Tailoring the magnetic anisotropy of thin films utilizing large persistent stress and pulsed laser irradiation

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1 Introduction

Any material having directional dependent properties is said to exhibit anisotropy. In the case of magnetic materials, the preferred direction (easy axis) for the orientation of the magnetization is determined by its magnetic anisotropy. The important magnetic properties like coercive field, remanent magnetization, saturation field of a material are governed by its magnetic anisotropy. The latter is the most important parameter of a magnetic material from both the fundamental and the application viewpoint. The magnetic properties of thin films, multilayers and nanoparticles are being utilized efficiently in various fields including automotive technology, data storage technology and biomedical applications. Development and optimization of new materials for the recording media, read head sensors and write heads is of current research interest to realize high-density data storage in excess of 1 TB/in$^2$.[1, 2] Magnetic anisotropy is an important parameter that has to be optimized to realize such a high-density recording media since it determines the stability of the stored information in the magnetic recording media. It also determines the coercivity and therefore the sensitivity and the operating range of a read head sensor. Moreover, it plays a vital role on down scaling the device feature size to overcome the super paramagnetic limit. Therefore, the main motivation behind this thesis work is to optimize the magnetic properties of magnetic thin films and multilayers by tailoring their magnetic anisotropy.

The total magnetic anisotropy energy density depends on the contributions from crystalline anisotropy, shape anisotropy, interface/surface anisotropy, magnetoelastic anisotropy and unidirectional exchange anisotropy. By tuning each of these anisotropy energy contributions, one can optimize the effective anisotropy determining the direction of magnetization. In this work, we are particularly interested in tailoring the magnetic properties of thin films and multilayers by varying the magnetoelastic and unidirectional exchange anisotropy contributions.

First part of the thesis deals with the optimization of magnetic properties by varying the magnetoelastic anisotropy energy contribution. Generally, the magnetization in ferromagnetic thin films tends to lie in the film plane in order to reduce the energy associated with the demagnetizing field. In certain magnetic thin films, however, there exists a spontaneous reorientation of magnetization from in-plane to perpendicular to the film plane; this phenomenon is called perpendicular magnetic anisotropy (PMA). PMA has been utilized in the field of perpendicular storage media [3-5] and magnetoresistive sensors.[6, 7] PMA can be observed for the samples with high crystalline anisotropy (eg. L1$_0$ ordered FePt and CoPt) with its crystallographic easy axis oriented normal to the sample plane.[8] When PMA is observed in ferromagnet/noble metal multilayers,[9-11] it can be attributed to the interfacial anisotropy. Whereas in ultra-thin FM films,[12, 13] it is
thought to be due to lattice-mismatch-induced strain across the film/substrate interface. Such strain can also be induced by an in-plane biaxial stress. So it is intriguing to study the influence of externally applied in-plane biaxial stresses on the PMA of ferromagnetic thin films.

Upon applying a biaxial stress, a uniaxial magnetoelastic anisotropy component \( K_{me} \) is induced in the direction normal to the sample plane. The induced isotropic magnetoelastic anisotropy energy can be written as,

\[
K_{me} = \frac{3}{2} \sigma \lambda
\]  

where, \( \sigma \) is the stress applied to the sample and \( \lambda \) is the magnetostriction coefficient. This equation shows that \( K_{me} \) depends on both the sign and the magnitude of the applied stress and the magnetostriction coefficient of the material. i.e. The degree to which \( K_{me} \) can be influenced is determined by the magnitude of the stress applied to the sample. Therefore, in this study a new method has been proposed by which a large biaxial stress can be applied in a more controlled way to the thin films and multilayers and thereby influencing the magnetoelastic anisotropy energy.

Second part of the thesis deals with the optimization of magnetic properties resulting from the unidirectional exchange anisotropy. This form of anisotropy arises due to an exchange coupling of an antiferromagnetic (AFM) layer with a ferromagnetic (FM) layer. This causes a shift in the hysteresis loop of the FM layer on the field axis, which is characterized by the exchange bias field \( H_{ex} \). The resulting unidirectional anisotropy has been used to control the direction of the magnetization of a FM layer in several applications like giant magnetoresistive spin valve sensors, magnetic tunnel junctions, and Magnetic random access memory. Recently, V. Skumryev et al. demonstrated a possibility on beating the super paramagnetic limit of the nanoparticles utilizing the extra source of anisotropy offered by the exchange bias effect.

The unidirectional anisotropy significantly depends on the microstructure of the AFM layer including texture, grain size and the crystalline phase. Most of these technically interesting AFM/FM bilayers require annealing step in the presence of an applied field to induce or to increase the existing unidirectional anisotropy. This enforces a challenge to influence the microstructure of AFM layer without significantly affecting the AFM/FM interface.

In this work we employed pulsed laser irradiation which provides an interesting alternative to conventional annealing due to the extremely fast heating (in the order of few ns) and cooling rates. This assists applying high temperatures without undesirable amounts of interfacial mixing during the short processing time. Several studies have been done on the microstructural phase transformation of FeNi films, PtMnSb films, and FePt
nanoparticles \cite{26} using laser irradiation. Recently, Schuppler et al. demonstrated magnetic patterning of Co/Pt ML using pulsed laser irradiation.\cite{27} The latter has also been utilized for tailoring the interfaces and the microstructure of the ferromagnetic/nonmagnetic multilayers.\cite{28, 29} Here, we present our study on influencing the microstructure of the AFM layer using nanosecond pulsed laser irradiation and thereby the associated magnetic properties of the exchange bias system.

In summary, in this thesis we present our work on the tailoring of magnetic properties of thin films and multilayers by optimizing the structural properties determining the unidirectional and the magnetoeelastic anisotropy. This thesis has been organized in such a way that chapter 2 provides a necessary theoretical insight on various forms of magnetic anisotropies associated with magnetic thin films and multilayers. The angular dependent various magnetic anisotropy contributions towards the effective magnetic anisotropy are explained using micromagnetic models. In addition, a detailed description on the origin of the unidirectional anisotropy is given using Meiklejohn-Bean model. Chapter 3 gives a general description on the primary experimental techniques used for the preparation and the characterization of the samples used in this study. Chapter 4 introduces a new method to apply a large biaxial stress along with the results and discussion on the influence of the stress induced magnetic anisotropy on the magnetic properties of thin films and multilayers. Chapter 5 starts with an introduction on the unidirectional anisotropy in NiMn based exchange bias system. It continues with an explanation for the temperature distribution in a material upon pulsed laser irradiation along with a quantitative argument on the advantage of using the pulse laser irradiation compared to the conventional heat treatment methods. The final two subsections are grouped with the experimental results and discussion on the effect of isothermal annealing and the pulsed laser irradiation on the structural and magnetic properties of the NiMn/Co bilayers.
2 Theoretical background

2.1 Effective magnetic anisotropy

In all the ferromagnetic thin films, the magnetization prefers to orient along certain direction termed as easy axis (e.a.). The direction along which a maximum energy is required to saturate the magnetization is termed as hard axis (h.a.). This excess energy required to change the orientation of the magnetization from easy to hard axis is termed as the effective magnetic anisotropy energy ($K_{\text{eff}}$). Descriptions for various anisotropy energy contributions are given in the following sections.

![Figure 2.1.1. Schematic illustration of the effective anisotropy energy associated with a ferromagnetic thin film. Easy axis (e.a.) is the direction along which magnetization prefers to orient, whereas hard axis (h.a.) is the direction along which a maximum energy is required to orient the magnetization.](image)

2.1.1 Demagnetizing energy/shape anisotropy

Among all the anisotropy energy contributions, the most important one in the case of thin films is the shape anisotropy that arises due to the demagnetizing field, $H_d$ given by,

$$H_d = -N_D M$$  \hspace{1cm} (2.1)

where, $M$ is the magnetization vector and $N_D$ is the demagnetizing tensor depends on the shape of the sample. In the case of thin films, the tensor elements $N_{xx}=N_{yy}=0$ and $N_{zz}=1$ i.e. $N_D=I$. Then, the demagnetizing energy associated with the influence of demagnetizing field on the direction of magnetization in thin films can be written as,

$$E_d = \frac{1}{2} \mu_0 M_s^2 \cos^2 \theta$$  \hspace{1cm} (2.2)
Theoretical background

where, $M_s$ is the saturation magnetization which subtends an angle $\theta$ with the film normal. According to this equation, the demagnetizing energy contribution favors the orientation of the magnetization along the sample plane. However, the roughness of the thin film samples significantly influences the demagnetizing factor $N_D$ as will be discussed in detail in section 4.2.3.

2.1.2 Magnetocrystalline and surface/interface anisotropy

The microscopic origin of magnetocrystalline anisotropy is the spin-orbit coupling. This interaction causes the alignment of the magnetic moment due to the spin of the electron with the magnetic moment due to the orbital motion of the electron. These are then coupled to the crystallographic axis by means of electrostatic field by the overlapping of the wave functions associated with neighboring atoms in the crystal lattice.\(^{[30]}\) This causes a preferred orientation of the magnetization along certain crystallographic direction. It is an intrinsic property of a crystalline ferromagnetic material and it reflects the symmetry of the crystal.

Néel in 1954 predicted that the reduced symmetry at the surface of the thin films would result in a different anisotropy compared to that of the bulk crystalline anisotropy.\(^{[31]}\) Therefore in the case of thin films, the total magnetocrystalline anisotropy energy has the contribution from the bulk or volume anisotropy, $K_{mc}$ per unit volume and the contribution from the surface anisotropy, $K_s$ per unit area.\(^{[12]}\) Similar situation is also encountered in the ferromagnetic/noble metal multilayers due to a lowered symmetry at the interface.\(^{[32, 33]}\)

A general expression for the total anisotropy energy in terms of the volume and the interface contributions describing the angular orientation of the magnetization in the case of polycrystalline thin film can be written as,

$$ E = -K_{tot} \cos^2 \theta $$ (2.3)

where,

$$ K_{tot} = K_{mc} + \frac{K_s}{t} $$ (2.4)

Here, $t$ is the thickness of the ferromagnetic thin films. The interfacial/surface anisotropy would make a significant contribution only in the case of ultrathin ferromagnetic layers. For the thick ferromagnetic films the Eq.(2.3) will be reduced to the following,

$$ E_{mc} = -K_{mc} \cos^2 \theta $$ (2.5)
2.1.3 Magnetostatic energy in an external field

The magnetostatic energy associated with the magnetization of the sample in the presence an external field $H$ is also referred as Zeeman energy. It can be expressed as,

$$E_{\text{zeeman}} = -\mu_0 M_s H \cos(\phi - \theta) \quad (2.6)$$

where, $\mu_0$ is the magnetic permeability of vacuum, $\phi$ and $\theta$ represents the angular orientation of the magnetization and the applied field with respect to the sample normal. According to this expression, the magnetization would align in the direction of the applied field to minimize the energy associated with the system.

2.1.4 Magnetoelastic anisotropy energy

The interaction between the magnetization and the lattice strain gives rise to an energy contribution via magnetostrictive effect and it is termed as magnetoelastic anisotropy energy. The phenomenon by which the change in the magnetization direction induces a dimensional change in a magnetic material is termed as magnetostrictive effect. For an isotropic material, the strain $\varepsilon$ experienced due to the magnetostrictive effect upon spontaneous magnetization in terms of magnetostriction coefficient $\lambda$ is given by $^{[34]}$

$$\varepsilon = \frac{3}{2} \lambda \left( \cos^2 \alpha - \frac{1}{3} \right) \quad (2.7)$$

where, $\alpha$ is the angle between the direction of magnetization and the direction along which the strain is measured.

In this study, we utilized the inverse magnetostrictive effect, where the preferred direction of magnetization can be influenced by applying stress. This effect can also be termed as stress induced magnetic anisotropy.

---

**Figure 2.1.2.** Schematic diagram showing the angular orientation of magnetization with respect to the plane subjected to an in-plane biaxial stress. The latter induces a uniaxial anisotropy in the direction normal to the sample plane.
Theoretical background

The work released by a strain $d\varepsilon$ in the presence of a uniform tensile stress $\sigma$ is given by $-\sigma d\varepsilon$. Therefore the associated magnetoelastic anisotropy energy is given by,

$$E_{me} = -\sigma \int d\varepsilon$$

Using Eq (2.7) the above equation can be rewritten as,

$$E_{me} = \frac{3}{2} \lambda \sigma \int 2 \sin \alpha \cos \alpha d\alpha$$

$$E_{me} = \frac{3}{2} \lambda \sigma \sin^2 \alpha$$

With the magnetoelastic anisotropy, $K_{me} = \frac{3}{2} \lambda \sigma$

$$E_{me} = K_{me} \sin^2 \alpha$$

where, $\alpha$ is the angle between the direction of magnetization and the direction of applied stress. The Eq (2.11) is commonly used to describe the uniaxial stress induced anisotropy. In our case, applying an in-plane biaxial stress ($\sigma_{xx}=\sigma_{yy}=\sigma$, $\sigma_z=0$) would lead to uniaxial magnetoelastic anisotropy in the direction normal to the sample plane (refer Appendix A) as depicted in Figure 2.1.2. According to Eq (2.10) magnetoelastic anisotropy energy depends on the sign and the magnitude of $\lambda$ and $\sigma$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.1.3.png}
\caption{Possible influence of the stress induced magnetoelastic anisotropy towards the energy associated with the system and the resulting orientation of the magnetization under the conditions (a) $\sigma \lambda < 0$ and (b) $\sigma \lambda > 0$.}
\end{figure}

Therefore, applying an in-plane biaxial tensile stress ($\sigma > 0$) to magnetic thin films would result in the following response depending upon their magnetostriction coefficient.
1. If \( \lambda < 0 \), it is easier to saturate the magnetization in the direction normal to the sample plane (perpendicular magnetic anisotropy) as depicted in Figure 2.1.3 (a).

2. If \( \lambda > 0 \), it is harder to saturate the magnetization in the direction normal to the sample plane (in-plane anisotropy) as depicted in Figure 2.1.3 (b).

The various magnetic anisotropy energy contributions towards the \( K_{\text{eff}} \) can be described using the micromagnetic Stoner Wohlfarth model.\(^{36}\) This model is based on the following assumption,

a) All the magnetic moments are oriented in the same direction within a particle (single domain particle).

b) The magnetization process involves coherent rotation of all the magnetic moments in response to the external applied field.

Based on the above descriptions, the angular dependent part of the anisotropy energy contributions associated with the sample subjected to an external field can be written as,

\[
E = E_{\text{zeeman}} + E_{mc} + E_{me} + E_d
\]  
(2.13)

\[
E = -\mu_0 M_s H_{FM} \cos(\phi - \theta) - K_c \cos^2 \theta + \frac{3}{2} \alpha \lambda \sin^2 \alpha + \frac{1}{2} \mu_0 M_i^2 N_d \cos^2 \theta
\]  
(2.14)

where, the angles \( \phi \) and \( \theta \) corresponds to the orientation of the applied field and magnetization with respect to the sample normal. The angle \( \alpha \) is angle between the magnetization and the direction of the applied stress. For the case of \( \sigma \) applied in the film plane (i.e. \( \alpha = 90^\circ - \theta \)) Eq. (2.14) can be written as

\[
E = -\mu_0 M_s H_{FM} \cos(\phi - \theta) - K_{\text{eff}} \cos^2 \theta
\]  
(2.15)

with

\[
K_{\text{eff}} = K_c - \frac{1}{2} \mu_0 M_i^2 N_d - \frac{3}{2} \sigma \lambda
\]  
(2.16)

The potential values of each anisotropy energy contribution towards the \( K_{\text{eff}} \) as in Eq. (2.16) are given below,

i) Shape anisotropy (\( K_d \)), which forces the magnetization in thin films to lie along the sample plane is usually of the order of \( 1.5 \times 10^5 \) J/m\(^3\) (Ni), \( 1.2 \times 10^6 \) J/m\(^3\) (Co), \( 1.8 \times 10^6 \) J/m\(^3\) (Fe).

ii) Magnetocrystalline anisotropy (\( K_{mc} \)) ranges from \( 10^3 \) J/m\(^3\) (Ni) to \( 10^6 \) J/m\(^3\) (L1\(_0\) ordered FePt)\(^{37}\).

iii) Interface/surface anisotropy (\( K_s \)) is of the order of 1 mJ/m\(^2\). In the case of ferromagnetic layer of thickness of 1nm, the contribution of \( K_s/t \) amounts to \( 10^6 \) J/m\(^3\) [see Eq (2.4)].
Theoretical background

iv) For the sample with high magnetostriction of the order of $10^{-4}$ or $10^{-3}$, application of a stress of the order of 1 GPa would give rise to a magnetoelastic anisotropy of about $10^5$ to $10^6$ J/m$^3$.

The magnetoelastic anisotropy contribution is significant for the samples with higher $\lambda$ as it is of the same order of magnitude as the others. This shows that it is possible to tailor the $K_{\text{eff}}$ of a material with high magnetostriction by applying a persistent biaxial stress. To achieve this it is necessary to apply a persistent biaxial stress in the thin films. In section 4.1, the proposed method of applying a large persistent biaxial stress to the functional layers has been discussed.
2.2 Origin of unidirectional anisotropy

The unidirectional anisotropy is an additional energy contribution towards the effective magnetic anisotropy of the FM layer (as mentioned in the previous section) and thereby influences the resulting orientation of the corresponding magnetization direction. This anisotropy arises from the interfacial phenomena of exchange coupling across the FM and the AFM layers termed as the exchange bias effect. This effect causes a displacement of the FM hysteresis loop along the field axis. This type of anisotropy was first observed by Meiklejohn and Bean in Co-CoO system.\textsuperscript{[38]}

2.2.1 Physical illustration of exchange bias

![Diagram showing exchange bias effect](image)

Figure 2.2.1. Schematic diagram depicting the response of exchange biased FM and AFM spins at various stages (1-4) of the negative shifted hysteresis loop after field cooling procedure. (Illustration was based on the reference\textsuperscript{[16]})

The shift in the hysteresis loop due to the exchange bias effect can be qualitatively understood assuming an exchange coupling between the FM and AFM spins at the interface. Let $T_N$ and $T_C$ be the Néel temperature of AFM layer and the Curie temperature of the FM layer, respectively. At the temperatures higher than $T_N$ and lower than $T_C$, all the FM spins align along the direction of the applied field, whereas the AFM spins are randomly oriented as shown in Figure 2.2.1. Upon reducing the temperature below $T_N$
Theoretical background

with an external field (field cooling), the AFM spins in the plane next to the FM layer at the interface align ferromagnetically or antiferromagnetic depending upon the exchange coupling energy) with the FM spins. The AFM spins in the next layer align in the opposite direction to follow the AFM order to produce zero net magnetization. When the applied field is reversed, the FM spins start to rotate to align themselves along the direction of the applied field. But the AFM spins with sufficiently large AFM anisotropy ($K_{AFM}$) will not respond to the applied field. Due to the exchange coupling at the AFM/FM interface, the AFM spins exerts a torque on the FM spins. This holds the FM spins in the direction of the field cooling and it results in an induced unidirectional anisotropy. Because of this effect the FM spins switch only at a large reverse field, which is sufficient to overcome the torque exerted by the AFM layer. This switching field or coercive field ($H_c$) is larger than the field ($H_c$) required to switch the FM spins in the absence of exchange coupling at the FM/AFM interface. The field ($H_c$) at which the FM spins switch back to their original direction is also reduced due to the exchange interaction at the interface, which acts as an internal field. As a result, the FM hysteresis loop is shifted in the field axis. The corresponding $H_{ex}$ and $H_c$ can be calculated using the formula,[39]

$$H_{ex} = \frac{H_c^+ + H_c^-}{2} \quad (2.17)$$

$$H_c = \frac{H_c^+ - H_c^-}{2} \quad (2.18)$$

2.2.2 The Meiklejohn-Bean model

Meiklejohn and Bean proposed a model to explain the shift in the hysteresis due to exchange bias effect.[40] This model is based on the Stoner Wohlfarth model[36] assuming single domain FM and AFM layer and a coherent rotation of the magnetization.

