$^{2+}$ and Fe$^{3+}$ ions penetrated deeply into the (002)-textured MgO underlayers,
which is different from the film on the amorphous MgO (Fig. 6.6). This serious interfacial diffusion may be through the grain boundary between MgO grains. As reported [1,2], diffusion occurs more rapidly along grain boundaries in polycrystalline materials than both through lattice in single crystal grain and amorphous disorder structure of the same compositions. Moreover, the serious interdiffusion can result in the relaxation of residual strain in films [3,4]. Accordingly, the Co-ferrite film on (002)-textured MgO possessed negligible residual strain, which was identified in the XRD patterns without peak shift.

![XPS depth profile](image)

**Fig. 6.9.** The XPS depth profile of the 40 nm Co-ferrite film on (002)-textured MgO underlayer.

### 6.4 Co-ferrite films on polycrystalline metal underlayers

In this work, Co-ferrite films with a thickness of 40 nm were also prepared on different metal underlayer (Au, Ag, and Cr). Due to the weak wettability of oxide (CoFe₂O₄) films on metal (Au and Ag), it was observed that the films on Au (Ag) were easily peeled off because of the weak adhesion force. But using a Cr metal layer,
the adhesion between films and Cr underlayer enhanced and the film on Cr was hardly exfoliated. As the XRD examination of the CoFe$_2$O$_4$ films (40 nm) on different metal underlayers (Fig. 6.10) indicated, the films on Au and Ag possessed an isotropic
orientation, while the film on Cr obviously presented a (111)-texture. No characteristic peaks from Cr were observed due to the thickness of Cr layer was very small (~ 5 nm), difficult for XRD method to detect. The hump in the spectra was from amorphous glass substrate. Furthermore, the (333) peak shift was observed for the film on Cr with an out-of-plane strain of 0.332 % whereas no peak shift and no strong intrinsic residual strain were observed for the films on Au and Ag.

![Graph showing magnetic hysteresis loops](image)

**Fig. 6.11.** The hysteresis loops of Co-ferrite films with a thickness of 40 nm on different metal underlayers.
Moreover, as hysteresis loops (Fig. 6.11) of these films showed, the films on the Au (Ag) showed isotropic magnetic texture with the $H_c$ of 5.0 kOe in both directions. In contrast, the film on the Cr layer exhibited perpendicular anisotropy with a $K_u$ of $1.2 \times 10^6$ ergs/cm$^3$ as well as $H_{c\perp}$ of 6.7 kOe and $H_{c\parallel}$ of less than 2.2 kOe.

### 6.5 Texture growth and strain induced magnetic anisotropy

<table>
<thead>
<tr>
<th>Substrates (or underlayers)</th>
<th>Orientation of CoFe$_2$O$_4$ films</th>
<th>$K_u$ ($10^6$ ergs/cm$^3$)</th>
<th>Measured out-of-plane Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystal (0001)-Al$_2$O$_3$</td>
<td>(111)-epitaxial</td>
<td>2.5</td>
<td>0.775</td>
</tr>
<tr>
<td>Single crystal (002)-MgO</td>
<td>(002)-epitaxial</td>
<td>1.1</td>
<td>-0.609</td>
</tr>
<tr>
<td>Single-crystal (001)-SiO$_2$</td>
<td>(111)-textured polycrystalline</td>
<td>1.6</td>
<td>0.551</td>
</tr>
<tr>
<td>Single-crystal (11-20)-SiO$_2$</td>
<td>(111)-textured polycrystalline</td>
<td>1.5</td>
<td>0.528</td>
</tr>
<tr>
<td>Single-crystal (1000)-SiO$_2$</td>
<td>(111)-textured polycrystalline</td>
<td>1.5</td>
<td>0.574</td>
</tr>
<tr>
<td>Amorphous Al$_2$O$_3$</td>
<td>(111)-textured polycrystalline</td>
<td>1.5</td>
<td>0.597</td>
</tr>
<tr>
<td>Amorphous MgO</td>
<td>(111)-textured polycrystalline</td>
<td>1.6</td>
<td>0.621</td>
</tr>
<tr>
<td>Amorphous SiO$_2$</td>
<td>(111)-textured polycrystalline</td>
<td>0.9</td>
<td>0.239</td>
</tr>
<tr>
<td>(002)-textured MgO</td>
<td></td>
<td>1.2</td>
<td>0.332</td>
</tr>
</tbody>
</table>

To summarize Co-ferrite films on different substrates or underlayers which were described in both Chapter 5 and Chapter 6, the texture and magnetic anisotropy, and strain state of CoFe$_2$O$_4$ films with a thickness of 40 nm are listed in Table 6.1. For the films on single crystal SiO$_2$ with different planes and amorphous oxide layers
including SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and MgO, the film texture formation follows the prediction in the texture map, which is shown in Fig. 5.10. Whereas, because the (002)-MgO plane has a small lattice mismatch with the (001)-CoFe\textsubscript{2}O\textsubscript{4} plane, the texture of Co-ferrite films on (002)-textured polycrystalline MgO preferred to the formation of (001)-texture as a result of a reduction in interfacial energy. However, compared to CoFe\textsubscript{2}O\textsubscript{4} films on oxide substrates or underlayers, the films on metal (Au and Ag) have a very weak adhesion to metal underlayers. Due to the weak adhesion, negligible constraint effects from substrate cause random growth of CoFe\textsubscript{2}O\textsubscript{4} grains on Au (or Ag) and the formation of isotropic orientation without residual strain. On the other hand, with a Cr underlayer acting as the adhesion layer to oxide and diffusion barrier, the CoFe\textsubscript{2}O\textsubscript{4} film on Cr obviously exhibit (111)-texture, following the texture map as shown in Fig. 5.10.

Furthermore, magnetic anisotropy of polycrystalline CoFe\textsubscript{2}O\textsubscript{4} films on different substrates or underlayers is certainly correlated with residual strain. As shown in Fig. 6.12, the $K_u$ of (111)-textured films is obviously correlated to out-of-plane tensile strain. (111)-textured Co-ferrite films with larger tensile strain possessed a larger $K_u$, which is consistent with what we have observed on (111)-epitaxial films on (0001)-Al\textsubscript{2}O\textsubscript{3}. In contrast, due to weak adhesion, isotropic polycrystalline CoFe\textsubscript{2}O\textsubscript{4} films on Au (or Ag) layers possessed very weak residual strain and then no magnetic anisotropy. Moreover, it needs to be highlighted that large $K_u$ of CoFe\textsubscript{2}O\textsubscript{4} films on oxide layers or on Cr layer is also strongly correlated with (111)-texture, which is clearly shown in Table 6.1. In addition, magnetic properties of films with a thickness of 40 nm prepared with different laser fluences (Table 5.5) also revealed that both (111)-texture and residual out-of-plane tensile strain are critical to achieve polycrystalline CoFe\textsubscript{2}O\textsubscript{4} films with high $K_u$. As indicated in Table 5.5, although
enhanced residual strain was obtained in the films deposited with large laser fluence over 3.5 J/cm², the decreased $K_u$ was observed because of degraded (111)-texture.

![Graph showing magnetic anisotropy $K_u$ versus out-of-plane strain for (111)-textured CoFe$_2$O$_4$ films (40 nm) on different substrates or underlayers.](image)

**Fig. 6.12.** The magnetic anisotropy $K_u$ versus out-of-plane tensile strain (%) for (111)-textured CoFe$_2$O$_4$ films (40 nm) on different substrates or underlayers.

### 6.6 Summary

In summary, in order to achieve nanocrystalline CoFe$_2$O$_4$ films with large perpendicular anisotropy and high coercivity, the key point is to fabricate highly (111)-textured films with large out-of-plane residual strain using PLD. However, achieving purely and excellently (111)-textured films normally requires high deposition temperature. Unfortunately, high temperature deposition is unfavorable for achieving small grain size and large residual strain due to strong diffusion of atoms at high deposition temperature. Therefore, the use of a suitable underlayer may be a possible method to induce the growth of highly textured films at a low temperature. The underlayer needs to meet the requirements: (1) strong adhesion to CoFe$_2$O$_4$ with
low interfacial energy; (2) easy to form texture with corresponding small lattice
mismatch to (111)-CoFe₂O₄, which can induce growth of (111)-textured CoFe₂O₄
films at low temperatures; (3) possessing microstructure with low atomic diffusion for
CoFe₂O₄ to maintain certain residual strain. In next chapter, because ZnO has a
hexagonal structure with lattice parameter (a=3.24 Å, c=5.20 Å) and (0001)-ZnO
shows the same hexagonal structure as (111)-CoFe₂O₄ with the lattice mismatch of
about 7.8 %, the use of ZnO underlayers was demonstrated to successfully obtain
highly (111)-textured CoFe₂O₄ films with large residual strain at low substrate
temperatures.