According to this model, the energy per unit area for an exchange coupled FM/AFM bilayer system can be written as

$$E = -\mu_0 M_{FM}^s H_{FM} \cos(\gamma - \beta) + K_{FM}^{eff} t_{FM} \sin^2 \beta + K_{AFM} t_{AFM} \sin^2 \alpha - J_{ex} \cos(\beta - \alpha) \quad (2.19)$$

where, the first term is the Zeeman energy with $H$, $M_{FM}^s$ and $t_{FM}$ being the applied field, saturation magnetization and the thickness, respectively of the FM layer. The second and the third terms are the anisotropy energies of FM and the AFM layer, respectively. The last term represents the exchange coupling energy at the FM and AFM interface with $J_{ex}$ being the exchange coupling energy (in this case it corresponds to a ferromagnetic coupling between the FM and AFM spins). The angles $\beta$ and $\gamma$ correspond to the orientation of the FM magnetization and the applied field $H$ with respect to the FM uniaxial anisotropy direction, respectively. The angle $\alpha$ defines to the orientation of the
magnetization of the AFM sublattice with respect to the AFM uniaxial anisotropy direction. Figure 2.2.2 shows the schematic of the angles and the vectors used in this model.

Figure 2.2.2. Schematic diagram showing the angular orientation of the applied field $H$, FM and AFM magnetizations ($M_{FM}$ and $M_{AFM}$) with respect to their corresponding anisotropy directions ($K_{FM}^{\text{eff}}$ and $K_{AFM}$) as in the Meiklejohn and Bean model. The two opposite directions of $M_{AFM}$ represent the orientation of sublattice magnetizations with respect to each other.

The induced FM uniaxial anisotropy direction upon field cooling procedure is assumed to be oriented parallel to the field cooling direction ($\gamma=0^\circ$). Both $K_{FM}^{\text{eff}}$ and $K_{AFM}$ assumed to be oriented parallel to the each other due to exchange coupling at the interface that determines the unidirectional anisotropy direction as depicted in Figure 2.2.2. In this model, the AFM magnetization is assumed to be fixed and does not respond to the applied field due to high AFM anisotropy energy (i.e $K_{AFM}^{\text{eff}}>J_{ex}$) and therefore $\alpha=0^\circ$. Then for the field applied along the FM uniaxial anisotropy direction (i.e. $\gamma=0^\circ$), Eq (2.19) can be written as,

$$E = -\mu_0 M_{FM}^t H_{FM} t_{FM} \cos(\beta) + K_{FM}^{\text{eff}} t_{FM} \sin^2 \beta - J_{ex} \cos(\beta)$$

(2.20)

Minimizing this equation with respect to $\beta$ results in the following expression

$$\cos \beta = \frac{\mu_0 H_{FM} M_{FM}^t t_{FM} + J_{ex}}{-2K_{FM}^{\text{eff}} t_{FM}}$$

(2.21)

The solutions can be obtained for the conditions $\beta=0^\circ$ and $180^\circ$ that corresponds to positive ($H^+_c$) and negative switching field ($H^-_c$), respectively. Therefore, for the FM layer exhibiting square hysteresis loop, the coercive fields $H^+_c (\beta=0^\circ)$ and $H^-_c (\beta=180^\circ)$ is given by,
Theoretical background

\[
H_c^+ = \frac{2K_{FM}^t t_{FM} + J_{ex}}{\mu_0 M_{FM}^t t_{FM}} \quad (2.22)
\]

\[
H_c^- = \frac{2K_{FM}^t t_{FM} - J_{ex}}{\mu_0 M_{FM}^t t_{FM}} \quad (2.23)
\]

By substituting these in the Eq. (2.17) and (2.18), we arrive at the following expressions for \(H_c\) and \(H_{ex}\) of the FM layers

\[
H_c = \frac{K_{FM}^t}{\mu_0 M_{FM}^t} \quad (2.24)
\]

\[
H_{ex} = \frac{-J_{ex}}{\mu_0 M_{FM}^t t_{FM}} \quad (2.25)
\]

Using this formula, the exchange coupling energy can be estimated from measured exchange coupling field. This formula also shows that the \(H_{ex}\) is inversely proportional to the thickness of the FM layer, which has already been verified experimentally.\(^{[41]}\)

According to this model the condition \(K_{AFM} t_{AFM} > J_{ex}\) has to be satisfied to observe the shift of the hysteresis loop. Because, if \(J_{ex} > K_{AFM} t_{AFM}\), the applied field \(H\) would rotate FM magnetization, which is accompanied by an irreversible change in the AFM (\(\alpha \neq 0^\circ\)), which would influence only the coercivity of the hysteresis loop without any shift of the hysteresis loop.
Sample preparation and characterization

This chapter describes the technique used for the sample preparation and the principal analytical tools used for the magnetic and the structural characterization of the magnetic thin films and multilayers in this study.

3.1 Sample preparation

All the samples in the present study were prepared by DC magnetron sputtering. The schematic sketch of the sputtering process is shown in the Figure 3.1.1. In DC sputtering, the target acts as cathode, which is held at high negative potential. A glow discharge (plasma) is formed due to the ionisation of inert atoms (Argon) by electrons. This plasma is basically a conducting gas with free electrons accelerating away from the target and the positively charged ions accelerating towards the target. When the positively charged Ar ions bombard the target, the atoms of the target are expelled out by momentum transfer. This process is known as sputtering. The sputtered atoms traverse in vacuum and get deposited onto the substrate.

In DC magnetron sputtering, magnets are placed behind the sputtering targets. The magnetic field produced by the magnets confines both the electrons emitted from the target and the secondary electrons produced during ionization of Ar atoms. This confinement of electrons increases the probability of ionisation. This also makes the plasma to be closer to the targets and hence increases the rate of sputtering.

The sputtering chamber consists of 4 positions for different sputter targets and eight sample positions. All the targets that have been used in this study are of 3” in diameter and all of them are about 99.95% pure. Co target is received from ChemPur, Karlsruhe and the
Sample preparation and characterization

CoFe alloy, Pd, Ni, Ta targets are received from Mateck, Jülich. The substrate can be placed in a rotating sample table, which is controlled by a computerized motor controller. Upon rotation of the sample table the substrate passes over all the 4 target positions in one complete rotation. This setup helps in the preparation of Co/Pd multilayers by rotating the substrate table continuously over the respective sputtering targets for a specific deposition rate of the corresponding materials. Sputter targets were mounted far from each other to avoid the deposition of the sputtered material on to the neighboring sputtering targets. The sputtering gas used in this process was high purity Argon (99.999%). The argon flow rate was controlled by a mass flow controller and the pressure in the sputtering chamber was controlled independently using a pressure controller.

*Table 3.1. Sputter parameter and the deposition rate for all the materials used in the present study.*

<table>
<thead>
<tr>
<th>Material</th>
<th>Ar pressure (mbar)</th>
<th>Power (kW)</th>
<th>Deposition rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>5.6×10⁻³</td>
<td>0.30</td>
<td>1.72</td>
</tr>
<tr>
<td>Ni</td>
<td>4.4×10⁻³</td>
<td>0.10</td>
<td>1.20</td>
</tr>
<tr>
<td>CoFe</td>
<td>2.4×10⁻³</td>
<td>0.15</td>
<td>1.22</td>
</tr>
<tr>
<td>Co</td>
<td>4.4×10⁻³</td>
<td>0.04-0.15</td>
<td>0.29-0.93</td>
</tr>
<tr>
<td>Pd</td>
<td>4.4×10⁻³</td>
<td>0.06</td>
<td>1.11</td>
</tr>
<tr>
<td>NiMn</td>
<td>2.3×10⁻³</td>
<td>0.25</td>
<td>2.80</td>
</tr>
</tbody>
</table>

All samples in our study were prepared with specified Argon flow rate of 10 sccm. The base pressure before sputtering was better than 10⁻⁸ mbar. The deposition rate of the materials was controlled by varying the sputter pressure and the sputtering power. The individual layer thicknesses were calibrated by performing small angle x-ray reflectometry.
3.2 Magnetic characterization

The magnetic properties of all the samples were measured using vibrating sample magnetometer (VSM), which is based on the induction technique. In VSM, the sample is placed between two pickup coils across the poles of an electromagnet, and the sample is vibrated at a fixed frequency. Two pickup coils experience a change of the magnetic flux due to the motion of the sample. According to Faraday's law of induction, an emf proportional to the rate of that change of flux is induced in the pickup coils. This induced voltage is proportional to the product of the magnetization and the volume of the sample being measured. For the sample vibrating at frequency $\omega$, the induced voltage $V$ at the pickup coil is given by,

$$V = g\mu A \omega \cos \omega t$$  \hspace{1cm} (3.1)

where, $\mu$ is the magnetic moment of the sample, $A$ is the amplitude of the sample vibration, $g$ is a geometric factor that is also depends on the position of the sample with respect to the sensing coil. This induced voltage is proportional to the projected component of the spontaneous magnetization in the direction normal to the plane of the pickup coils as shown in Figure 3.2.1.

![Figure 3.2.1. Schematic illustration of the magnetization measurement in VSM. The pickup coils measure the projected component of the magnetization of the sample perpendicular to the plane of the coil.](image)

The vibrating sample magnetometer consists of a mechanical resonator (LakeShore 735 VSM controller), which oscillates the sample in the vertical direction at a fixed frequency. An external field is applied by variable-gap electromagnet, which provides a maximum magnetic field of about 2.2 T (depends on gap between the poles of the electromagnet). The equipment has an experimental flexibility, both in terms of achievable field strengths, and in terms of allowable sample sizes since the pole gap can be adjusted.
Determination of the effective magnetic anisotropy

The effective magnetic anisotropy ($K_{\text{eff}}$) can be determined from the magnetization curves using following two methods.\cite{15}

1. Area method.
2. Saturation field ($H_s$) method.

To determine the PMA of a sample by the area method, magnetic measurements have to be carried out with the external magnetic field applied parallel ($H_{//}$) and perpendicular ($H_{\perp}$) to the sample plane. The schematic of the M/H loop of the sample with in-plane anisotropy (magnetization prefers to lie along the sample plane) and out-of-plane anisotropy (magnetization prefers to orient perpendicular to the sample plane) are shown in Figure 3.2.2. The area enclosed between the corresponding magnetization curves (shaded region) is proportional to the effective PMA. This is based on the energy required to change the magnetization of the sample by an applied field $H$ by an amount of $dM$, which is given by,

$$K_{\text{eff}} = \mu_0 \int_0^M H dM$$  \hspace{1cm} (3.2)

**Figure 3.2.2. Schematic diagram of M/H loops with field applied perpendicular and parallel to the sample with (left) in-plane anisotropy and (right) out-of-plane anisotropy**

Determination of $K_{\text{eff}}$ by the $H_s$ method can be understood based on the micromagnetic Stoner Wohlfarth model \cite{36} involving minimization of the total energy of a magnetic system. The angular dependent part of the anisotropy energy contributions associated with the sample subjected to an external field can be written as [see section 2.1]
Sample preparation and characterization

\[ E = -\mu_0 M_s H_{FM} \cos(\phi - \theta) - K_{eff} \cos^2 \theta \]  

(3.3)

where,

\[ K_{eff} = K_e - \frac{1}{2} \mu_0 M_s^2 N_D - \frac{3}{2} \sigma \lambda \]  

(3.4)

For the samples with in-plane anisotropy \((K_{eff}<0)\), the magnetization would prefer to lie along the sample plane. Therefore the magnetostatic energy does not need to be overcome to saturate the sample parallel to the sample plane. This is valid only if, \(K_e < |K_d|\), which is the case for most of the thin films.

For the field applied perpendicular to the sample plane \((\phi=0^\circ)\), the energy minimization of Eq (3.3) with respect to \(\theta\) yields

\[ M_s \cos \theta = \frac{-2K_{eff}}{\mu_0 H} \]  

(3.5)

This corresponds to the parameter measured in VSM. (see Figure 3.2.1) Upon saturating the magnetization perpendicular to the sample plane, \(\theta=0^\circ\) and \(H=H_s\), then the \(K_{eff}\) can be estimated from the following equation,

\[ K_{eff} = -\frac{1}{2} \mu_0 M_s H_s \]  

(3.6)

For the samples exhibiting PMA \((K_{eff}>0)\), the field required to magnetize the layer perpendicular to the sample plane is zero. For the field applied parallel to the sample plane \((\phi=90^\circ)\), the energy minimization of Eq (3.3) with respect to \(\theta\) yields

\[ \sin \theta = \frac{2K_{eff}}{\mu_0 M_s H} \]  

(3.7)

At saturation, \(\theta=90^\circ\) and \(H=H_s\). Then the \(K_{eff}\) is estimated from the following equation,

\[ K_{eff} = \frac{1}{2} \mu_0 M_s H_s \]  

(3.8)

In this work, the \(K_{eff}\) has been measured by both the area and the saturation field methods and the validity of these methods is discussed in the chapter 4.2. Recently, A. S. H. Rozatian et al. showed that the \(K_{eff}\) measured by the area method using VSM are consistent with that of the measurements using Torque magnetometer,[44] which is one of the commonly used techniques to measure the \(K_{eff}\).[45]
3.3 Structural characterization

X-ray diffraction (XRD) technique has been utilized to characterize the crystal structure and the texture of the thin films. X-ray reflectivity measurements (XRR) were performed for the thickness measurement and to determine the surface and the interfacial roughness of the samples.

Microstructure and the lattice parameter of the samples were studied using a Panalytical X’Pert Pro x-ray diffractometer having standard 0-20 geometry. The measurements were carried out with either Cu or Co radiation. The radiation passes through the 0.04 rad soller slit and the divergence of the incident beam can be adjusted using programmable divergence slit and a mask at the end of the primary beam. The width of the divergence slit and the mask has been chosen in such a way that the irradiated area is not larger than the sample. In the case of Cu radiation, the measurements were performed with 40 kV high tension and 40 mA anode current and the diffracted beam passes through a parallel plate collimator and a monochromator in order to cancel the Cu-Kβ and any possible fluorescence radiation. In the case of Co anode, the measurements were performed with 40 kV high tension and 35 mA anode current and the diffracted beam passes through the programmable anti-scatter slit and 0.04 rad soller slit before impinging on the position sensitive “X’Celerator Scientific” detector.

Texture analysis (rocking curve) and small angle x-ray reflectometry to study the layer structure has been performed using Siemens D5005 diffractometer outfitted with Cu x-ray tube. All the measurements were usually performed with 40 kV high tension and 40 mA anode current. A high intensity, parallelized and almost monochromatic X-ray beam is obtained using a Göbel mirror. The reflected beams were collimated using 0.6 and 0.1 mm slits for higher angular resolution.

3.3.1 X-Ray diffraction (XRD)

When the x-rays are irradiated on a sample, they will be scattered by the atoms and the coherently scattered x-rays undergo the phenomena of diffraction. The measured XRD pattern reflects the atomic arrangement of the crystal.

Let M and N be the monochromatic x-ray beams with wavelength \( \lambda \) impinging on the sample at an angle of \( \theta \) as shown in Figure 3.3.1. The path difference between the reflected x-ray beams M’ and N’ is equal to \( (a+b) \). If this path difference between M’ and N’ is equal to an integral multiple of the wavelength of the x-ray beam then they are in-phase with each other and will undergo constructive interference. Similarly, if the path difference \( (a+b) \) is not equal to an integral multiple of \( \lambda \), then the reflected beams will undergo destructive interference.
Therefore the condition to observe constructive interference is given by,

\[ a + b = n\lambda \quad (3.9) \]

![Diagram of Bragg condition](image)

*Figure 3.3.1. A schematic illustration to derive Bragg condition (see below text for the explanation).*

From Figure 3.3.1 one can realize that the path difference \((a+b)\) is equal to \(2d\sin\theta\) with \(d\) being the lattice spacing, then the Eq. (3.9) can be written as,

\[ 2d\sin\theta = n\lambda \quad (3.10) \]

This expression is termed as Bragg’s equation. For cubic crystal structure, the interplanar distance between consecutive planes of atoms is a function of the Miller indices \((h,k,l)\) and the lattice parameter \(a\) and it is given by,

\[ d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3.11) \]

For tetragonal crystal structure, the interplanar lattice spacing \(d\) is related to the lattice parameters \(a\) and \(c\) as,

\[ d = \frac{ac}{\sqrt{c^2(h^2 + k^2) + a^2l^2}} \quad (3.12) \]

### 3.3.1.1 Biaxial stress analysis

Biaxial stress induced elastic deformation of polycrystalline thin films causes a change in the lattice spacing of the constituent grains from the stress free state to a value corresponding to the applied stress. When the strained lattice spacing is same for all the grains having similar orientation with respect to the direction of the applied stress, then it is termed as uniform strain (macrostrain). This causes a shift in the diffracted peak to a new 2\(\theta\) value.
The effect of uniform in-plane strain on the position of the XRD peak is illustrated in Figure 3.3.2. An in-plane tensile strain causes a perpendicular Poisson contraction, which reduces the lattice spacing and according to Bragg’s law, this would shift the diffracted peak to higher 2θ values. Therefore, by measuring the shift in the diffraction peak one can determine the strain in the direction normal to the sample plane.

Figure 3.3.2. Schematic representation of the effect of in-plane uniform strain in thin film on the out-of-plane lattice spacing (left) and the corresponding diffraction peak (right).