6.7 References


Chapter VII Effects of ZnO underlayers on growth and magnetic anisotropy of polycrystalline Co-ferrite films

In this chapter, ZnO underlayer was demonstrated to achieve Co-ferrite films with excellent texture, high coercivity, and large perpendicular anisotropy on inexpensive amorphous glass at low temperatures.

7.1 Textured growth and magnetic properties of Co-ferrite films on ZnO underlayers

As reported previously, ZnO films with (0001)-oriented texture have been fabricated at a low deposition temperature as low as 300 °C [1,2]. Since the (0001)-ZnO plane has a similar hexagonal structure as the (111)-CoFe₂O₄ plane with a rather small lattice mismatch of 7.8 %, the ZnO underlayers were utilized to induce (111)-textured growth of Co-ferrite films.

Fig. 7.1(a) shows the XRD pattern of the ZnO target, which was well indexed as PDF No.36-1451 [3]. Fig. 7.1(b) shows the XRD patterns of the ZnO film with a thickness of approximate 50 nm deposited on glass (amorphous SiO₂) at 300 °C. The diffraction peaks of this film exhibited only a family of {0002} peaks, indicating a pure (0001)-textured structure. The XPS composition analysis (Fig. 7.1(c)) of the ZnO film revealed that the composition ratio between Zn and O of 49.9: 50.1, which was close to 1:1 of the ZnO target.

Fig. 7.2 shows the XRD patterns of the Co-ferrite films deposited on glass with a ZnO underlayer at different substrate temperatures. The thickness of Co-ferrite films was measured to be 40 nm.
Fig. 7.1. The XRD patterns of the ZnO target (a), the XRD patterns (b) and XPS survey scan spectra (c) of the ZnO film on glass at 300 °C.

The formation temperature of the crystalline Co-ferrite phase on ZnO underlayers started at 150 °C. The patterns only exhibited a series of \{111\} peaks from Co-ferrite phase besides the peaks for the ZnO underlayer, suggesting a pure (111)-texture. The rocking curve (Fig. 7.2(d)) of the film deposited at 300 °C showed...
Fig. 7.2. The XRD patterns (a) and the rocking curve (b) of the 40 nm Co-ferrite film deposited directly on glass, and the XRD patterns (c) and the rocking curve (d) of the 40 nm Co-ferrite films deposited on glass with a ZnO underlayer deposited at different substrate temperatures (the rocking curve was taken for the film at 300 °C).

a FWHM of 4.3°. For comparison, the 40-nm Co-ferrite films were also deposited directly on glass substrates at different temperatures without a ZnO underlayer in this work, which was previously described in Chapter 5. Without ZnO underlayers, the formation of the crystalline Co-ferrite phase started at 400 °C. Compared to the isotropic Co-ferrite target, the Co-ferrite films without ZnO underlayers possessed preferred (111)-orientation (Fig. 7.2(a)). But, other peaks (e.g., (311)) were present together with the {111} family, indicating a relatively poor texture and the FWHM showed a large value of 8.9° (Fig. 7.2(b)). These results above clearly indicated that enhanced (111)-oriented Co-ferrite films were formed with a textured (0001)-ZnO underlayer. The excellent (111)-textured growth may be attributed to the small misfit
between the (111)-plane of Co-ferrite and (0001)-plane of ZnO. The small misfit can also account for the reduced formation temperature of crystalline Co-ferrite phase. Previous studies have also reported the oriented growth of (0001)-BaFe_{12}O_{19} at a low temperature on silicon substrates with a (0001)-ZnO underlayer, which had the lattice misfit of 9.0 % with (0001)-BaFe_{12}O_{19} [4,5].

As Fig. 7.2(c) also indicates, a peak shift of the (222) diffraction peaks was observed (compared to the \(2\theta = 37.14^\circ\) of the Co-ferrite target). As shown in Table 7.1, the peak position for the film at 300 °C was 36.34°. The peak shift decreased with increasing deposition temperature.