The perpendicular Poisson ($\varepsilon_z$) of the functional layer subjected to a biaxial in-plane tensile stress is given by,

$$
\varepsilon_z = \frac{d_N - d_0}{d_0}.
$$

(3.13)

where, $d_N$ and $d_0$ are the lattice spacing at strained and unstrained states, respectively. The corresponding in-plane strain and stress can be determined using the following generalized Hook’s law.

$$
\varepsilon_i = \frac{1}{E} \left[ \sigma_i - \nu (\sigma_j + \sigma_k) \right]
$$

(3.14)

For the case of biaxial stress state ($\sigma_x=\sigma_y=\sigma_z=0$), the in-plane strain, $\varepsilon_x$ and the out-of-plane strain, $\varepsilon_z$ are given by,

$$
\varepsilon_x = (1-\nu) \frac{\sigma}{E}
$$

(3.15)

$$
\varepsilon_z = -2\nu \frac{\sigma}{E}
$$

(3.16)

From Eq (3.15) and (3.16) we arrive at the following relation
Sample preparation and characterization

\[ \varepsilon = -\varepsilon_z \frac{(1 - \nu)}{2\nu} \quad (3.17) \]

Using this equation, the in-plane strain can be determined from the out-of-plane strain evaluated from the measured changes in the lattice spacing. The corresponding biaxial stress can be calculated from the following equation,

\[ \sigma = \frac{E\varepsilon_x}{(1 - \nu)} \quad (3.18) \]

It has to be kept in mind that any non-uniform strain (microstrain) in the sample would lead to peak broadening instead of peak shift. This will be addressed in the chapter 4.3.

3.3.1.2 Grain size analysis

As we discussed earlier, in order to observe a Bragg peak due to the constructive interference of the scattered x-rays from a crystal, the Bragg condition has to be satisfied. Where, the angle of incidence \( \theta \) must be equal to the Bragg angle, \( \theta_B \) and the path difference between the first two successive atomic planes has to be an integral multiple of the wavelength i.e. \( n\lambda \). When the angle of incidence slightly varies from \( \theta_B \), the x-rays scattered from the first atomic plane will undergo destructive interference with the x-rays scattered by the atomic plane, which has exactly one-half the wavelength (out of phase).

For smaller difference between the angle of incidence and \( \theta_B \), the plane of atoms scattering the x-rays exactly out of phase with that of the corresponding incident ray will lie deeper in the crystal and in the case of samples with small grains, these planes may not exist. Therefore for such samples, at this angle of incidence there will be non-zero intensity due to the diffracted beams and this causes the broadening of Bragg peak. This gives rise to a relation between the width of the Bragg peak and the grain size given by the following Scherrer’s formula, \(^{[46]}\)

\[ t_g = \frac{K\lambda}{B\cos\theta_B} \quad (3.19) \]

where, \( t_g \) is the grain size, \( B \) is the full width at half maximum of the Bragg peak and \( K \) is a factor that depends upon the crystal structure (for cubic crystal it is approximately equal to 0.9).
3.3.2 Small angle X-ray Reflectometry (SAXR)

The reflection of x-rays at the surface and interfaces is due to the different electron densities in the different layers, which correspond to different refractive indices in classical optics. For X-rays striking an ideally flat surface at low angle of incidence \( \theta \), the reflectivity \( R_F \) is given by the Fresnel equation,

\[
R_F = \left( \frac{\sin \theta - \sqrt{n^2 - \cos^2 \theta}}{\sin \theta + \sqrt{n^2 - \cos^2 \theta}} \right)^2
\]

(3.20)

where, \( n \) is the refractive index of the material.

![Kiessig fringes](image)

*Figure 3.3.3. The specular x-ray reflectivity scans for single layer showing Kiessig fringes.*

The reflectivity \( R \) of a rough surface or interface can be calculated by adding a Debye-Waller like attenuation factor to account for roughness.

\[
R = R_F \exp \left( \sigma^2 Q_\perp Q'_\perp \right)
\]

(3.21)

where, \( \sigma \) is the root mean square roughness, \( Q_\perp \) and \( Q'_\perp \) are the components of the wave vector normal to the interface above and below the interface respectively.

For incident angles \( \theta \) below a critical angle \( \theta_c \), total external reflection occurs, as shown in Figure 3.3.3. The critical angle \( \theta_c \) for most materials is less than 0.5°. The electron density \( \rho_e \) of the material is related to the critical angle \( \theta_c \) as,

\[
\theta_c = \sqrt{\rho_e}
\]

(3.22)
Above $\theta_c$, the reflected beams from the different interfaces interfere with each other and give rise to interference fringes (Kiessig fringes). The period of the interference fringes and the decay of the intensity are related to the thickness and the roughness of the layer, respectively (refer Eq. (3.21))

The position of the incident angle $\theta_m$ at which an interference maximum of the order $m$ occurs is related to layer thickness $d$ by,

$$\sqrt{\sin^2 \theta_m - \sin^2 \theta_c} = \frac{m\lambda}{2d} \quad (3.23)$$

The typical range for these measurements is between 0.2° and 4° in Theta. To determine thickness and roughness, it is essential to precisely align the sample to the X-ray beam. In order to achieve that, rocking curve measurements (fixed $2\theta$, varying $\theta$) have been performed for each sample. The offset of the theta value (determined from the peak position) was added to the starting $\theta$ value of the measurement. The specular X-ray scans which are obtained using this technique have been analyzed by fitting with a simulated multilayer reflectivity curve using the software REFSIM, which is based on Parratt formalism.\[47\] This program can be used for single layer as well as multilayer structure to determine the parameters like thickness, roughness and density.
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4 Biaxial stress induced magnetic anisotropy

Stress-induced anisotropy arising from the inverse magnetoelastic effect has been an active area of study for several decades.\cite{48} Several studies showed that it plays a vital role in thin films and the multilayers exhibiting PMA i.e. for the reorientation of the magnetization from in-plane to the out-of plane direction of the sample.\cite{49-51} Here, we are interested to influence the stress induced anisotropy contribution towards PMA by applying an external permanent biaxial stress to the functional layers. Since the strain associated with the magnetoelastic energy can be easily varied; it gives an additional degree of freedom to optimize the magnetic properties of thin films and multilayers with high yield strength.

Several investigations have been reported on the effect of stress on the magnetic properties of thin films. In these studies the stress is applied to the thin film by hydrostatic pressure,\cite{52} lattice mismatch with the substrate,\cite{53} by alloying elements with different lattice parameter,\cite{54} or by using piezo-substrates, for which the electrically induced strain is controlled by varying the potential across the substrate.\cite{55} L. Callegero et al.\cite{56} proposed a new manner for inducing biaxial strain in which a substrate is inflated by subjecting it to a pressurized fluid on one side. The inflation leads to an isotropic in-plane tensile stress being exerted on a film deposited on the opposite side of the substrate. All of these methods have primarily been used to study the influence of biaxial stress on magnetic anisotropy. But they cannot modify the magnetic anisotropy permanently, as the techniques do not apply a permanent stress to the thin-film sample. This limits the usage of characterization tools to study structural and magnetic characteristics. Therefore, it is necessary to have an alternate method to apply a large permanent stress to the samples in a more controlled manner.

Here, we present our new method of depositing thin films on the Ta substrates, which are then loaded with hydrogen. By this approach, a persistent in-plane biaxial tensile stress can be applied to the thin-film sample and this method is described in detail in section 3.1. Our method of applying stress has been employed on the films with a different magnetostriction coefficient and a different saturation magnetization. Thereby, we studied the factors influencing the contribution of the magnetoelastic anisotropy towards the effective magnetic anisotropy. The corresponding experimental results along with discussions are grouped in section 3.2. In section 3.3, we present the study on the optimization of the magnetic properties of the Co/Pd multilayer, which is a potential candidate for the ultra high-density recording media.
4.1 A new method of applying biaxial stress to the thin films

In all the metal-hydrogen systems, the dissolution of hydrogen results in the crystal lattice distortion.\(^{[57]}\) In this work, the strain due to such a lattice distortion has been utilized to apply the biaxial stress in the functional layers. Hydrogen loading of thin films and multilayers clamped to the substrate causes an in-plane compressive stress of several GPa as lateral expansion is hindered as the films are clamped to the substrate;\(^{[58, 59]}\) In all those studies, the observed strain is only due to the lattice expansion in the direction perpendicular to the sample plane.\(^{[60, 61]}\) But in this study, we propose a method by which the volume expansion of the substrate upon hydrogen loading causes an in-plane stress to the functional layers.

4.1.1 Lattice strain due to hydrogen in metals

It is well known that the hydrogen diffuses into the metals and occupies the interstitial sites, which is accompanied by the lattice expansion. The change in the volume of the host metal by the dissolution of \(n\) hydrogen atoms is given by

\[
\Delta V = n \Delta v
\]

where, \(\Delta v\) is the change in the volume per hydrogen atom (H). For a metal crystal with \(N\) metal atoms (M) and a mean atomic volume of \(V_m\), the total volume, \(V=NV_m\). Then, the relative change in the volume of the metal due to atomic fraction of hydrogen \((c=n/N)\) is

\[
\frac{\Delta V}{V} = \frac{n \Delta v}{NV_m} = c \frac{\Delta v}{V_m}
\]

The metal lattice volume increases with an increasing hydrogen concentration by approximately 2 to 3 Å\(^3\) per hydrogen atom.\(^{[62]}\) The dissolved hydrogen occupies octahedral interstitial sites in Pd and Ni (FCC), and tetrahedral interstitial sites in V, Nb and Ta (BCC). A relatively large amount of hydrogen up to ratio H/M\(\sim\)1 can be dissolved in these systems.\(^{[63, 64]}\)

In the present study, Ta has been chosen as the substrate because the formation of a single \(\alpha\)-TaH phase (solid-solution) occurs over a wider range of the hydrogen concentration \((c<0.16)\) at room temperature (see Figure 4.1.5). Whereas in the case of other transition metals, the \(\alpha\) phase exist over only a narrow range of the hydrogen concentration at room temperature. The relative volume change \(\Delta v/V_m\) in \(\alpha\)-TaH phase due to hydrogen is about 0.15.\(^{[57]}\)
Biaxial stress induced magnetic anisotropy

For the metals with cubic crystal structure and random intermetallic site occupancy for hydrogen, the Eq. 4.2 can be written as,

$$\frac{\Delta a}{a} = \frac{1}{3} c \frac{\Delta \nu}{\nu_m}$$  \hspace{1cm} (4.3)

Figure 4.1.1. Ta lattice expansion vs hydrogen concentration.\(^{[57]}\)

where, \(\Delta a/a\) is the relative lattice parameter change of the host metal. From Eq (4.3), it is possible to evaluate the atomic concentration of hydrogen in the host metal by precisely measuring the lattice parameter change using x-ray diffractometer. Figure 4.1.1 shows the relative lattice parameter change of Ta as a function of the atomic fraction of hydrogen. The relative change in the lattice parameter is isotropic only in the \(\alpha\)-TaH phase \((c<0.16)\). At higher hydrogen concentration, there is a formation of tantalum hydride phases with tetragonal (TaH\(_{0.5}\)) or orthorhombic (TaH\(_{0.8}\)) crystal structures, and the corresponding lattice parameters are given in Table 4.1.

Table 4.1. Crystal structure and the corresponding lattice parameter of the tantalum hydride phases.\(^{[65]}\)

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td>Ta metal</td>
<td></td>
</tr>
<tr>
<td>TaH(_{0.5})</td>
<td></td>
</tr>
<tr>
<td>TaH(_{0.8})</td>
<td></td>
</tr>
</tbody>
</table>

\[\text{\footnotesize Reference:}\]
Biaxial stress induced magnetic anisotropy

Figure 4.1.2 shows the proposed method of applying an in-plane biaxial stress by loading the Ta substrate with hydrogen. The absorption of hydrogen in the Ta substrate causes a volumetric lattice expansion. This expansion would apply an in-plane biaxial stress to the functional layers deposited on the substrate. Also, the proposed method does not require solubility of hydrogen in the functional layer itself and may therefore be applied to a wide variety of systems.

![Diagram showing volumetric expansion of Ta substrate upon hydrogen loading](image)

*Figure 4.1.2. Schematic drawing shows a volumetric expansion of the Ta substrate upon hydrogen loading. The strain transfer from the substrate would cause expansion of the functional layer in the film plane, which is accompanied by the Poisson’s contraction in the vertical direction.*

4.1.2 Surface activation of metal

The absorption of hydrogen in metals involves physisorption of the hydrogen molecules on a metal surface. This depends on the sticking coefficient of hydrogen molecules on the metal surface.\(^{[66]}\) The adsorbed hydrogen atoms have to overcome the activation energy barrier to dissociate into chemisorbed hydrogen atoms.\(^{[67]}\)

\[
H_2 \rightarrow 2H \tag{4.4}
\]

The height of this activation energy barrier depends on the surface elements. Usually the oxidized or the contaminated surface passivates the metallic surface towards hydrogen.\(^{[68]}\) But these oxide layers do not hinder the diffusion of atomic hydrogen.\(^{[69]}\) So in this case, it requires an activation treatment to make the surface reactive towards hydrogen. This can be achieved by (1) thermal treatment at 400°C or above in reducing atmosphere or (2) etching the surface impurity by ion sputtering\(^{[70]}\) or (3) by coating the surface with the suitable materials which dissociates the hydrogen molecules to their atomic entities, which further diffuses in to the metallic layer.\(^{[71]}\) In the first and the second methods, further processing (e.g. hydrogen loading) is possible only in the inert atmosphere in order to avoid any further contamination upon exposing to air. In the present study, third method has been used to assist the loading of the Ta substrate with hydrogen.
In the case of Ta substrates, the tantalum oxide at the surface significantly increases the hydrogen loading temperature to about 500˚C. Such an elevated temperature would deteriorate the magnetic properties of the functional layers due to interfacial diffusion. Therefore, one side of the Ta substrate was coated with 100 nm of Pd by DC magnetron sputtering at room temperature, which acts as an activation layer to promote the diffusion of hydrogen into the Ta at relatively low temperature of about 80°C. The Pd layer catalyzes the dissociation of hydrogen molecule into individual hydrogen atoms, which diffuse further into the Ta substrate.

### 4.1.3 Absorption of hydrogen in metals

The chemisorbed hydrogen atoms diffuse through the subsurface layer and into the bulk and they dissolve exothermically in the Ta host metal. The hydrogen absorption process is reversible, in which two chemisorbed hydrogen atoms recombine at the surface of the metal and desorb as hydrogen molecule. The hydrogen absorption and desorption processes strongly depend on the pressure and temperature.

![Figure 4.1.3. Ideal pressure-composition isotherm of metal hydride system.](image)

The influence of the pressure and the temperature on the hydrogen absorption in metals and the resulting metal-hydride formation can be understood by pressure-composition isotherms. An ideal set of pressure-composition isotherms is shown in Figure 4.1.3, where the equilibrium hydrogen pressure, $P_{H_2}$, in a host metal is plotted against the hydrogen concentration, $c$, at different temperatures, $T_1 < T_2 < T_3$. The hydrogen dissolves in the host metal and forms $\alpha$-phase, the fraction of which increases with increasing pressure. At some pressure the host metal saturates with $\alpha$-phase and a strong H-H interaction leads to the formation of hydride phase ($\beta$-phase). The dashed curve in Figure 4.1.3 corresponds to the boundary between the single phase region ($\alpha$ or $\beta$) and region of co-existence of $\alpha$.
Biaxial stress induced magnetic anisotropy

and β phases below T_c. The plateau in the isotherms, where both α and β phases coexist is termed as plateau pressure. The plateau pressure, $P_{eq}$ significantly depends on the temperature and they are related via van’t Hoff equation,

$$\ln P_{eq} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (4.5)$$

where $\Delta S$ is the entropy of formation, $R$ is the gas constant and $\Delta H$ is the heat of formation, which determines the stability of the metal hydrides. The $\Delta H$ of tantalum metal hydride is -36 kJ/mol H. [75, 76]

As the temperature increases, the width of the plateau pressure decreases resulting in an increased solubility of hydrogen in α-phase. In pure β-phase region, the concentration of hydrogen increases with increasing hydrogen pressure. At a very high hydrogen pressure, further hydride phases may form.

4.1.4 Hydrogen loading setup

Figure 4.1.4 shows a schematic representation of the hydrogen loading setup. The chamber was evacuated to vacuum better than $10^{-4}$ mbar and the sample was heated at required loading temperature. Then, the chamber was filled with hydrogen at the pressure of 1.5 Bar. The temperature for hydrogen loading has been chosen to be 80ºC so that the tantalum hydride exists in a single phase for the entire hydrogen concentration at this temperature (see Figure 4.1.5). At constant pressure and temperature the hydrogen concentration in the Ta increases with time until the solubility limit of the hydrogen in the Ta substrate is reached (see Figure 4.1.3). By changing the hydrogen loading time, a different hydrogen concentration in the Ta substrate corresponding to different strain can be achieved.

![Schematic diagram of hydrogen loading setup](image)

*Figure 4.1.4. Schematic diagram of hydrogen loading setup.*
Upon cooling to room temperature, there is a formation of α-phase or the coexistence of α-phase with one or several tantalum-hydride phases depending on the concentration of hydrogen. Figure 4.1.5 shows that at room temperature α-phase extends up to H/Ta ratio of 20 % (the corresponding atomic fraction of H in Ta is 0.16). Therefore, according to Eq. (4.3) the maximum expansion in the Ta lattice spacing in α-phase amounts to about 0.8 %. But the formation of tantalum-hydride phases with a higher concentration of hydrogen would cause a maximum expansion of the Ta lattice spacing to about 2 to 3 % (see Table 4.1). This value corresponds to a theoretical limit of a maximum in-plane strain that can be induced in the functional layers deposited on the Ta substrate upon hydrogen loading.

*Figure 4.1.5. Tantalum-Hydrogen binary phase diagram.*[64]
4.2 Influencing magnetic anisotropy of Ni and CoFe films

In this chapter, the results of our study on the influence of biaxial tensile stresses on the effective PMA of magnetic thin films is presented. The shape anisotropy which forces the magnetization to lie in the film plane depends upon the saturation magnetization of the magnetic thin film.[see Eq. (2.2)] Therefore, Ni and Co$_5$Fe$_{50}$ having different saturation magnetization have been chosen as model systems for the current study. Ni has low saturation magnetization of 485 emu/cc and a negative magnetostriction constant,\cite{77} whereas Co$_5$Fe$_{50}$ has high saturation magnetization of 1950 emu/cc and a positive magnetostriction constant.\cite{78}

![Figure 4.2.1. Model of the samples used in the experiment.](image)

Annealed Ta foils (99.95% purity) of 25 µm and 125 µm thickness were used as substrates. A Ta buffer layer of 30 nm thickness was deposited on one side of the Ta substrate in order to provide an oxide-free surface for 50 nm thick Ni and 20 nm thick Co$_5$Fe$_{50}$ layers to grow upon.

4.2.1 Structural investigation

XRD was carried out in 0-2θ geometry in order to determine the amount of strain induced in the magnetic layer from a measurement of the corresponding change in lattice constant. The XRD scan (Figure 4.2.2) of the 50 nm thick as-prepared Ni sample shows that it grew with predominantly (111) texture on the Ta substrate. After 30 min of hydrogen loading, the Ta (110) peak shifts to lower 2θ values. This is caused by an isotropic increase in the Ta lattice spacing as hydrogen occupies the Ta interstitial sites [see Figure 4.1.1]. With increasing hydrogen loading time to 1 hr, there is a formation of Ta$_2$H phase and with further increasing the hydrogen loading time to 3hrs, there is a formation of tantalum hydride (TaH$_{0.9}$) with higher atomic concentration of hydrogen. This volumetric expansion of the Ta substrate transfers an in-plane biaxial tensile stress to
the as-deposited magnetic thin-films, which leads to a lattice contraction in the direction normal to the film plane [refer Eq. (3.16)]. This contraction can be observed in the shift of the Ni (111) peaks to higher 2θ values.

![Graph](image)

**Figure 4.2.2.** Wide-angle XRD scans of an as-prepared and the hydrogen loaded Ni films on a 25µm thick Ta substrate. The intensity is plotted on a logarithmic scale and the scans of the hydrogen loaded samples have been shifted for better visibility and comparison of the Ni peak shift.

Figure 4.2.3 shows x-ray scans of 20 nm thick Co$_{50}$Fe$_{50}$ samples before and after hydrogen loading. The as-prepared sample shows that Co$_{50}$Fe$_{50}$ layer grew with predominantly (110) texture on the Ta substrate. The continuous shift of the Ta (110) peak to lower 2θ values with increasing hydrogen loading time shows that the hydrogen concentration in the Ta substrate increases continuously. The increasing volumetric expansion applies an in-plane biaxial stress to the Co$_{50}$Fe$_{50}$ film and the resulting lattice contraction in the direction normal to the sample plane (Poisson’s contraction) leads to a continuous shift of the Co$_{50}$Fe$_{50}$ (110) peak shifts to higher 2θ values [refer Eq. (3.16)].

In the case of Co$_{50}$Fe$_{50}$ films, the Ta$_2$H phase appears only after loading the hydrogen for 5 hrs, whereas in the case of Ni samples we observed the tantalum hydride phase just after loading for 1 hr. The reason for the difference in the hydrogen loading time must be due to the catalytic activity of Ni toward the chemisorption of the hydrogen atoms.$^{[79]}$ Previous studies showed that the kinetics of hydrogen adsorption is enhanced by the Ni layer.$^{[80]}$ This would reduce the time required for the hydrogenation of the Ta substrate coated with Ni since the hydrogen diffuses into the Ta from both the sides (activated by Pd and Ni). But the hydrogen diffuses out of the Ni at room temperature,$^{[81]}$ whereas the hydrogen desorption from Ta occurs only at an elevated temperature of about 500°C.$^{[82]}$
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This is also evident from the observed shift of the Ta (110) peak to lower 2θ values in ex-situ (after exposing the sample to air). XRD scan (Figure 4.2.2) due to the strain induced by the interstitial hydrogen atoms.

![Figure 4.2.3. Wide-angle XRD scans of an as-prepared Co50Fe50 sample and the samples loaded with hydrogen. The intensity is plotted on a logarithmic scale and the scans of the hydrogen loaded samples have been shifted for better visibility and comparison of the Co50Fe50 peak shift.](image)

The strain $\varepsilon_z$ in the Ni and Co50Fe50 due to the lattice contraction in the direction normal to the sample surface has been calculated using following equation.

$$\varepsilon_z = \frac{d_L - d_0}{d_0}$$

where, $d_L$ and $d_0$ are lattice spacings of the magnetic films normal to the sample plane in the hydrogen-loaded and as-prepared states, respectively. By applying Hooke's law to the biaxial stress state, the in-plane biaxial strain $\varepsilon_x$ in the Ni and the Co50Fe50 thin films has been determined from the Eq (3.17) using a Poisson's ratio of 0.31.

The calculated values of strain, $\varepsilon_x$ in the Ni and the Co50Fe50 thin films are plotted in Figure 4.2.4 (a) and (b), respectively against the Ta strain. The plots have been divided into two regions depending upon the observed the tantalum hydride phases in the corresponding samples (refer XRD scans in Figure 4.2.2 and Figure 4.2.3). The strain in the Ta substrate in region with the $\alpha$TaH phase alone is isotropic, whereas the strain in region with coexistence of $\alpha$TaH with TaH$_{0.5}$ or TaH$_{0.9}$ phases is anisotropic as these phases have tetragonal and orthogonal crystal structures, respectively [refer Table 4.1]. The solid line in both the plots has been drawn for 1:1 strain transfer from the Ta.
substrate. The in-plane strain in both Ni and Co\textsubscript{50}Fe\textsubscript{50} increases with an increasing Ta strain. As all the data points lie below the solid line, we can conclude that the strain transfer is not 100%. The maximum strain $\varepsilon_x$ induced in the Ni layer was found to be 0.42%, whereas in the case of Co\textsubscript{50}Fe\textsubscript{50}, a maximum strain $\varepsilon_x$ of 0.6% was induced upon hydrogen loading. The reason for a higher amount of strain in Co\textsubscript{50}Fe\textsubscript{50} than that of Ni could be the solid solution hardening in the CoFe alloy or the lower thickness of the Co\textsubscript{50}Fe\textsubscript{50} film compared to that of the Ni film, which would increase its yield strength.\[83\] This shows that the maximum amount of strain that can be induced is limited by the mechanical properties of the film.

The corresponding in-plane biaxial stress in the Ni and Co\textsubscript{50}Fe\textsubscript{50} layers were estimated using Eq (3.18). In the case of Ni, the maximum biaxial stress was found to be 1.24 GPa,
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and it was calculated using a value of 200 GPa \[^{[84]}\] for the Young’s modulus and a Poisson’s ratio of $\nu=0.31$. In the case of Co$_{50}$Fe$_{50}$, a maximum stress was about 1.79 GPa and it was calculated for the volume weighted average of the Young’s modulus of the bulk Co (206 GPa) and Fe (205 GPa)\[^{[85]}\] and a Poisson’s ratio of $\nu=0.31$.

From the present investigation, it cannot be completely excluded that some hydrogen diffuses into the magnetic layer as well. However, the observed shift of the Ni and Co$_{50}$Fe$_{50}$ peak to higher 2$\theta$ values cannot be attributed to hydrogen dissolution in the magnetic layers but only to the in-plane biaxial stress state. Hence, we assume that there is no significant amount of hydrogen dissolved in the Ni or Co$_{50}$Fe$_{50}$ layer. XRD measurements on the hydrogen-loaded samples exposed to air for 6 months showed no change in the induced strain values. This indicates that no hydrogen desorbs from the Ta substrate at room temperature on this time scale.

### 4.2.2 Magnetic characteristics of Ni

In order to study the influence of biaxial stress on the PMA of the magnetic layer, magnetic measurements were performed. Figure 4.2.5 shows M-H hysteresis loops of the 50 nm thick Ni film for the case of the magnetic field applied perpendicular to the sample plane for an as-prepared sample as well as for samples with different biaxial stress values; in addition, an M-H loop is shown for the magnetic field oriented parallel to the plane of the as-prepared sample.

![Figure 4.2.5. M-H loops of Ni films on a Ta substrate with magnetic field applied perpendicular to the plane of an as-prepared sample (open circles) as well as of samples with biaxial stresses of 0.86 GPa (open triangles) and 1.24 GPa (open squares); a hysteresis loop was also recorded with the magnetic field applied in the plane of the as-prepared sample (solid line).\[^{[86]}\] ](image)

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All the samples exhibit in-plane anisotropy due to dominant shape anisotropy. There was no observable difference in the M-H loops with field applied parallel to the film plane for samples with increasing biaxial stress (not shown in figure). Whereas, in M/H loops with field applied perpendicular to film plane, the saturation field \( H_s \) decreases with increasing biaxial stress.

The area enclosed between the magnetization curves with field parallel and perpendicular to the sample plane is proportional to the effective anisotropy energy \( K_{\text{eff}} \) of the sample [see section 3.2]. The M-H loops with field perpendicular to the sample plane show that there is a decrease in this area with increasing biaxial stress. This observation can be explained by the applied stress inducing an additional anisotropy component in the direction normal to the film plane, thus changing the value of \( K_{\text{eff}} \). The latter is the sum of the magnetocrystalline anisotropy \( K_c \), the shape anisotropy \( K_d \), and the magnetoelastic anisotropy \( K_{\text{me}} \), which in case of PMA can be written as in Eq. (2.16),

\[
K_{\text{eff}} = K_c + K_d + K_{\text{me}} = K_c - \frac{1}{2} \mu_0 N_D M_s^2 - \frac{3}{2} \sigma \lambda
\]  

(4.7)

where \( M_s \) is the saturation magnetization, \( \mu_0 \) is the magnetic permeability, \( N_D \) is the demagnetizing factor, \( \sigma \) is the applied stress and \( \lambda \) is the magnetostriction coefficient. Interfacial and surface anisotropy contribute significantly only for the magnetic layers with thickness of few monolayers. \(^{10, 11}\) As in our study the Ni and the Co\(_{50}\)Fe\(_{50}\) layers have a thickness of 50 nm and 20 nm, respectively, the interfacial and the surface anisotropy are negligible. Here, \( K_{\text{eff}} > 0 \) implies that the sample has a perpendicular easy axis, whereas \( K_{\text{eff}} < 0 \) corresponds to an in-plane easy axis as mentioned earlier in section 3.2. The \( K_{\text{eff}} \) has been determined by both the area method and the saturation field method.

![Figure 4.2.6. Illustration of the method used to determine the saturation field \( H_s \) from the M/H loop.](image)
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In the case of saturation field method, the field corresponding to the intercept of the line drawn at 95% of $M_s$ with the M/H loop has been taken as $H_s$ (see Figure 4.2.6) and the corresponding value of $K_{eff}$ has been calculated using Eq (3.6). The $K_{eff}$ obtained from both the methods have been plotted in Figure 4.2.7 as a function of applied biaxial stress. The $K_{eff}$ increases with increasing biaxial stress and these data were fitted to Eq. (1), which predicts a linear dependence with a slope proportional to the $\lambda$ of Ni. The values calculated for $\lambda$ from the linear fit of the data obtained by the area method and the saturation field method were $(-2.3 \pm 0.2) \times 10^{-5}$ and $(-2.5 \pm 0.3) \times 10^{-5}$, respectively. The magnitude and the sign of the measured values of $\lambda$ are in good agreement with the literature value $^{[77, 78]}$ of $-3.4 \times 10^{-5}$ for the bulk Ni. This agreement shows that the biaxial stress induced anisotropy component is the primary reason for the observed increase in the $K_{eff}$.

![Graph](image)

Figure 4.2.7. The effective perpendicular anisotropy energy $K_{eff}$ as a function of in-plane biaxial tensile stress applied to a Ni thin film calculated by area method and $H_s$ method. The slope of the linear fit of Eq. (1) to the data points is proportional to the magnetostriction coefficient.

The value of $K_{eff}$ (y-intercept) of the as-prepared samples calculated by two different methods differ significantly for each method. In the case of saturation field method, the Eq (3.6) for calculating the $K_{eff}$ is derived from the Stoner Wohlfarth model $^{[36]}$ for a single domain particle. According to this model, the change in magnetization as function of field applied along the hard axis (in our case it is along the direction of the sample normal) must be linear. But it is clear from Figure 4.2.5 that there is a non-linear change in the magnetization with the applied field, which indicates a distribution of the saturation field. The latter has no influence on the value estimated by the saturation field method because
the calculated $K_{eff}$ corresponds to the maximum field required to saturate the magnetization along the hard axis. Whereas, the distribution of $H_s$ influences the $K_{eff}$ values derived using the area method since the area method gives energy, which averages over regions with different $H_s$. Therefore, the $K_{eff}$ obtained from the area method is more reliable than the other.

The data obtained from the area method show that the $K_{eff}$ increases from $-0.98 \times 10^5$ J/m$^3$ in the as-prepared sample to $-0.68 \times 10^5$ J/m$^3$ at an applied stress of about 1.24 GPa. A shape anisotropy energy $K_d$ of $1.48 \times 10^5$ J/m$^3$ was calculated using $M_s=485$ kA/m for bulk Ni$^{[87]}$ and assuming $N_D=1$. The value of $K_c$ calculated from the linear fit was $(50 \pm 6) \times 10^3$ J/m$^3$ and this value is significantly larger than the literature value of $K_c^{\text{bulk}} = 4.5 \times 10^3$ J/m$^3$.\[10] Up to now, we did not consider the anisotropy energy arising from intrinsic stress in the Ni layer. It is well known that DC magnetron-sputtered Ni thin films possess intrinsic tensile stress.\[88] So the intrinsic stress in the sample has been calculated by comparing the Ni (111) peak position ($2\theta=52.20^\circ$) of the as-prepared sample to the reference value of $2\theta=52.17^\circ$. The difference in the two values corresponds to a tensile stress of 96 MPa and a corresponding contribution to $K_{me}$ of $-5 \times 10^3$ J/m$^3$; however, the latter cannot account for the discrepancy between $K_c^{\text{bulk}}$ and the value calculated for $K_c$. It is likely that this deviation originates from our assumption that $N_D=1$. It is known that $N_D$ depends on the surface roughness of the sample. In next section, we will discuss about the influence of the substrate roughness on the magnetic anisotropy of thin films.

![Figure 4.2.8. FRT optical profilometer image of the Ta substrate.](image)

4.2.3 Influence of the roughness of the substrate

Chappert and Bruno$^{[12]}$ have explained that the roughness of the sample gives rise to an additional anisotropy term due to an in-plane demagnetizing field that reduces the
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The actual demagnetizing energy. M. Li \textit{et al}. \cite{89} and Y.-P. Zhao \textit{et al}.\cite{90} showed that the in-plane demagnetizing field of the magnetic films increases with increasing roughness of the substrate due to an increase in the in-plane demagnetizing factors $N_{xx}$ and $N_{yy}$ of the demagnetizing tensor. This leads to a decrease in the demagnetizing factor $N_{zz}$ normal to the film plane according to the sum rule $N_{xx}+N_{yy}+N_{zz}=1$. Henceforth, the shape anisotropy decreases due to a decrease in $N_{zz}$ with increasing roughness, i.e. $N_D<1$. Several studies have reported demagnetizing factors less than unity owing to the roughness of the sample.\cite{10, 11}

The rms surface roughness of the Ta substrate upon which the Ni layer has been deposited is 1.52 $\mu$m, which was measured using an optical profilometer (Figure 4.2.8). The large rms surface roughness of the Ta substrate may therefore be responsible for a decrease in $K_d$. Since $K_c = K_{eff} + K_d$, a reduced $K_d$ would yield a lower calculated value for $K_c$. The large surface roughness of the Ta substrate also influences the M/H loop with field applied parallel to the sample plane (Figure 4.2.5) where a ratio of $M_r/M_s$ less than 1 is observed. This may be interpreted as an effect of out-of-plane anisotropy components reducing the parallel magnetization component in the remanent state.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{magnetization_curve.png}
\caption{Magnetization curves of Ni (50 nm) deposited on Si substrate with field applied parallel and perpendicular to the sample plane. \cite{86}}
\end{figure}

In order to clarify the influence of roughness, a 50 nm-thick Ni layer has been deposited on a polished Si wafer (rms surface roughness < 1 nm) with a Ta buffer layer of 30 nm thickness under the same sputter conditions. X-ray scan showed that the sample exhibits a predominant Ni (111) texture, similar to that of Ni deposited on a Ta substrate. The M-H measurements with magnetic field applied parallel and perpendicular to the sample surface are shown in Figure 4.2.9; the corresponding value for $K_{eff}$ is $(-1.35\pm0.03)\times10^5$ J/m$^3$. The calculated value for $K_c$ is $8\pm3\times10^3$ J/m$^3$ (corrected for the $K_{me}$ of $-5\times10^3$ J/m$^3$ due to intrinsic stress), which is close to the bulk value of Ni.
Therefore, in the case of the Ni film deposited on a Ta substrate, we can conclude that the discrepancy between $K_c$ bulk and the calculated value for $K_c$ is mainly due to the large rms surface roughness of the Ta substrate.

### 4.2.4 Magnetic characteristics of Co$_{50}$Fe$_{50}$

![Figure 4.2.10. M-H loops of Co$_{50}$Fe$_{50}$ films on a Ta substrate with magnetic field applied perpendicular to the plane of an as-prepared sample (open circles) as well as of the sample with biaxial stress of 1.79 GPa (open triangles); a hysteresis loop was also recorded with the magnetic field applied in the plane of the as-prepared sample (solid line).]

Figure 4.2.10 shows M-H hysteresis loops of 20 nm thick Co$_{50}$Fe$_{50}$ film for the case of the magnetic field applied perpendicular to the sample plane for an as-prepared sample as well as for a sample with biaxial stress of 1.79 GPa; in addition, an M-H loop is shown for the magnetic field oriented parallel to the plane of the as-prepared sample. The hysteresis observed in the M/H loops with field applied perpendicular to the sample plane can be attributed to the out-of-plane magnetization component due to the large surface roughness of the Ta substrate as explained earlier. Upon applying biaxial stress there was no observable change in the magnetization curve with field applied parallel to the sample plane (not shown in figure). But there was an observable change in the $K_{eff}$ (area enclosed between the M/H loops with field applied parallel and perpendicular to the sample plane) upon applying a biaxial stress of 1.79 GPa due to the stress induced anisotropy component.