![Fig. 7.3. The XPS depth profiles of the 40 nm Co-ferrite films deposited at 300 °C on glass with a ZnO underlayer.](image)

In order to observe the CoFe_{2}O_{4}/ZnO/glass film architecture further, the XPS depth profile was measured (Fig. 7.3). A sharp interface between Co-ferrite and ZnO underlayer was well defined for the film with the ZnO underlayer. The interdiffusion
between the film and the ZnO underlayer at the interfacial area was not serious in this film structure.

The examination of surface morphology of films using AFM is shown in Fig. 7.4. Fig. 7.4(d) showed the AFM image of the 40 nm Co-ferrite film deposited directly on glass at 550 °C (which was the optimized temperature to achieve the optimal $K_u$) without a ZnO underlayer. Non-regular and elongated grains were observed.

![Fig. 7.4. The AFM images of the 40 nm Co-ferrite films deposited on glass with a ZnO underlayer at 300 °C (a), 400 °C (b), 500 °C (c), and directly on glass without a ZnO underlayer at 550 °C (d).](image)
In contrast, Fig. 7.4(a)-(b) showed the AFM images of the 40 nm Co-ferrite films deposited at 300 °C and 400 °C, respectively, on glass substrates with ZnO underlayers. The images revealed grains with a granular structure and circular shape. The grains were well separated from each other. Moreover, the rms surface roughness for both two films was less than 1 nm, and the particle size distribution was narrow with a mean diameter of around 20 nm. The particles intended to agglomerate with the deposition temperature up to 500 °C (Fig. 7.4(d)), suggesting that deposition temperature less than 500 °C is suitable to obtain isolated grain structure with small grain size without agglomeration with ZnO underlayers.

Table 7.1. Magnetic properties of Co-ferrite films with a thickness of 40 nm deposited on glass with a ZnO underlayer at different substrate temperatures [Coercivity $H_c$, the remanence ratio $(M_r/M_s)$, $K_u$, and $2\theta$ positions of the (222) peaks].

<table>
<thead>
<tr>
<th>Substrate temperature ($^\circ$C)</th>
<th>$H_c$∥ (kOe)</th>
<th>$(M_r/M_s)$∥ (%)</th>
<th>$H_c$⊥ (kOe)</th>
<th>$(M_r/M_s)$⊥ (%)</th>
<th>$K_u$ ($10^6$ ergs/cm$^3$)</th>
<th>$2\theta$ positions of (222) peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.4</td>
<td>23.4</td>
<td>2.4</td>
<td>32.9</td>
<td>0.2</td>
<td>----</td>
</tr>
<tr>
<td>150</td>
<td>3.4</td>
<td>32.7</td>
<td>8.2</td>
<td>75.2</td>
<td>1.3</td>
<td>36.26</td>
</tr>
<tr>
<td>300</td>
<td>2.5</td>
<td>16.3</td>
<td>10.7</td>
<td>84.5</td>
<td>2.3</td>
<td>36.34</td>
</tr>
<tr>
<td>400</td>
<td>2.7</td>
<td>26.8</td>
<td>9.5</td>
<td>80.5</td>
<td>2.0</td>
<td>36.53</td>
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<tr>
<td>500</td>
<td>4.1</td>
<td>45.6</td>
<td>7.2</td>
<td>64.3</td>
<td>1.8</td>
<td>36.71</td>
</tr>
</tbody>
</table>

Table 7.1 gives the magnetic properties (coercivity and remanence) of the 40-nm films deposited at different temperatures with a ZnO underlayer. All the films showed perpendicular anisotropy. The ratio $(M_r/M_s)$⊥/$(M_r/M_s)$∥ (as an indicator of perpendicular anisotropy) is highly correlated to the substrate temperature, increased from 1.4 at 150 °C to 5.2 at 300 °C (as the maximum), and then decreased to 1.4 at
500 °C. The films possessed a large $H_{c\perp}$ over 8.0 kOe with the substrate temperature at 150 °C or higher as well as $H_{c\parallel}$ below 4.1 kOe. The Co-ferrite films with high coercivity, large perpendicular anisotropy and low formation temperature are interesting for potential applications including magnetic recording and magneto-optical recording.