Figure 4.2.11 shows the measured value of $K_{eff}$ as a function of the applied biaxial tensile stress. The $K_{eff}$ of Co$_{50}$Fe$_{50}$ decreases from $-14 \times 10^5$ J/m$^3$ to $-16 \times 10^5$ J/m$^3$ upon applying a maximum biaxial stress of 1.79 GPa. The data were fitted to Eq. (1) and the
calculated value for $\lambda$ is $(8\pm2)\times10^{-5}$. The magnitude and the sign of $\lambda$ are in good agreement with the literature value for Co$_{50}$Fe$_{50}$ alloy of $10\times10^{-5}$.\textsuperscript{[78]}

Figure 4.2.11. The effective perpendicular anisotropy energy $K_{\text{eff}}$ of Co$_{50}$Fe$_{50}$ as a function of the applied in-plane biaxial tensile stress.\textsuperscript{[86]}

The relative change of the $K_{\text{eff}}$ of Ni is about 40% upon applying a biaxial stress of 1.2 GPa, whereas in the case of Co$_{50}$Fe$_{50}$ it is only about 15% even at the higher biaxial stress of 1.79 GPa and the larger value of $\lambda$. According to the Eq (4.7), the relative change in the $K_{\text{eff}}$ can be expressed as follows;

$$\frac{\Delta K_{\text{eff}}}{K_{\text{eff}}^0} = \frac{-3}{2} \frac{\sigma \lambda}{K_c - \frac{1}{2} \mu_0 N_D M_s^2}$$

where, $K_{\text{eff}}^0$ is the effective PMA at zero stress state and $\Delta K_{\text{eff}}$ is the change in the $K_{\text{eff}}$ upon applying a biaxial stress. Since $K_{\text{eff}}^0$ of the Co$_{50}$Fe$_{50}$ is $-14\times10^5$ J/m$^3$ in comparison with the value of only about $-1\times10^5$ J/m$^3$ for Ni, it is clear that the main reason for the lower relative change of $K_{\text{eff}}$ in the case of the Co$_{50}$Fe$_{50}$ is the large $K_{\text{eff}}^0$. The latter is a result of the high $M_s$ value of Co$_{50}$Fe$_{50}$ of $1.9\times10^6$ A/m,\textsuperscript{[35]} which leads to a large shape anisotropy contribution. Therefore, Eq. (2) predicts that the $K_{\text{eff}}$ of a thin film can be influenced most significantly by the magnetoelastic anisotropy if it possesses both a high $\lambda$ and a low $M_s$.

In conclusion, a persistent in-plane biaxial stress has been applied to the Ni and the Co$_{50}$Fe$_{50}$ layers by loading the corresponding Ta substrate with hydrogen. A maximum biaxial tensile stress of 1.24 GPa and 1.79 GPa was applied to Ni and Co$_{50}$Fe$_{50}$ thin films,
respectively. The applied biaxial stress induces an additional anisotropy component perpendicular to the sample surface, which influences the $K_{eff}$ of the sample. In case of Ni, the $K_{eff}$ increases from $-0.98 \times 10^5$ J/m$^3$ to a maximum value of $-0.68 \times 10^5$ J/m$^3$, whereas for Co$_{50}$Fe$_{50}$ it decreases from $-14 \times 10^5$ J/m$^3$ to $-16 \times 10^5$ J/m$^3$ with the applied biaxial stress.

In these systems, the maximum amount of in-plane strain in the Ni and Co$_{50}$Fe$_{50}$ films is significantly smaller than the maximum strain in the Ta substrate. This limits the maximum relative change of $K_{eff}$ that can be achieved by the stress applied to the film, which itself is a result of the strain transferred from the Ta substrate. Since the yield strength of thin films increases with decreasing films thickness or grain size, larger magnetoelastic anisotropy contributions may be achieved in the nanostructured materials with grain sizes in the range of a few nanometers. Also, the multilayer systems with high yield strength and a high $\lambda$ are promising candidates for optimizing PMA by an applied biaxial stress. Therefore, in next section the influence of biaxial stress on the Co/Pd multilayers is investigated.
4.3 Influencing magnetic anisotropy of Co/Pd multilayers

Co/Pd multilayers (ML) exhibiting perpendicular magnetic anisotropy (PMA) are promising candidates for continuous and patterned perpendicular magnetic recording media. Enhancement of PMA is essential to further increase of the storage density of such media. Many studies have been carried out to optimize the magnetic properties of Co/Pd ML by introducing an appropriate underlayer, or by varying the sputter conditions of the Pd underlayer. S. Okamoto et al. showed that PMA of Pd/Co/Pd trilayers increases by hydrogenation of the Pd layer or by addition of Sm to the Co layer. P. Poulopoulos et al. demonstrated an enhancement of PMA in Pd/Co ML with intentionally alloyed layers.

The PMA observed in Co/Pd ML has been attributed to Néel surface magnetic anisotropy in terms of reduced symmetry of Co atoms at Pd/Co interface. In the Co/Pd ML PMA increases with decreasing thickness of the Co layer due to increasing interfacial to volume anisotropic contribution. Several reports claim that the stress induced anisotropy also plays a major role in PMA. Using electronic structure calculations in combination with a simple linear theory Victoria et al. showed that the epitaxial strain in the Co/Pd superlattices significantly influences the interfacial anisotropy. Kim et al. showed that an alloy like Co environment at the Co/Pd interface yields PMA through the stress induced anisotropy. Since Co/Pd MLs exhibit large negative magnetostriction of the order of $10^{-4}$, an in-plane isotropic tensile stress in the ML leads to a positive contribution to the PMA. This would provide an additional degree of freedom to optimize the PMA of the Co/Pd MLs.

In this chapter, our first attempt to enhance the PMA of Co/Pd MLs by applying an external in-plane biaxial tensile stress is reported. The biaxial stress is applied to the Co/Pd ML by loading the Ta substrate with hydrogen. This approach differs from the earlier work of hydrogenation of the functional layers since it leads to a different state of deformation of the films. In the case of hydrogenation of the functional layers, the volume expansion of the layers is constrained by the substrate leading to an expansion in the direction perpendicular to the film plane. In the case of the hydrogenation of the Ta substrate, the volume expansion of the substrate leads to an expansion of functional layer in the plane of the film associated with a Poisson’s contraction in the direction perpendicular to the film plane. The different deformation states may lead to a different effect on the PMA of the MLs.

The Co/Pd MLs were prepared on the 125µm thick Ta substrate. All the Co/Pd MLs were grown on 9nm thick Ta buffer layer and were protected by a 3 nm thick Ta cap layer. The ML films consisting of 30 bilayers of Pd(0.96 nm)/Co(t nm) were prepared with two different Co sub-layer thicknesses ($t_{Co}=0.26$ and 0.53 nm), resulting in different values of
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the magnetostriction constant. The reason for the latter is that at larger thickness of the Co layer, the magnetostriction constant is mainly determined by the pure Co atoms positioned away from the interface. Whereas at smaller Co layer thickness, the contribution from the interfacial Co atoms having a similar environment as that of the CoPd alloy with a very large negative magnetostriction dominates.

4.3.1 Structural characteristics

XRD scans of [Pd(0.98 nm)/Co(0.53 nm)]₃₀ MLs before and after hydrogen loading are shown in Figure 4.3.2. It is observed that the Co/Pd ML has predominant (111) texture due to the absence of (200) peak (not shown in figure).
The (111) peak position of the ML is related to the average lattice spacing of the Co and Pd layers. The measured value of the average lattice spacing from the XRD scans was 0.2183 nm, which is in good agreement with the calculated value of 0.2176 nm obtained using the step model.\textsuperscript{[106]} The shift of the Ta (110) peak to lower 2θ values upon hydrogen loading is caused by an isotropic expansion of the Ta lattice spacing, as the hydrogen atoms occupy the interstitial sites in the Ta lattice. The continuous shift of the Ta (110) peak with increasing loading time shows that the hydrogen concentration in the Ta substrate increases continuously. This volumetric expansion transfers in-plane biaxial tensile stress to the as-deposited Co/Pd ML, which leads to a lattice contraction in the direction normal to the film plane. This contraction can be observed from the shift of the Co/Pd (111) peak to higher 2θ values.

The corresponding in-plane biaxial strain $\varepsilon_x$ was calculated from the strain $\varepsilon_z$ in the direction normal to the sample surface using Eq (3.15) and (3.16), respectively. The maximum in-plane strain $\varepsilon_x$ induced in the Co/Pd ML was found to be 1.22%. The corresponding biaxial stress of 2.8 GPa was calculated using a volume weighted average of Young’s modulus of bulk Co (210 GPa) and bulk Pd (121 GPa) and a Poisson’s ratio of $\nu=0.31$.\textsuperscript{[107]} The $\text{[Pd(0.98 nm)/Co(0.26 nm)]_{30}}$ MLs also exhibit prominent (111) peak that shifts to higher 2θ values with increasing hydrogen loading time (Figure 4.3.3).

![Figure 4.3.3](Image)

*Figure 4.3.3. Wide-angle XRD scans of $\text{[Pd(0.98 nm)/Co(0.26 nm)]_{30}}$ MLs in the as-prepared state and after hydrogen loading for the times indicated.*

The maximum strain $\varepsilon_x$ calculated from the peak shift was 1.05% and the corresponding biaxial stress was 2.1 GPa. The maximum amount of strain induced in the
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Co/Pd ML was found to be 3 times higher than the value observed for a 50 nm thick Ni layer [see section 4.2.1], which may be attributed to the higher yield strength of the ML system. There was a significant increase in the full width at half maximum (FWHM) of the Co/Pd (111) peak from 0.609° (as-prepared) to 0.84° after 7 hours of hydrogen loading for the sample with $t_{Co}=0.53$ nm. For the sample with $t_{Co}=0.26$ nm FWHM of Co/Pd (111) peak increases from 0.53° to maximum of about 0.86°.

Figure 4.3.4. Rocking curves of [Pd(0.98 nm)/Co(0.52 nm)]$_{30}$ MLs in the as-prepared state and after hydrogen loading.

This increase in the FWHM of the Co/Pd (111) peak could be due to change in the crystallite size or due to the inhomogeneous strain distribution. A possible reason for the change in the crystallite size of the Co/Pd ML could be due the breakdown of its coherent structure due to hydrogen absorption.\cite{108} The break up of Co/Pd ML into small crystallites would change the mosaicity of the sample. In order to study that rocking curve measurement has been performed for the Co/Pd ML before and after hydrogen loading and the corresponding scans are shown in Figure 4.3.4. There was no observable change in the FWHM of the rocking curves. Therefore, the broadening of Co/Pd (111) peak can only be attributed to the inhomogeneous strain (microstrain) distribution in the Co/Pd ML due to the coexistence of several tantalum hydride phases with different crystal structures (Table 4.1) would lead to a distribution of strain. This is evident from the significant increase in the FWHM upon the formation of TaH$_{0.5}$ and TaH$_{0.9}$ phases.

Figure 4.3.5 shows the amount of strain transferred from the Ta substrate to the [Pd(0.98 nm)/Co(t nm)]$_{30}$ ML. With increasing hydrogen loading time there was a formation of Ta$_{2}$H phase (Figure 4.3.2 and Figure 4.3.3), which has a tetragonal crystal structure differing from the cubic structure of the $\alpha$Ta phase. Therefore, the formation of
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Ta$_2$H phase may lead to an anisotropic Ta lattice expansion compared to an isotropic expansion of the $\alpha$Ta phase. This leads to an uncertainty of the estimation of strain in the Ta substrate in the two phase region. Therefore, the strain transfer from the Ta substrate to the Co/Pd ML has been plotted only in the region of the $\alpha$-TaH phase. The dotted line corresponds to a linear fit with a slope of 0.98, which indicates complete strain transfer from the Ta substrate to the Co/Pd ML.

![Graph showing strain in Co/Pd (%)](image)

Figure 4.3.5. In-plane biaxial tensile strain in the [Co(t nm)/Pd(0.96 nm)]$_{30}$ MLs vs strain in the Ta substrate.

In the case samples with an inert substrate (no absorption of hydrogen), hydrogenation of a Co/Pd ML would cause an expansion of its lattice spacing in the direction normal to the film plane, and the corresponding strain can be written as,

\[ \varepsilon_{z,\text{hyd}} = \varepsilon_0 + \frac{2\nu}{1-\nu} \varepsilon_0 \]

where, $\varepsilon_0$ corresponds to an isotropic lattice expansion in the Co/Pd ML upon hydrogenation. The second term corresponds to an additional lattice expansion in the direction normal to the film plane due to the suppression of the lateral expansion in $x$ and $y$ direction. Eq. (4.9) shows that the dissolution of hydrogen in the Co/Pd ML would shift the Co/Pd (111) peak to a lower value of 2$\theta$ due to the lattice expansion in the direction normal to the film plane. S. Okamoto et al. have observed a similar behavior upon hydrogenation of the Co/Pd ML deposited on a Si substrate. In our case, we observe a shift of the Co/Pd (111) peak to higher 2$\theta$ values that can be attributed only to the in-plane biaxial tensile stress state. Moreover, the complete strain transfer from the Ta substrate to the Co/Pd MLs shows that there is no significant amount of hydrogen in the Co/Pd ML,
which otherwise would decrease the slope of the strain transfer curve (shown in fig. 2). However, it is well known that Pd can be easily loaded with hydrogen.\textsuperscript{[110]} Therefore, the presence of hydrogen in the Co/Pd ML has been investigated by studying the corresponding structural changes by in situ XRD during hydrogen loading and unloading sequence.

### 4.3.2 In situ XRD investigation during hydrogen absorption and desorption

An environmental chamber for hydrogen loading and temperature control was mounted in a Philips X’pert 0-2θ x-ray diffractometer using Mo radiation and a solid state detector. Before supplying hydrogen the chamber was flushed with pure Ar and the temperature was raised to 70°C. Then, the hydrogen loading was carried out in a continuous flow of hydrogen at atmospheric pressure.

![In-situ XRD scans of the sample](image)

*Figure 4.3.6. In-situ XRD scans of the sample (a) in Ar atmosphere at 70°C, (b) 30 min after introducing hydrogen into the loading chamber, (c) after 5 hrs of hydrogen loading, (d) after cooling down to room temperature in Ar atmosphere.*

Figure 4.3.6 shows the in-situ XRD curves of the $t_{Co}=0.26$ nm sample under various environmental conditions. When comparing the XRD scan of the sample measured in air at room temperature (a) and in Ar atmosphere at 70°C (b) there is no observable Co/Pd
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(111) peak shift. Upon introducing hydrogen at 70°C (c) the Co/Pd (111) peak shifts to lower 2θ angles (after 30 min). This testifies to a noticeable expansion of Co/Pd average lattice spacing and, hence, to hydrogenation. There was no observable change in the Ta peak position at this time, which indicates that hydrogen diffuses into the Co/Pd ML faster than into the substrate. After exposure to hydrogen for 5 hrs (d) an observable shift of the Ta (110) peak to lower 2θ. This indicates lattice expansion of the Ta substrate due to the diffusion of hydrogen. After flushing out the hydrogen with Ar and cooling down to room temperature, there was a large shift of the Co/Pd (111) peak to higher 2θ values indicating a lattice contraction of the Co/Pd ML (e).

![Graph](image)

**Figure 4.3.7.** Lattice spacing of the Ta substrate and the Co/Pd ML calculated from in-situ XRD scans measured during hydrogen loading.

Figure 4.3.7 summarizes the change in out-of-plane interplanar spacing of the substrate as well as ML, as computed from the Bragg reflection positions. The plot can be divided into the following three regions;

1. Hydrogen is introduced into the chamber which is maintained at 70°C. No significant change in the lattice spacing of the Ta substrate is observed but an increase in the out-of-plane lattice spacing of Co/Pd due to the uptake of hydrogen in the ML is found. Although a volumetric expansion of the Co/Pd takes place, the Co/Pd ML can only expand in the direction perpendicular to the film plane since the lateral expansion is constrained by the substrate. (i.e. $\varepsilon_x^{\text{film}} = \varepsilon_x^{\text{substrate}}$, $\varepsilon_y^{\text{film}} = \varepsilon_y^{\text{substrate}}$)

2. Linear isotropic expansion of the lattice spacing of the Ta substrate due to the hydrogen loading. At the same time, a decrease in the out-of-plane lattice spacing of the Co/Pd ML is found. This is readily understood as follows: The isotropic lattice expansion of Ta substrate leads to an in-plane biaxial tensile stress in the Co/Pd ML. This causes the
observed shift of the Co/Pd (111) peak to higher 20 values, due to the Poisson’s contraction perpendicular to the film plane and the accompanying reduction of the lattice spacing. The linear change in the lattice spacing of the Co/Pd ML with the Ta lattice spacing shows that the deformation is still elastic. The decrease in the out-of-plane lattice spacing also shows that any possible volume expansion of the Co/Pd ML induced by further hydrogen incorporation is over-compensated by the lattice contraction due to the biaxial strain induced by the Ta substrate.

3. The loading chamber was flushed with Ar and the sample is cooled down to room temperature. No significant change in the lattice spacing of the Ta substrate is observed. This indicates that hydrogen does not desorb from the substrate under the conditions applied here. This observation is consistent with earlier reports that the hydrogen desorbs from the Ta only at an elevated temperature of about 500°C. On the other hand, there is a significant reduction in the Co/Pd lattice spacing indicating that hydrogen desorbs from the Co/Pd ML. As the corresponding volume reduction of the Co/Pd ML is again hindered by the substrate, the lattice parameter can only contract in the direction perpendicular to the film plane. The decrease in the lattice spacing of the Co/Pd ML during unloading of hydrogen (region 3) was found to be much larger than the previous increase during loading (region 1). A similar behavior has been observed for the sample with larger thickness (t_Co=0.53 nm) of the Co layer. This indicates that some additional amount of hydrogen is dissolved in region 2, which is released again in region 3.

In order to estimate the change in the concentration of hydrogen in the Co/Pd ML, the strain due to volumetric expansion of the Co/Pd ML during loading and unloading of hydrogen has to be derived. Since the Co/Pd ML deforms elastically during the hydrogen loading and unloading process, the volumetric expansion can be derived from a linear elastic model\cite{112,113} The total out-of-plane strain in the Co/Pd ML in region 1 (ε_z,1) of Figure 4.3.7 is the sum of the original strain due to volumetric expansion during hydrogen loading ε_{Pd,i,1} and the additional expansion Δε_{z,1} due to lateral confinement, which can be derived from the appropriate version of Hooke’s law:\cite{see section 3.3.1.1}

\[
ε_{z,1} = ε_{Pd,i,1} + Δε_{z,1} = ε_{Pd,i,1} + \frac{2ν}{1-ν} ε_{Pd,i,1} = \frac{1+ν}{1-ν} ε_{Pd,i,1} \tag{4.10}
\]

\[
ε_{Pd,i,1} = \frac{1-ν}{1+ν} ε_{z,1} \tag{4.11}
\]

The total out-of-plane strain in the Co/Pd ML in region 2 (ε_z,2) of Figure 4.3.7 is the sum of isotropic strain due to volumetric expansion during hydrogen loading ε_{Pd,i,2} and the additional Poisson’s contraction Δε_{z,2} due to the in-plane biaxial stress induced by the expansion of the Ta substrate due to hydrogen loading. Here, we assume that the in-plane
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strain in the Co/Pd ML is equal to the volumetric strain in the Ta during hydrogen loading ($\varepsilon_{x,\text{Pd}}=\varepsilon_{y,\text{Pd}}=\varepsilon_{x,\text{Ta}}=\varepsilon_{y,\text{Ta}}=\varepsilon_{z,\text{Ta}}$):

$$\varepsilon_{z,2} = \varepsilon_{z,1} + \Delta \varepsilon_{z,2} - \frac{2\nu}{1-\nu} \varepsilon_{Ta,L}$$

(4.12)

$$\varepsilon_{Pd,L,2} = \varepsilon_{z,2} + \frac{2\nu}{1-\nu} \varepsilon_{Ta,L}$$

(4.13)

Figure 4.3.8. (a) Stress free Co/Pd ML deposited on the Ta substrate. (b) Strain ($\varepsilon_{\text{Pd,L1}}$) due to lattice expansion upon diffusion of hydrogen into the Co/Pd ML and the biaxial compressive stress ($-\varepsilon_{\text{Pd,L2}}$) in x-y plane due to lateral constraint leads to an additional strain ($\Delta \varepsilon_{z,1}$) in z-direction (Corresponds to region (1) in figure 2). (c) Isotropic lattice strain ($\varepsilon_{\text{Ta,L}}$) in the Ta substrate due to hydrogen loading, strain ($\varepsilon_{\text{Pd,L2}}$) due to lattice expansion upon diffusion of hydrogen into the Co/Pd ML, which is superimposed by the strain ($\Delta \varepsilon_{z,2}$) due to an in-plane biaxial tensile stress ($\varepsilon_{\text{Ta,L}}$) imposed by the Ta lattice expansion (Corresponds to region (2) in figure 2). (d) Strain ($\varepsilon_{\text{Pd,UL}}$) due to lattice contraction as the hydrogen diffuses out of the Co/Pd ML and the biaxial tensile stress ($\varepsilon_{\text{Pd,UL}}$) in x-y plane due to lateral constraint leads to an additional strain ($\Delta \varepsilon_{z,3}$) in z-direction (Corresponds to region (3) in figure 2).

The total out-of-plane strain in Co/Pd ML in region 3 ($\varepsilon_{z,3}$) of Figure 4.3.7 is the sum of isotropic strain due to hydrogen unloading $\varepsilon_{\text{Pd,UL}}$ and the additional Poisson’s contraction $\Delta \varepsilon_{z,3}$ due to the lateral tensile stress:

$$\varepsilon_{z,3} = \varepsilon_{\text{Pd,UL}} + \Delta \varepsilon_{z,3} = \varepsilon_{\text{Pd,UL}} + \frac{2\nu}{1-\nu} \varepsilon_{\text{Pd,UL}} = \frac{1+\nu}{1-\nu} \varepsilon_{\text{Pd,UL}}$$

(4.14)
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\[ \varepsilon_{Pd,UL} = \frac{1 - \nu}{1 + \nu} \varepsilon_{z,3} \]  \hspace{1cm} (4.15)

Table 4.2 shows the calculated values of strain due to isotropic volumetric distortion when the hydrogen diffuses in \( (\varepsilon_{Pd,L1} \text{ and } \varepsilon_{Pd,L2}) \) or out \( (\varepsilon_{Pd,UL}) \) of the Co/Pd ML using equations (2), (4), and (6), respectively.

Table 4.2. Strain due to volumetric expansion of Co/Pd MLs with different thickness of the Co layer during loading and unloading of hydrogen.

<table>
<thead>
<tr>
<th>( t_{Co} )</th>
<th>Hydrogen loading</th>
<th>Hydrogen unloading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \varepsilon_{Pd,L1} )</td>
<td>( \varepsilon_{Pd,L2} )</td>
</tr>
<tr>
<td>0.26 nm</td>
<td>0.07%</td>
<td>0.16%</td>
</tr>
<tr>
<td>0.53 nm</td>
<td>0.03%</td>
<td>0.11%</td>
</tr>
</tbody>
</table>

The hydrogen fraction, \( c \), in Pd (number of H atoms per Pd atoms) can be estimated using the following formula, [see section 4.1.1] which relates \( c \) to the corresponding lattice strain \( \varepsilon_{Pd} \):\[ \hspace{1cm} (4.16) \]

Although this equation is strictly valid only for pure Pd, it will be used here as an approximation to estimate the amount of hydrogen in the Co/Pd ML from the calculated values of the isotropic strain (Table 1) upon loading and unloading of hydrogen. It must be kept in mind that the constant of proportionality between \( c \) and \( \varepsilon \) might differ slightly for the Co/Pd ML due to the different chemical composition. However, Eq. (4.16) will allow us to do a qualitative discussion of the hydrogen concentration in the Co/Pd ML samples.

The estimated values of \( c \) (using Eq. 7) in the Co/Pd ML with different Co layer thickness as a function of loading time are shown in Figure 4.3.9. It shows that in region (1) after 30 min \( c \) in the Co/Pd ML reaches a value of about 0.012. We have observed at the beginning of the loading sequence that the diffusion of hydrogen into the Ta substrate occurs on a time scale of hours, whereas the hydrogen diffuses into the Co/Pd ML on a time scale of minutes (see Figure 4.3.7 for \( t=30 \) min). Therefore, we can assume that the hydrogen concentration in the Co/Pd ML represents the equilibrium concentration of hydrogen under the condition used here. In region (2), the equilibrium \( c \) in the Co/Pd ML increases with increasing in-plane biaxial stress applied by the isotropic lattice expansion of the Ta substrate. This can be understood based on the influence of stress on the chemical potential of the system. Any change in the applied in-plane biaxial stress (by the
volumetric expansion of Ta substrate) would lead to a change in the chemical potential, $\mu$ of the hydrogen in the system by the additional work done, which is given by

$$\Delta \mu = \Delta P \Omega$$  \hspace{1cm} (4.17)

where, $\Delta P$ is the pressure change (hydrostatic part of the tensor) and $\Omega$ is the partial molar volume of hydrogen.\cite{113,114} This change in the chemical potential modifies the driving force for the diffusion of hydrogen into the Co/Pd ML and the solubility of the hydrogen at a given external hydrogen pressure. In region (3), the hydrogen completely diffuses out of the Co/Pd ML after exposing it to Ar atmosphere as can be seen from the decrease of $c$ to zero within the error limits. We point out here that this result does not depend on the particular value of the proportionality constant in Eq. (7).

The maximum value of $c$ in our system is $\approx 0.04$, which is small when compared to the bulk Pd where the equilibrium $c$ is $\approx 0.6$ at 1atm. In an earlier study, Okamoto \textit{et al.} reported that the maximum concentration of hydrogen in a Pd/Co/Pd trilayer system was very similar to that of bulk Pd under similar loading condition.\cite{61} However, in the present work the thickness of the Pd layer is only about 1nm compared to 20 nm in Okamoto \textit{et al.}'s work. Therefore, the reduced $c$ can be attributed to the alloying effect of Co at the interfaces of the Co/Pd ML.\cite{115,116} The latter would reduce the vacancies in the Pd 4d band due the transfer of valence electrons from the Co atoms,\cite{117} which leads to the reduction of the solubility of hydrogen.
4.3.3 Magnetic characteristics

The magnetic reversal in the Co/Pd ML proceeds via the nucleation of the reversal domains and the domain wall motion. Nucleating field, $H_n$ is the critical reverse field at which reversal domains nucleate and $H_w$ is the field required to unpin the domain walls.\cite{118}

![Figure 4.3.10. Schematic diagram of magnetization reversal in Co/Pd MLs.](image)

When $H_n > H_w$, the sample would exhibit square hysteresis loop because once the domain nucleation occurs, the reversed domains grow immediately as they already overcome the domain wall critical field. It is also referred as nucleation dominated magnetization reversal. If $H_n < H_w$, the sample would exhibit sheared hysteresis loop showing characteristic nucleating field for the reversed domains and the motion of which is restricted due to the domain wall pinning that causes the sheared part of the M/H loop as shown in Figure 4.3.10.

![Figure 4.3.11. Magnetization curves of the as-prepared sample of the form [Co(0.26 nm)/Pd(0.98 nm)]$_{30}$ as well as the samples with varying biaxial stress with the field applied perpendicular to the sample plane.](image)

The magnetization curves of the as-prepared sample of the form [Co(0.26 nm)/Pd(0.98 nm)]$_{30}$ as well as the samples with varying biaxial stress with the field applied perpendicular to the sample plane.\cite{105}
In order to study the influence of biaxial stress on the magnetic anisotropy of the Co/Pd ML, magnetic measurements were performed. Figure 4.3.11 shows that the magnetization reversal in $[\text{Pd}(0.98 \text{ nm})/\text{Co}(0.26 \text{ nm})]_{30}$ MLs occurs via domain nucleation at a distinct nucleation field followed by domain wall motion and rotation processes.

Figure 4.3.12. (a) Graphical procedure for the determination of the squareness factor $S^*$ from the hysteresis. (b) and (c) corresponds to the hysteresis loops with $S^*$ of 1 and 0, respectively.

The M-H loops show that the stress induced anisotropy influences the nucleation field but does not significantly affect the domain wall motion and rotation processes during the magnetization reversal. For both the as-prepared as well as for the samples with varying biaxial stress, the $M_r/M_s$ ratio is equal to 1 within the experimental errors. But, there is a significant change in the squareness of the hysteresis loop that corresponds to the transition width for switching the magnetization direction near the coercive field.

Figure 4.3.13. The change of $H_c$ and $S^*$ as a function of applied values of biaxial stress for the sample $[\text{Co}(0.26 \text{ nm})/\text{Pd}(0.98 \text{ nm})]_{30}$. 58
The squareness of the hysteresis loop can be expressed with the parameter, \( S^* \) as follows,\[^{119}\]

\[
S^* = 1 - \left( \frac{M_r}{H_c} \left( \frac{dM}{dH} \right)_{H=H_c} \right)
\]

(4.18)

Figure 4.3.12 (a) shows the graphical procedure for the determination of \( S^* \) from the hysteresis loops. It is a dimensionless quantity that varies between 0 and 1, with 1 corresponding the sharpest transition of the magnetization direction as shown in Figure 4.3.12 (b). Figure 4.3.13 shows the change of \( H_c \) and \( S^* \) as a function of the applied biaxial stress. Upon applying a biaxial stress of 2.1 GPa, \( H_c \) increases from 1.36 kOe to 2.14 kOe and \( S^* \) increases from 0.70 to 0.87.

![Figure 4.3.12](image)

**Figure 4.3.12.** Magnetization curves of the as-prepared sample of the form [Co(0.53 nm)/Pd(0.98 nm)]\(_{30}\) as well as the samples with varying biaxial stress with the field applied perpendicular to the sample plane.\[^{105}\]

Figure 4.3.14 shows M-H loops for the case of the magnetic field applied perpendicular to the sample plane for [Pd(0.98 nm)/Co(0.53 nm)]\(_{30}\) MLs with different values of in-plane biaxial stress. The magnetization curve shows a positive nucleation field (indicated by the solid arrows) as the applied field is reduced from the saturation field and at zero field, the as-prepared sample is nearly in the demagnetized state with relatively small remanence compared with the samples subjected to the in-plane biaxial stress.

The corresponding coercive field and the remanent magnetization normalized to the saturation magnetization (\( M_r/M_s \)) were estimated and are shown in Figure 4.3.15 as a function of applied biaxial stress. \( H_c \) increased from 220 Oe to 444 Oe and \( M_r/M_s \) increased from 0.17 to 0.76 with an applied biaxial stress of 2.8 GPa.
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Figure 4.3.15. The change of $H_c$ and $M_r/M_s$ as a function of applied values of biaxial stress for the sample $[\text{Co}(0.53 \text{ nm})/\text{Pd}(0.98 \text{ nm})]_{30}$.

Figure 4.3.14 shows that the biaxial stress induced anisotropy significantly influences the nucleation field but does not affect the domain wall motion process. Therefore, a small increase of the applied stress (region 1 in Figure 4.3.15) hardly influences both the coercivity and the normalized remanent magnetization, as they are mainly determined by the unaltered domain wall motion process in this region. But for a larger increase of the applied stress (region 2 in Figure 4.3.15), the coercivity as well as the $M_r/M_s$ ratio are mainly determined by the decreasing nucleation field. This leads to the non linear increase of $H_c$ with increasing stress as compared to an almost linear increase of the $H_c$ in the case of the $[\text{Pd}(0.98 \text{ nm})/\text{Co}(0.26 \text{ nm})]_{30}$ MLs (see Figure 4.3.13).

Figure 4.3.16. The magnetization curves with field applied perpendicular ($\perp$) and parallel ($/\!/\!$) to the sample plane of the as-prepared $[\text{Co}(t \text{ nm})/\text{Pd}(0.98 \text{ nm})]_{30}$ MLs.$^{[105]}$

These results show that it is possible to optimize $H_c$ and $S^*$ of Co/Pd ML by applying a persistent in-plane biaxial tensile stress. The increase of $H_c$ can be attributed to an
increase of $K_{\text{eff}}$ due to an additional uniaxial anisotropy component induced by the applied biaxial stress. The $K_{\text{eff}}$ was derived from the area enclosed by the magnetization curves with field applied perpendicular and parallel to the sample plane. Figure 4.3.16 show the magnetization curves of [Pd(0.98 nm)/Co(t nm)]$_{30}$ MLs with field applied perpendicular and parallel to the sample plane.

In the case of the samples showing hysteresis, the latter has been removed by averaging the two halves of the hysteresis loop as suggested by de Jonge et al.\cite{120} For some samples, the applied field was not sufficient to saturate the sample in the hard axis direction. In these cases, the magnetization curve was extrapolated linearly to the saturation magnetization. It is well known that there are some uncertainties in the evaluation of anisotropies by the area method in case of sheared hysteresis curves.\cite{15} However, the values of $K_{\text{eff}}$ at zero stress state calculated in this way were of the same order of magnitude as the values reported in the earlier work on similar Co/Pd ML structures measured using torque magnetometer.\cite{9, 121, 122}

![Graph showing the effective anisotropy energy $K_{\text{eff}}$ plotted as a function of in-plane biaxial tensile stress applied to [Co(t nm)/Pd(0.98 nm)]$_{30}$ MLs. The slope of the linear fits to the data points is proportional to the corresponding magnetostriction coefficients.\cite{105}](image)

The values of $K_{\text{eff}}$ of [Pd(0.98 nm)/Co(t nm)]$_{30}$ MLs derived from their corresponding magnetization curves are shown in Figure 4.3.17 as a function of applied biaxial stress. There exists a linear increase in $K_{\text{eff}}$ with increasing biaxial stress. In the case of [Pd(0.98 nm)/Co(0.53 nm)]$_{30}$ MLs, $K_{\text{eff}}$ increases from $3.5 \times 10^5$ J/m$^3$ to a maximum value of $7.0 \times 10^5$ J/m$^3$, and in the case of [Pd(0.98 nm)/Co(0.26 nm)]$_{30}$ ML it increases from...
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$4.7 \times 10^5 \text{ J/m}^3$ to a maximum value of $10.3 \times 10^5 \text{ J/m}^3$. The data are fitted to the following relation,

$$K_{\text{eff}} = K_{\text{eff}}^0 - \frac{3}{2} \sigma \lambda$$ (4.19)

where, $\sigma$ is the value of applied biaxial stress, $\lambda$ is the magnetostriction coefficient and $K_{\text{eff}}^0$ is the effective magnetic anisotropy at zero stress state. The slope of the linear fit is proportional to $\lambda$ and the y-axis intercept corresponds to the $K_{\text{eff}}$ at zero stress state. The latter increases with decreasing thickness of the Co layer $t_{\text{Co}}$ due to the interfacial anisotropy $K_s$ according to the equation

$$K_{\text{eff}}^0 = K_s + 2K_s/ t_{\text{Co}}$$ (4.20)

where, $K_s$ is the volume contribution to the effective PMA. The calculated values of $\lambda$ for the Co/Pd MLs with Co thicknesses of 0.26 nm and 0.53 nm derived from the slope of the linear fit are $-1.7 \times 10^{-4}$ and $-0.8 \times 10^{-4}$, respectively. These values are in good agreement with the values in the literature.[9] This agreement confirms that the applied in-plane biaxial tensile stress is the primary reason for the observed increase in the $K_{\text{eff}}$, which in turn enhances the magnetic properties of the Co/Pd MLs.

### 4.3.4 MFM characterization

To study the influence of the applied stress on the magnetic domains, MFM characterization was performed in Co/Pd MLs ($t_{\text{Co}}$=0.53 nm) in demagnetized state. and the latter was carried out by the process called DC cyclic erasure. This process involves subjecting the samples to a series of minor loops (magnetization cycle) with a small stepwise reduction in the applied field, $\Delta H$.

![MFM images](image)

*Figure 4.3.18. MFM images of the Co/Pd ML ($t_{\text{Co}}$=0.53 nm) sample subjected to different in-plane biaxial stresses in demagnetized state. (a) zero stress, (b) 1.2 GPa and (c) 2.8 GPa.*
The obtained MFM domain images of the Co/Pd MLs (Figure 4.3.18) show a distinctive stripe domain pattern, which arises in order to reduce the demagnetizing field.\[^{124}\] We can observe that the domain width increases with increasing biaxial stress. The change in the domain width is driven by the minimization process of the two competing energies (1) the domain wall energy, and (2) magnetostatic energy. The wall energy $E_w$ is reduced when the domains are larger due to the reducing domain wall area. Similarly the demagnetizing energy or the magnetostatic energy $E_{mag}$ is reduced when the domains are smaller, which would allow the stray field to be closer to the sample.

Domain wall energy, $E_w$ per unit area is given by,\[^{87}\]

$$E_w = f_w \frac{t}{d} \quad (4.21)$$

where, $t$ is the thickness of the film, $d$ is the width of the domain, and $f_w$ is the domain wall energy density, which is related to the exchange stiffness constant $A$ and the effective uniaxial anisotropy $K_{eff}$ according to the following equation.\[^{124}\]

$$f_w = \sqrt{AK_{eff}} \quad (4.22)$$

Demagnetizing energy, $E_{mag}$ associated with an alternating parallel strips normal to the film plane is given by,\[^{87}\]

$$E_{mag} = 1.7\mu_0 M_s^2 d \quad (4.23)$$

The total energy per unit area is

$$E_{tot} = E_w + E_{mag} \quad (4.24)$$

$$E = f_w \frac{t}{d} + 1.7\mu_0 M_s^2 d \quad (4.25)$$

Minimizing the total energy with respect to the domain width $d$ leads to following dependence of domain width on the domain wall energy.

$$d = \frac{f_w t}{\sqrt{1.7\mu_0 M_s^2}} \quad (4.26)$$

The above equation shows that the domain width is directly proportional to the square root of the domain wall energy $f_w$. The latter depends on the biaxial stress, as the $K_{eff}$ depends on the applied in-plane stress according to the Eq (4.19). Therefore, the observed increase in the domain width is due the magnetoelastic energy contribution towards the $K_{eff}$. 