Fig. 7.5. The hysteresis loops of the 40 nm Co-ferrite films deposited (a) directly on glass at 550 °C, and (b) on glass deposited at 300 °C with a ZnO underlayer.
Fig. 7.5(a) shows the hysteresis loops of the 40 nm Co-ferrite films after deposition at the optimized temperature (300 °C with a ZnO as the underlayer and 550 °C without the ZnO underlayer). Without ZnO underlayer, the $H_{c\perp}$ and $H_{c\parallel}$ were 8.4 kOe and 4.0 kOe with the remanence ratio of 73.4 % in the out-of-plane direction and 58.6 % in the in-plane direction, respectively. The $K_u$ for the film was $0.9 \times 10^6$ ergs/cm$^3$. Whereas, the hysteresis loops of the 40-nm film with a ZnO underlayer at 300 °C (Fig. 7.5(b)) showed a higher $H_{c\perp}$ value of 10.7 kOe and a larger $(M_r/M_s)_\perp$ of 84.5 %. The $K_u$ was $2.3 \times 10^6$ ergs/cm$^3$. The results obviously revealed that a ZnO underlayer can strongly enhance perpendicular anisotropy ($K_u$) of Co-ferrite films, even at a low temperature of 300 °C. The large $K_u$ is certainly correlated with the excellent (111)-texture at such a low temperature. The correlation between $K_u$ and (111)-texture is consistent with the previously description in Chapter 6.

In order to further understand the effects of residual strain on magnetic properties, Co-ferrite films with different thicknesses (20-400 nm) on a ZnO underlayer at the optimal temperature of 300 °C. Fig. 7.6(a) shows coercivities of Co-ferrite films on ZnO underlayers with different thicknesses. The optimal thickness for the film with the largest $H_c$ and highest remanence ratio was 40 nm. With further increasing of film thickness to 400 nm, the $H_{c\perp}$ decreases from 10.7 kOe to 6.6 kOe while $H_{c\parallel}$ increased from 2.5 kOe to 4.2 kOe. Meanwhile, as indicated in Table 7.2, the $K_u$ degraded from $2.3 \times 10^6$ ergs/cm$^3$ for the film (40 nm) to $0.4 \times 10^6$ ergs/cm$^3$ for the film (400 nm), suggesting that the perpendicular anisotropy becomes weaker in thicker films. The thickness-dependent $H_{c\perp}$ and $K_u$ are certainly related to the relaxation of residual strain. This relaxation of residual strain was clearly identified with the XRD patterns (Fig. 7.6(b)).
In this work, when a (0001)-ZnO underlayer was used, highly (111)-textured Co-ferrite films were successfully obtained with a thickness up to 400 nm. As shown in Fig. 7.6(c), the peak shift reduced when the film thickness increased. The reduction in peak shift suggested residual strain relaxation, which caused the reduction of strain-
induced stress anisotropy. The gradual relaxation of residual strain with increasing film thickness is possible due to grain growth and grain boundary diffusion [6].

Table 7.2. Coercivity $H_c$, strain, and $K_u$ of CoFe$_2$O$_4$ films with different thicknesses (25-400 nm) deposited with (0001)-ZnO underlayers.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$H_{c\parallel}$ (kOe)</th>
<th>$H_{c\perp}$ (kOe)</th>
<th>In-plane Strain (%)</th>
<th>Out-of-plane Strain (%)</th>
<th>$K_u$ (10$^6$ ergs/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>4.2</td>
<td>6.6</td>
<td>-0.142</td>
<td>0.088</td>
<td>0.4</td>
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<td>200</td>
<td>3.7</td>
<td>7.2</td>
<td>-0.292</td>
<td>0.208</td>
<td>0.9</td>
</tr>
<tr>
<td>100</td>
<td>2.9</td>
<td>8.6</td>
<td>-0.726</td>
<td>0.484</td>
<td>1.4</td>
</tr>
<tr>
<td>40</td>
<td>2.5</td>
<td>10.7</td>
<td>-1.072</td>
<td>0.706</td>
<td>2.3</td>
</tr>
<tr>
<td>20</td>
<td>2.0</td>
<td>8.8</td>
<td>-1.077</td>
<td>0.715</td>
<td>1.7</td>
</tr>
</tbody>
</table>