4.3.5 Switching field distribution (SFD)

The switching field of a hysteresis loop is proportional to the effective anisotropy energy associated with the material. Therefore, the measurement of the distribution of the switching field of a material would provide a direct measure of the distribution of the associated effective anisotropy energy. The hysteresis loop measures both reversible and irreversible changes in the magnetization, whereas the DC remanent curve measures only the irreversible changes in the magnetization.

![Diagram of magnetic field and remanent magnetization](image)

*Figure 4.3.19. Schematic representation of the measurement of the DC remanent curve. The measurement starts from the positive saturated remanent state, which is measured after applying a positive saturation field, $H_s$. After positive saturation, the remanent magnetization of the sample at zero field is measured (solid circular dot) as a function of the negative field (solid square dot) until the negative remanent saturation is reached.*

The SFD associated with the irreversible magnetization reversal was studied from the DC remanent curves. The starting point of these DC remanent curves is from the positively saturated remanent state, and it provides information on the response of the magnetization of Co/Pd ML to an increasing negative field until the reverse saturation is applied. These DC remanent curves were obtained by applying and removing a negative field, (in small steps) after saturating the sample with a positive saturation field $H_s$ as shown in Figure 4.3.19.

The DC remanent curves obtained for the Co/Pd MLs ($t_{Co}=0.26$ nm) subjected to a different in-plane biaxial stress are shown in Figure 4.3.20. The characteristic features like the onset of the nucleating field and the sheared region of remanent curves are similar to the features observed in their corresponding hysteresis loops [Figure 4.3.11]. This shows that these features that are observed in the hysteresis loops are irreversible.
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Figure 4.3.20. DC remanent curves of the Co/Pd ML ($t_{Co}=0.26$ nm) subjected to different in-plane biaxial stress.

Differentiation of these normalized DC remanent curves gives the irreversible susceptibility $\chi_{irr}$ defined as $^{125}$

$$\chi_{irr} = \frac{d\left(M_r/M_s\right)}{dH} \hspace{1cm} (4.27)$$

It gives a direct measure of SFD or the distribution of the energy barrier during magnetization reversal. The $\chi_{irr}$ obtained from the measured DC remanent curves are shown in Figure 4.3.21. It follows that the peak at low field side (solid arrows) corresponds to the domain nucleation field, $H_n$ and the one at high field side (black dotted line) correspond to the critical field for the domain wall motion, $H_w$.

Figure 4.3.21. Irreversible susceptibility curves derived from the corresponding DC remanent curves of the Co/Pd ML ($t_{Co}=0.26$ nm). The peaks corresponding to the domain nucleation field, $H_n$ are marked by the solid arrows. The broad peak (as-prepared) at the high field side marked by the dotted line corresponds to the field, $H_w$ required to unpin the domain walls.
As-prepared sample shows a highly asymmetric distribution of the energy barriers that is much broader at the high field side (2.1 kOe). The peak position corresponding to $H_n$ at 1.13 kOe is much smaller than its coercive field of 1.36 kOe (Figure 4.3.11). This shows that the growth of the nucleated domains is hindered due to domain wall pinning. The next energy barrier at an applied field of 2.1 kOe corresponds to the critical field $H_w$ required to unpin the domain walls, which ultimately helps the magnetization to reach the saturation value.

Figure 4.3.22. MFM images of the Co/Pd ML ($t_{Co}=0.26$ nm) sample subjected to different in-plane biaxial stresses in demagnetized state. (a) zero stress and (b) 2.1 GPa.

Upon applying the biaxial stress of 1.4 GPa and 2.1 GPa the nucleating field increases significantly to 1.7 kOe and 1.9 kOe, respectively due to an increase in the $K_{eff}$. Whereas, there is no significant change in the energy barrier corresponding to the field, $H_w$ required to unpin the domain walls and as a result the difference between the $H_n$ and $H_w$ decreases. This decrease contributes to an increase in the hysteresis squareness of the sample subjected to the biaxial stress due to the reduction in the sheared part of the hysteresis loop.[see Figure 4.3.10] But the FWHM of the energy barrier for the nucleation of domains increased from 0.35 kOe for the as-prepared sample to 0.47 kOe upon applying the biaxial stress of 2.1 GPa. This cannot be explained by a decrease in the intergranular coupling because the MFM images of these samples (Figure 4.3.22) show that the stripe domains run through the sample, which reveals a strong intergranular exchange coupling. For the samples with low intergranular exchange coupling (decoupled grains) one would not observe the stripe domain pattern.[126, 127] Therefore, this increase in the FWHM reflecting the distribution of the nucleation field can be attributed only to the distribution of the magnetoelastic anisotropy contributions towards $K_{eff}$.
The reason for the distribution of the stress induced magnetic anisotropy energy contributions must be due to the inhomogeneous in-plane strain in the Co/Pd ML. This is also evident from the XRD measurements (Figure 4.3.3), where the FWHM of the Co/Pd (111) peak increases at higher biaxial stress (higher loading time). Both the SFD and the corresponding XRD scans indicate that there is a distribution of stress induced anisotropy due to non-uniform strain transfer to the Co/Pd ML at higher biaxial stress (higher concentration of hydrogen in Ta substrate). A possible reason is that at higher hydrogen concentration, the formation of tantalum hydrides with locally different crystal structures would induce an inhomogeneous strain to the Co/Pd MLs.

In conclusion, a maximum biaxial stress of 2.8 GPa has been applied to the Co/Pd MLs. In-situ XRD measurements showed that hydrogen diffuses into the Co/Pd ML as well as the Ta substrate, and hydrogen diffuses out of Co/Pd ML upon exposing the sample to Ar atmosphere/air. The applied biaxial stress increases $H_c$ and the squareness of the M/H loops due to the stress induced anisotropy energy contribution. In case of [Pd(0.98 nm)/Co(0.26 nm)]$_{30}$ MLs, about 100% increase of $H_c$ was observed upon applying a stress of 2.1 GPa. Analyzing the $K_{eff}$ data in terms of a simple micromagnetic model yields a magnetostriction constant that is in good agreement with the literature value. SFD measurements in combination with the XRD measurements showed a possible distribution in stress induced anisotropy due to an inhomogeneous strain transfer from the Ta substrate upon formation of multiple tantalum hydride phases.
4.4 Conclusions

A new method of applying an in-plane biaxial stress to the functional layers by loading a Ta substrate with hydrogen has been successfully demonstrated. The magnitude of the applied stress was altered by varying the concentration of hydrogen in the Ta that causes the volumetric expansion of the Ta lattice spacing. The amount of strain induced in the Co$_{50}$Fe$_{50}$ films is larger than that of the strain induced in Ni films. But in both the cases, the maximum amount of strain in the films is significantly smaller than the maximum strain in the Ta substrate. The reason for the difference is most likely the limited strength of the films.

A maximum biaxial tensile stress of 1.24 GPa and 1.79 GPa was applied to Ni and Co$_{50}$Fe$_{50}$ thin films, respectively. The applied biaxial stress induces an additional anisotropy component perpendicular to the sample surface, which influences the $K_{\text{eff}}$ of the sample. In case of Ni, the $K_{\text{eff}}$ increases from $-0.98 \times 10^5$ J/m$^3$ to a maximum value of $-0.68 \times 10^5$ J/m$^3$, whereas for Co$_{50}$Fe$_{50}$ it decreases from $-14 \times 10^5$ J/m$^3$ to $-16 \times 10^5$ J/m$^3$ with the applied biaxial stress. The maximum relative change of $K_{\text{eff}}$ that can be achieved is also limited by the stress applied to the film, which itself is a result of the strain transferred from the Ta substrate and restrained by the strength of the film.

In the case of Co/Pd ML, a maximum in-plane strain of about 1.22% has been induced and this value is significantly larger than the maximum amount of strain induced in Ni and Co$_{50}$Fe$_{50}$ thin films. This shows that Co/Pd ML has higher yield strength, which could be due to the hindrance for the dislocations to pass through the entire ML structure. A complete transfer of the biaxial strain from the Ta substrate (in the $\alpha$-TaH phase) shows that there is no significant amount of hydrogen dissolved in the Co/Pd ML. XRD measurements revealed an inhomogeneous strain in the Co/Pd MLs that has been attributed towards coexistence of tantalum hydrides with different crystal structure at higher hydrogen concentration. This also defines the limitation of our method of applying the biaxial stress i.e. homogeneous strain transfer can only be achieved in the single phase region. Moreover, In situ XRD scans during hydrogen loading revealed that the hydrogen diffuses into the Co/Pd ML prior to the loading of the Ta substrate. Upon exposing the sample to pure Ar or air the hydrogen diffuses out of the Co/Pd ML but remains in the Ta substrate.

Upon applying biaxial stress to the Co/Pd MLs, $K_{\text{eff}}$ increases which leads to an increase in $H_c$ and the squareness of the M/H loops. In case of [Pd(0.98 nm)/Co(0.26 nm)]$_{30}$ MLs, $H_c$ increases from 1.36 kOe in the as-prepared state to 2.14 kOe upon applying a stress of 2.1 GPa. MFM measurements showed that the domain width of the Co/Pd MLs increases with increasing biaxial stress. These results showed a direct contribution of the increased $K_{\text{eff}}$ due to the stress induced anisotropy toward the domain.
wall energy. SFD measurements revealed the distribution of stress induced anisotropy energy contribution due to the inhomogeneous strain transfer at higher biaxial stress state. Analyzing the $K_{\text{eff}}$ data in terms of a simple model yields a magnetostriction constant that is in good agreement with the literature value. This agreement proves that the increase in $K_{\text{eff}}$ upon applying biaxial stress is primarily due to the stress induced perpendicular anisotropy. The new approach introduced therefore can be utilized for the optimization of PMA in magnetic thin films and MLs.
Biaxial stress induced magnetic anisotropy
5 NiMn/Co exchange bias system

AFM materials such as FeMn, NiMn, IrMn, PtMn, PtPdMn, RhRuMn, CoNiO, NiO, TbCo have been exploited as pinning layer in giant magneto resistive spin valve sensors. \cite{128-131} Thermal stability is one of the important criteria, which has to be addressed when it comes to an application. For example in the case of spin valve read head sensors, the magnetotransport properties should not change over the time at an elevated temperature due to heating by the sensing current \cite{132} and electrostatic discharge \cite{133}. Among all the AFM materials NiMn with L1\textsubscript{0} structure is a promising candidate for the exchange bias systems due to its excellent magnetic and thermal properties.\cite{134} However, ordering of the NiMn requires an annealing treatment of the as deposited material. \cite{135} It can be done by short time annealing at temperature greater than 350°C \cite{136} or for a long time annealing at 300°C.\cite{137}

C.-H. Lai \textit{et al.} observed an enhancement of the $H_{ex}$ by altering the NiMn orientation from (001) to (111).\cite{138} B. Y. Wong \textit{et al.} also reported that the $H_{ex}$ is closely associated with the (111) texture of NiMn.\cite{139} M. F. Toney \textit{et al.} showed the existence of a strong correlation between the exchange coupling and the L1\textsubscript{0} ordering in NiMn based spin valve systems.\cite{22} B. Dai \textit{et al.} observed a reduction in the $H_{ex}$ due to undesirable interfacial diffusion in the NiMn based exchange bias systems upon annealing.\cite{139} These studies reveal that the strength of exchange bias field (unidirectional anisotropy) induced by NiMn is governed by its microstructure, degree of ordering, and the interfacial mixing across the NiMn and FM layer. Therefore, modifying the microstructure of NiMn without affecting the interface would influence the associated magnetic properties. Pulsed laser irradiation offers an interesting unconventional heat treatment method with fast heating and cooling rates. It can be utilized for the application of high temperature to modify the microstructure of NiMn without affecting the interfaces due to extremely short processing time. In addition, it allows the possibility to limit the heat load by optimizing the thermal diffusion length (will be discussed in detail in section 5.2.1).

In this chapter, the influence of pulsed laser irradiation on magnetic (unidirectional anisotropy) and structural characteristics of the NiMn/Co exchange bias system has been reported. Possible origin of the unidirectional anisotropy in NiMn/Co exchange bias system is discussed in section 5.1 that is followed by an explanation on the correlation between the microstructure and the $H_{ex}$. In section 5.2, the distribution of the temperature in thin films upon pulsed laser irradiation is discussed. Section 5.3 and 5.4 are grouped with the results and discussion on the effect of conventional annealing and pulsed laser irradiation on the structural phase transformation of NiMn and its effect on the exchange bias effect.
NiMn/Co exchange bias system

5.1 NiMn as an antiferromagnet

NiMn based exchange bias systems show a large exchange bias field, high blocking temperature, and excellent thermal stability combined with a good corrosion resistance.\textsuperscript{[132, 140]} Also, the E. Linville et al. reported that the NiMn based spin valve system are less susceptible to an external stress, which is one of the necessary requirements to fabricate GMR sensor with better sensor characteristics.\textsuperscript{[141].}

![Figure 5.1.1. Binary phase diagram of NiMn alloy.\textsuperscript{[142]}](image)

The equiatomic NiMn alloy exists in three phases, which is evident from the binary phase diagram shown in Figure 5.1.1. The NiMn thin films prepared by most of the conventional techniques (DC magnetron sputtering or electrodeposition) have disordered fcc phase (Figure 5.1.2), which has paramagnetic properties. Upon annealing at an elevated temperature, it transforms to L1\textsubscript{0} ordered fct tetragonal phase with $c=3.524$ Å and $a=3.714$ Å. This phase is antiferromagnetic with a very high $T_N$ of 800°C \textsuperscript{[143]} due to its large crystalline anisotropy energy of $9.7 \times 10^5$ J/m\textsuperscript{3}.\textsuperscript{[144].}

Neutron diffraction studies of Kasper and Kouvel revealed that in ordered equiatomic NiMn, the Mn and Ni occupies the alternating planes with their moments aligned perpendicular to the tetragonal c-axis \textsuperscript{[145]}. The magnetic moments of the nearest neighbouring Mn atoms are arranged antiparallel to each other, with $\mu_{\text{Mn}}$ of about 4.0 $\mu_B$ whereas $\mu_{\text{Ni}}$ is smaller than 0.6 $\mu_B$. The analysis of exchange pair interactions showed that the Ni magnetic moments are almost completely quenched by the frustrated interactions.
between Mn-Mn, Ni-Ni, and Ni-Mn coupling.\cite{146} Therefore, it is more likely that the Mn magnetic moments play a vital role in determining exchange coupling across the FM/AFM interface.

![Image of crystal lattice structure](image)

Figure 5.1.2. Crystal lattice structure of disordered and ordered equiatomic bulk NiMn alloy.

### 5.1.1 Unidirectional anisotropy in NiMn/Co bilayer

In this work, in order to observe the exchange bias effect in NiMn/Co, the samples were subjected to the field annealing procedure. This procedure is very similar to the field cooling procedure described earlier in section 2.2.1, with only difference being that the annealing temperature is lower than the \( T_N \) of NiMn.

Field annealing procedure leads to,

1. Uniaxial field induced anisotropy in the Co layer.
2. Structural phase transformation of NiMn from paramagnetic fcc to L\( _{10} \) ordered fct phase with its anisotropy direction being determined by the induced uniaxial anisotropy direction of the FM Co layer.

After cooling down to room temperature, the exchange coupling across the NiMn/Co bilayer leads to an induced unidirectional anisotropy that can be understood based on the possible AFM interfacial spin configuration at the FM/AFM interface as depicted in Figure 5.1.3. In the case of compensated interfacial spin configuration [Figure 5.1.3 (a)], the net AFM magnetization is zero and hence the field exerted on the FM layer would be zero. In the case of uncompensated spin configuration [Figure 5.1.3 (b)], all the interfacial AFM spins are aligned parallel to the FM spins (assuming ferromagnetic coupling between FM and AFM spins at the interface) resulting in a non-zero net AFM magnetization. This would hold the FM spins along the induced AFM anisotropy direction.
Takano et al. proposed that the interfacial uncompensated spins are responsible for the unidirectional anisotropy.[147] The existence of these uncompensated AFM interfacial spins has been experimentally verified by several groups on several FM/AFM exchange bias systems. Hase et al. showed the existence of small net magnetization in IrMn AFM layer due to the presence of uncompensated Mn spins at IrMn/Co interface.[148] Antel et al. found that in FeMn/Co exchange bias system, Fe spins form an uncompensated interface with their spins aligned parallel with the Co spins.[149] Recently, Schmid et al. demonstrated the existence of uncompensated AFM spins in IrMn and CoO based exchange bias systems.[150]

Figure 5.1.3. Schematic illustration of possible spin configuration in FM/AFM bilayer. a) Compensated interfacial spins cause the net AFM magnetization to be zero. (b) Uncompensated interfacial spins with all the AFM magnetic moments oriented in the same direction cause a non-zero net AFM magnetization.

Ohldag et al. observed a correlation between the observed exchange bias field and the uncompensated spins in NiO/Co, IrMn/Co and PtMn/Co$_{0.9}$Fe$_{1.0}$ exchange bias systems.[151] Their study on the influence of applied external field for the magnetization (FM layer) reversal showed that most of the uncompensated spins followed the ferromagnetic Co spin, whereas a part of the uncompensated interfacial AFM spins are held (pinned) in their sublattices during magnetization reversal. They proposed that only the uncompensated pinned interfacial AFM spins are responsible for the exchange bias effect. The resulting unidirectional anisotropy in the case of the AFM/FM interface with uncompensated pinned magnetic moments can be easily understood with the Meiklejohn-Bean model presented in section 2.2.2.

So far nobody has reported any experimental proof on the arrangement of the interfacial spins in the NiMn/Co exchange bias system. Kilian and Victora treated the exchange coupling in (111) textured NiMn based exchange bias systems by including the number of interfacial uncompensated spins in their micromagnetic modeling.[152] Recently,
Saha and Victora showed that it is possible to explain the dependence of $H_{ex}$ on the temperature, thickness of the AFM layer and the number of grains using micromagnetic simulation by including the uncompensated spins corresponding to the number of Mn atoms in the NiMn (111) plane. The above mentioned experimental observations on the Mn based exchange bias systems along with the micromagnetic simulations on the NiMn/Co systems suggest that the uncompensated pinned interfacial spins could be responsible for the phenomenon of exchange bias in the NiMn/Co bilayers.

### 5.1.2 Correlation between the microstructure and $H_{ex}$

In the case of NiMn based exchange bias systems several groups have reported that the $H_{ex}$ increases with increasing (111) texture. A possible reason for the influence of texture on the exchange bias field can be understood based on the angle between the FM and AFM spins.