In order to study the thickness-dependent residual strain, the $\sin^2 \psi$ technique was used [7]. For our measurement, the (422) plane was selected for all the films with different thicknesses with tilting the samples with both $\psi = 19.44^\circ$ and $61.86^\circ$. The measured (422) peaks for the 40 nm at varying $\psi$ are shown in Fig. 7.8(a). With the accurately measured peak positions, the calculated interplanar spacings of (422) planes for the films with different thicknesses were plotted in Fig 7.8(b). The in-plane and out-of-plane strain were fitted and listed in Table 7.2. The results directly indicated that the residual strain relaxed with increasing thickness and the strain was highly correlated with the $K_u$, which is consistent with what we have proposed in Chapter 6 that residual strain-induced stress anisotropy plays critical role in tuning magnetic anisotropy of polycrystalline Co-ferrite films in this work.
Fig. 7.7. The XRD patterns of the asymmetric (422) peaks for the 40-nm film with the varying $\psi$ angle (a), and the plotting and linear fitting of the values $(d_\psi - d_0)/d_0$ against $\sin^2 \psi$ for CoFe$_2$O$_4$ films with different thicknesses on ZnO underlayers (b).

### 7.2 Summary

In summary, Co-ferrite films with purely (111)-textured structure have been fabricated on inexpensive amorphous glass with a ZnO underlayer using PLD. It has
been found that the presence of a ZnO underlayer could result in a reduction of the formation temperature of textured films. $H_{c,\perp}$ of 10.7 kOe has been achieved in the 40-nm Co-ferrite film with a ZnO underlayer deposited at 300 °C. The films with CoFe$_2$O$_4$/ZnO/glass structure have been demonstrated to possess a large perpendicular magnetic anisotropy $K_u$ of $2.3 \times 10^6$ ergs/cm$^3$, small grain size (around 20 nm), and smooth surface. This work has shown that the ZnO underlayer is an appropriate seed layer to induce highly (111)-textured Co-ferrite films with promising magnetic properties, which are interesting for many applications including magnetic recording, magneto-optical recording, and MEMS devices.

7.3 References

8 Chapter VIII Conclusions and future works

8.1 Conclusions

This thesis mainly focused on fabricating nanocrystalline Co-ferrite films with large perpendicular anisotropy and high coercivity using pulsed laser deposition (PLD), investigating mechanisms for thin film growth and magnetic anisotropy, and tuning crystallographic orientation and magnetic properties of Co-ferrite films. The details of the study are summarized below:

(1) Polycrystalline and crystallographically isotropic Co-ferrite films were prepared by PLD at room temperature followed by post-annealing. The films showed an isotropic crystallographic orientation and isotropic magnetic properties. The study of magnetic properties of these films indicated that controlling grain size close to single domain size of Co-ferrite materials is critical to obtain high coercivity films. Thus, film deposition using PLD with post-annealing is not suitable to achieve textured Co-ferrite films with large perpendicular anisotropy.

(2) Thin film growth mechanisms for both epitaxial and polycrystalline Co-ferrite films with in-situ heating were summarized. Firstly, when using oxide substrates (single crystal (0001)-Al₂O₃, (002)-MgO) with corresponding small lattice mismatch with CoFe₂O₄, the (001)-epitaxial films on (002)-MgO and the (111)-epitaxial films on (111)-Al₂O₃ formed even at a low temperature and the epitaxial structure could keep for the film with a thickness of 700 nm. Secondly, if using amorphous oxide layers (Al₂O₃, MgO, and SiO₂) or single crystal SiO₂ with different planes, which have no corresponding lattice
matching with any plane of CoFe2O4, polycrystalline Co-ferrite films formed. The texture map about predicted texture evolution of these polycrystalline films was developed based on the competition between surface or interfacial energy and strain energy density. When film thickness is small or substrate temperature is high, the texture tends to be (111)-texture. Whereas, when thickness is thick or substrate temperature is low, the film leads to form (311) and/or (220)-texture. Thirdly, the texture evolution of Co-ferrite films on different metal layers was found to give evidence for prediction by the texture map. If using metal layers (Au or Ag) with weak adhesion to Co-ferrite materials, the films tended to be isotropic orientation. Whereas, if using Cr metal underlayers, which shows strong adhesion force to Co-ferrite materials, the texture tended to follow that of the films on amorphous oxide layers. Furthermore, the residual strain in polycrystalline Co-ferrite films was investigated to be due to the shot-peening effects during PLD process itself. The strain was found to be relaxed due to either grain growth (grain boundary diffusion) or interfacial diffusion.

(3) The mechanisms for magnetic anisotropy of both epitaxial and polycrystalline Co-ferrite films with in-situ heating were investigated. Firstly, thickness-dependent magnetic anisotropy of both (111) and (001)-epitaxial films illustrates that strain-induced stress anisotropy is critical to be considered for the interpretation of thickness-related reorientation of magnetic anisotropy. With out-of-plane and in-plane strain measured using HRXRD for the epitaxial films, the calculated values for $K_u$ based on a phenomenological model is well consistent with the measured ones. Secondly, the evolution of magnetic anisotropy of polycrystalline films can also be explained with stress anisotropy induced by residual strain. Perpendicular anisotropy $K_u$ was found to be
proportional to out-of-plane strain in polycrystalline Co-ferrite films. Finally, it is concluded that both residual strain and (111)-texture are prerequisite to achieve polycrystalline Co-ferrite films with high coercivity and large perpendicular anisotropy.

(4) Based on the previous predictions, (0001)-ZnO layer was demonstrated as an effective underlayer to obtain excellent (111)-textured Co-ferrite films with room temperature high coercivity and large perpendicular anisotropy. It has been found that the presence of a ZnO underlayer can cause a reduction of the formation temperature to 300 °C. The films (40 nm) with CoFe₂O₄/ZnO/glass structure has been demonstrated to possess a high coercivity of 10.7 kOe, a large perpendicular magnetic anisotropy $K_u$ of $2.3 \times 10^6 \text{ergs/cm}^3$, small grain size (around 20 nm), and smooth surface.

8.2 Future works

As demonstrated in this work, textured polycrystalline Co-ferrite films with large perpendicular anisotropy and high coercivity were achieved on inexpensive amorphous SiO₂ with ZnO underlayers. However, there are still more works we can conduct in the future to realize the potential applications of Co-ferrite films.

Firstly, the practical implementation of perpendicular recording with Co-ferrite films acting as magnetic recording media requires films to have uniform grain size less than 15 nm and have the trilayer structure: soft magnetic underlayer (SUL) /ZnO/CoFe₂O₄. It is believed that the SUL layer is prerequisite for enhancing the writing field and increasing the readback signal amplitude. Accordingly, in the future, more experimental works need to target on further reducing grain size with doping non-magnetic oxide (such as SiO₂) around grain boundary of Co-ferrite grains to
isolate them and optimizing the film growth the trilayer film structure (SUL) /ZnO/CoFe$_2$O$_4$ with promising magnetic properties.

Secondly, potential applications of CoFe$_2$O$_4$ films as magneto-optical devices require both large perpendicular anisotropy and large Kerr rotations in the spectra ranges of 400~500 nm. In the future, more experimental works need to focus on fabricating Co-ferrite films with enhancing Kerr effects under different conditions, such as, doping different heavy rare earth elements, such as Ho, Er, Tm, Yb, Lu.

Thirdly, as generally reported, epitaxial spinel ferrite materials (Fe$_3$O$_4$, NiFe$_2$O$_4$, CoFe$_2$O$_4$) and ZnO materials are promising as the candidates used in spintronics devices. As also shown in the thesis, excellent (111)-epitaxial CoFe$_2$O$_4$ films with large perpendicular anisotropy were achieved on (0001)-Al$_2$O$_3$. Thus, we propose, the epitaxial film system combining spinel ferrites and ZnO, such as Fe$_3$O$_4$/ZnO/CoFe$_2$O$_4$/Al$_2$O$_3$, may be of great interest for spin filter, magnetic tunnel junction, and other magneto-electronics devices in the future.

Lastly, besides potential applications of nanocrystalline ferrite thin films in magnetic recording, magneto-optic, MEMS and spintronics devices, the miniaturization in the field of microwave devices (circulators, isolators, and phase shifters) employing ferrite components compatible with monolithic microwave integrated circuits (MMICs) is one of the driving forces for the future growth of ferrite thin film technology. Thus, PLD with in-situ heating used in this work can be extended for the fabrication of nanocrystalline ferrite (LiFe$_2$O$_4$, NiZnFe$_2$O$_4$) thin films at a low temperature in the future.