The FM-AFM spin-spin interaction which is proportional to $H_{ex}$ is given by,

$$\vec{S}_{FM} \cdot \vec{S}_{AFM} = |S_{FM}| |S_{AFM}| \cos \alpha$$

(5.1)

where, $\alpha$ is the angle between the FM and AFM spins at the FM/AFM interface. Based on the assumption that the FM spins lie in the film plane due to shape anisotropy, there are two possible extreme conditions. (1) In the case of AFM spins oriented normal to the sample plane ($\alpha=90^\circ$), the FM-AFM spin-spin interaction would be zero resulting in no $H_{ex}$. (2) In the case of AFM spins oriented parallel to the FM spins ($\alpha=0^\circ$), the non zero FM-AFM spin-spin interaction would induce a unidirectional anisotropy and hence an observable $H_{ex}$. Therefore, a random textured NiMn layer would result in a distribution of the FM-AFM spin-spin interaction at the interface and that would influence the resulting $H_{ex}$. But the arrangement of spins in NiMn (111) planes is still unclear.

Previous investigations reporting an increase in $H_{ex}$ with increasing (111) texture of NiMn suggest the possibility of the spins being oriented along the (111) plane. It is known from neutron diffraction studies that in L1$_0$ ordered NiMn, the spins are aligned perpendicular to the tetragonal c-axis. The configuration with spins orienting parallel to the NiMn (111) plane would result only if they are directed along the face diagonal perpendicular to c-axis.

M. Tsunoda et al. showed that the $H_{ex}$ increases with increasing lateral grain size of NiMn. Similar dependency of $H_{ex}$ on AFM grain size has also been observed in IrMn based exchange bias systems. The influence of grain size on the $H_{ex}$ can be understood based on the similar effect as that of the thickness of AFM on $H_{ex}$. In section 2.2.2, it has been mentioned that $K_{AFM} t_{AFM}>J_{ex}$ condition has to be satisfied to observe the exchange bias effect. Any decrease in $t_{AFM}$ would impede this condition and would result...
NiMn/Co exchange bias system

in the reduction or the absence of the exchange bias effect. M. F. Toney et al. showed that the $H_{ex}$ increases with increasing thickness of NiMn.\textsuperscript{[22]} Moreover, the influence of grain size or thickness of AFM on $K_{AFM}$ which has not been studied may also influence $H_{ex}$. Tsunoda et al. observed that the blocking temperature of the exchange bias system increases with an increasing AFM grain size. \textsuperscript{[23]} They suggest that it could be due to an increase in the effective magnetic anisotropy of NiMn with increasing grain size.

To summarize, in the case the NiMn based exchange bias system, the interfacial pinned uncompensated spins could be a possible reason for the resulting unidirectional anisotropy. Previous studies showed a strong influence of thickness, texture and grain size of NiMn on the resulting magnetic and thermal properties. Therefore influencing the microstructure of NiMn would significantly influence the unidirectional anisotropy of the NiMn/Co exchange bias system.
5.2 Laser material interaction

Upon irradiating a metal (sufficiently thick to be opaque) with laser, a part of energy is absorbed and a part is reflected. Optical absorption is accounted by the vibration of the free electrons near the surface of the metal. The electron gas in the metals hinders the penetration of the light to any significant depth (attenuation). The variation of the amplitude of the electric field of the propagating wave as a function of the depth $z$ upon laser irradiation is given by Beer-Lambert’s law.

$$E = E_0 \exp\left(-\frac{2\pi \kappa}{\lambda} z\right)$$

(5.2)

where, $\lambda$ is the wavelength of the laser and $\kappa$ is the imaginary part of the complex index of refraction (absorption index). The intensity that is proportional to the square of the amplitude of the field is given by,

$$I = E^2 = I_0 \exp(-az)$$

(5.3)

where, $a$ is the absorption coefficient and the inverse of which gives the optical penetration depth ($a^{-1}=\lambda/4\pi\kappa$) of the laser in a metal. The latter can be defined as the distance at which the intensity decreases by $1/e$ of its original value. For example, the optical penetration depth in Ni for the wave length of 1064 nm is about 14 nm.$^{[156]}$

![Image](image.png)

**Figure 5.2.1. Reflection and absorption upon laser irradiation on a metallic sample.**

The oscillation of the free electrons upon laser irradiation that are in phase with the wavefront of the incident light causes the re-radiation of the light (reflection). The reflectivity $R$ from a metal surface for normal angle of incidence can be deduced from the refractive index $n$ and the absorption index $\kappa$ of the corresponding material using the following formula.$^{[157]}$

$$R = \frac{(1-n)^2 + \kappa^2}{(1+n)^2 + \kappa^2}$$

(5.4)
For an opaque material the absorptivity, $A$ is given by

$$A = 1 - R$$  \hspace{1cm} (5.5)

Upon laser irradiation, the absorbed energy is transformed to the thermal energy and depending upon the energy the material may undergo melting or ablation. In the case of pulsed laser irradiation of thin films, the ablation limit depends on the laser fluence (pulse energy per unit area) and the thickness of the film \cite{158} with the total thickness of the film being less than the thermal diffusion length (will be addressed in the next section). In the case of pulsed laser processing of thin films, it is important to understand the spatial distribution of temperature and the evolution of surface temperature as a function of time.

### 5.2.1 Temperature distribution in a material during laser irradiation

The temperature distribution caused by the absorption of laser light in a material can be described by the heat conduction differential equation for a point source as

$$\rho c_p \frac{\partial T}{\partial t} = k \nabla^2 T + \dot{Q}(\bar{r}, t)$$  \hspace{1cm} (5.6)

where, $k$, $\rho$, $c_p$ are the thermal conductivity, density and the specific heat of the material, respectively and $\dot{Q}$ is the energy per unit volume from the laser light source.

When the radius of the beam is larger than the thermal diffusion length ($l_{th}$), the lateral heat flow can be ignored and the temperature distribution in $z$-direction can be obtained from one dimensional heat diffusion equation. In the case of an infinite plane source, one dimensional heat equation is given by

$$\rho c_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial z^2} + \dot{Q}_a \delta(z, t)$$  \hspace{1cm} (5.7)

where, $\dot{Q}_a$ is the energy per unit area and the accumulation of heat at the surface of the material is denoted by $\delta(z, t)$. The fundamental solution for the above equation is \cite{156}

$$T(z,t) = \frac{\dot{Q}_a}{\rho c_p (4\pi \alpha t)^{1/2}} \exp \left( - \frac{z^2}{4\alpha t} \right)$$  \hspace{1cm} (5.8)

where, $\alpha$ is the thermal diffusivity which is related to the thermal conductivity, the density and the specific heat of the material as

$$\alpha = \frac{k}{\rho c_p}.$$  \hspace{1cm} (5.9)
It plays the role of diffusion constant for heat energy. In general, the thermal diffusion length can be derived by applying the condition, \( T(l_{th}, t)/T(0, t) = 1/e \) to the Eq (5.8). Then, we arrive at the following equation describing thermal diffusion length, \( l_{th} \) for any given time \( t \) after laser irradiation.

\[
l_{th} = 2\sqrt{\alpha t} \tag{5.10}
\]

This thermal diffusion length may vary significantly depending upon the boundary condition of the problem. In the case of pulse laser irradiation (for a single laser pulse) with circular beam profile, the source term has to be modified by using the Heaviside step function as,

\[
\dot{Q}_a(x,t) = AI_0 [H(t) - H(t - \tau)] \tag{5.11}
\]

where, \( A \) is the absorptivity, \( I_0 \) is the intensity of the laser and \( \tau \) is the laser pulse duration.

![Figure 5.2.2. Graphical illustration of the modified source term (Eq.(5.11)) with Heaviside step function as a function of time.](image)

The Heaviside function indicates that the heat is applied continuously for the time \( 0 < t < \tau \) as shown in Figure 5.2.2.

Several groups have derived an analytical solution for the heat conduction differential equation by including Heaviside step function in the source term to study the temperature distribution upon pulsed laser irradiation.\[^{159}\] In this work, we referred to the analytical solution derived by J. C. Conde \textit{et al.} using Green function.\[^{160}\] The solution for the temperature distribution in \( z \)-direction at the centre of the laser pulse (circular beam of radius \( R \)) upon irradiation (for a single pulse) is given by

\[
T(z, t) = T_0 + \frac{AI_0 R^2}{k} \sqrt{\frac{\alpha}{\pi t}} \times \int_{\tau - t}^{\tau} \frac{\exp(-z^2/4\alpha(\tau - t))}{\sqrt{[\tau - t(4\alpha(\tau - t) + R^2)]}} \times \{H(t) - H(t - \tau)\} dt. \tag{5.12}
\]
Using Eq (5.12) the distribution temperature in the sample upon laser spot of diameter of 11 mm has been determined.

Figure 5.2.3. Temperature rise over room temperature (298 K) at the surface (z=0) of the sample upon pulse laser irradiation as a function of time.

Figure 5.2.3 shows the time dependent rise in the surface temperature of the NiMn thin film at the centre of the laser spot, upon irradiating the sample with one laser pulse at fluence of 0.3 J/cm$^2$ and with pulse duration of 9 ns. The values for the thermal conductivity and the thermal diffusivity used in the calculation are 0.78 W/cmK and 0.2 cm$^2$/s, respectively.\cite{161} Here, we assume that the absorptivity to be 0.5 because it is difficult to estimate the exact value for reflectivity since it significantly depends on the surface roughness and the thickness of the natural oxide on the surface of the film. Moreover, it is not necessary to know the exact value of reflectivity of equiatomic NiMn as we are only interested in the distribution of the temperature. It can be observed from Figure 5.2.3 that the surface temperature increases up to the pulse width of 9 ns where it reaches the maximum temperature of 1350 K. At the end of the pulse, the temperature decreases rapidly indicating a very fast cooling rate.

Figure 5.2.4 shows the temperature rise over the room temperature vs the depth $z$ at the end of 1 laser pulse (after 9 ns). The estimated value of the thermal diffusion length (1/e decay) from the plot is about 410 nm. This value is significantly smaller than the value of 850 nm estimated from the Eq (5.10) for the laser dwell time (pulse duration) of 9 ns and the thermal diffusivity value of 0.2 cm$^2$/s. This difference must be due to the assumption in deriving the equation (5.10) that the temperature is constant for the entire pulse width, which is not the actual case as we observe in the Figure 5.2.3. Moreover, the
thermal diffusion length will also decrease further upon consideration of the temperature dependence of the thermal conductivity.\textsuperscript{[162]}

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{figure5_2_4}
\caption{Temperature rise over room temperature (298 K) against the depth of the sample upon laser irradiation (single pulse).}
\end{figure}

\subsection*{5.2.2 Estimation of diffusion length}

The diffusion of Mn into the FM layer upon post annealing treatment of Mn based exchange bias system would deteriorate the device properties. In order to avoid that several attempts have been made to optimize the post treatment procedure in Mn based exchange bias system. M. Rickart \textit{et al.} reported exchange bias in ordered antiferromagnet (PtMn) based exchange bias system by performing rapid thermal annealing.\textsuperscript{[131]} C.-H. Lai \textit{et al.} demonstrated the structural modification and the magnetic properties of NiMn exchange bias system using C ion irradiation prior to annealing treatment.\textsuperscript{[163]} In this work, the main aim is to modify the microstructure of the NiMn in NiMn/Co exchange bias system and therefore its unidirectional anisotropy without significantly affecting the interfaces using pulsed laser irradiation. Here, a quantitative argument to support our proposed idea on restricting the interfacial diffusion using pulsed laser irradiation is presented. The change in the diffusion length upon laser irradiation compared with that of conventional furnace annealing can be explained by the following example.

The diffusion coefficient, $D$ of an impurity atom in bulk is given by \textsuperscript{[164]}

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right).$$

(5.13)
NiMn/Co exchange bias system

The activation energy, $E_a$ and preexponential factor, $D_0$ for the diffusion of Mn as an impurity in the Co bulk are 2.2 eV and $1.1 \times 10^{-2}$ cm$^2$/s$^{[107]}$. From the estimated value of the diffusion coefficient of Mn into the Co bulk using Eq (5.13), the corresponding diffusion length can be calculated using the formula

$$l_d = 2\sqrt{Dt}.$$  \hspace{1cm} (5.14)

The estimated value of the diffusion length of Mn in to the bulk Co upon conventional annealing at the temperature of 673 K for $t=10$ min is 0.3 nm. The diffusion length along the grain boundaries must be even larger due to the low activation energy compared to that of the bulk.

Similarly, the diffusion length of Mn into the bulk Co upon pulse laser irradiation was estimated assuming the time of heating to be the pulse width of 10 ns (due to high cooling rate, the diffusion after the laser pulse is negligible, refer Figure 5.2.3) and a temperature of 1350 K (near the melting point of NiMn at 50:50 composition). The value of the diffusion length amounts to 0.015 nm. This value is over estimated, as the calculation is based on the assumption that the temperature is constant for entire time of irradiation [see previous section]. However, the diffusion length of Mn in to the bulk Co upon laser irradiation is significantly smaller than that of the conventional annealing.

![Figure 5.2.5. Schematic representation of the dependence of the diffusion coefficient on the annealing temperature for the processes with two different activation energies $E_{a1}$ and $E_{a2}$.

The laser irradiation technique would play a significant role to optimize a property of the system involving different events with different activation energies where one of the latter is preferred over the other. For example, let us consider a system involved with the processes activated at two different activation energies $E_{a1}>E_{a2}$. Figure 5.2.5 shows a schematic representation of the dependence of diffusion coefficient on the annealing temperature for the processes with different activation energies. At higher temperature, the
diffusion coefficient values for both the processes approaches each other, whereas at low temperature the process with low activation energy will be dominated. Therefore, a long-term isothermal annealing treatment would significantly favour the processes with low activation energy and a rapid high temperature heat treatment would favour the processes with high activation energy.

Upon nanosecond pulsed laser irradiation, the process with high activation energy will be significantly influenced, while the other process with low activation energy freezes out due extremely fast heating and cooling rates. In the case of Ni$_{50}$Mn$_{50}$, the activation energy for self-diffusion of Ni and Mn is about 3.25 eV and 2.4 eV, respectively and the activation energy for fcc to L1$_0$ ordered fct phase is about 1.45 eV. But the activation energy for the diffusion of Ni and Mn along the grain boundary of the adjacent layer (in this case Co) can be an order of magnitude lower than in the bulk.$^{[165]}$ Therefore, using pulsed laser irradiation it could be possible to influence the microstructure of NiMn without any significant interdiffusion across NiMn/Co particularly along the grain boundaries.
5.3 Isothermal annealing experiments

In this chapter, the changes in the structural and the magnetic properties of NiMn/Co exchange bias system upon isothermal annealing treatment are reported. The samples of the form Si/Ta(9.3nm)/Co(8.5nm)/NiMn(25nm) were prepared for this study. The chemical composition of the NiMn thin film is Ni (47 at%) and Mn (53 at%), measured using EDX analysis.

All the samples have an induced in-plane uniaxial anisotropy in the as-prepared state.[166] The hysteresis loops of the as-prepared sample with the field applied perpendicular and parallel to the induced easy axis (uniaxial anisotropy) direction of the Co layer are shown in Figure 5.3.2.

Along easy axis they exhibit a square hysteresis loop with a sharp switching field, whereas the M/H loop with the field applied perpendicular to the easy axis shows a typical hard axis loop (sheared hysteresis). The observed in-plane uniaxial anisotropy could be due to one of the following reasons.

Figure 5.3.1. Model layer structure of NiMn/Co bilayer system used in the experiments.

Figure 5.3.2. Magnetization curves obtained by applying field parallel and perpendicular to the induced in-plane uniaxial anisotropy direction (easy axis for magnetization).
1. The magnetic field experienced by the sample during magnetron sputtering would induce the magnetic field induced uniaxial anisotropy.\cite{34, 166} 

2. Any internal stress involved in the FM layer during deposition would lead to an induced anisotropy via inverse magnetoelastic effect.\cite{167, 168} 

3. The formation of columnar grains of the FM layer would result in shape anisotropy and the orientation of these columnar structures along one direction would lead to an induced uniaxial anisotropy.\cite{169, 170} 

There is no observable $H_{ex}$ in the as-prepared sample, which must be due to the paramagnetic fcc phase of NiMn. The samples are post-annealed in order to achieve ordered fct phase of NiMn. As our samples possess an in-plane easy axis, the post annealing treatment has been carried out without applying an external field. The remanent magnetization state of the Co layer would define the direction of the unidirectional anisotropy due to exchange coupling. S. Groudeva-Zotova et al. showed that the NiMn based exchange bias system with an induced in-plane uniaxial anisotropy in the FM layer exhibits a similar $H_{ex}$ upon annealing with and without applying an external field.\cite{136} 

5.3.1 Optimization of annealing temperature 

Samples were subjected to conventional heat treatment in a vacuum better than $10^{-6}$ mbar. Figure 5.3.3 shows the x-ray scans of the as-prepared sample and the samples annealed at different annealing temperatures for 30 min. NiMn layer grew with predominant (111) texture on the Co layer.

![XRD scans of NiMn Co bilayer annealed at different temperatures for 30 min each.](image)

*Figure 5.3.3. XRD scans of NiMn Co bilayer annealed at different temperatures for 30 min each.*
The NiMn (111) peak shifts to higher 2θ values upon annealing at an elevated temperature without any significant change in the Co (111) peak position. This shift of NiMn (111) shows the contraction of perpendicular lattice spacing. This change in the lattice spacing must be the result of the change in the crystal structure due to the structural transformation of NiMn from fcc to L1₀ ordered fct phase. This peak shift increases with increasing annealing temperature. At elevated temperatures, any change in the concentration of NiMn due to possible interfacial diffusion across the layers would also influence the NiMn (111) peak positions. Therefore, it is important to note that the shift in NiMn (111) peak cannot be solely attributed to the phase transformation.

The calculated values of NiMn (111) lattice spacing ($d_{111}^{NiMn}$) from the corresponding XRD peaks are shown in Figure 5.3.4 as a function of annealing temperature. It shows that the lattice spacing decreases with increasing annealing temperature. This decrease is significant upon increasing the temperature beyond 300°C. The estimated value of $d_{111}^{NiMn}$ lattice spacing using Vegard’s law for the alloy composition of Ni (47 at%) and Mn (53 at%) was 2.122 Å. The reason for the deviation of measured $d_{111}^{NiMn}$ of the as-prepared sample from that of the estimated value could be due to the presence of an intrinsic in-plane tensile stress in the sputtered NiMn film.

Figure 5.3.5 shows the magnetization loops (field applied parallel to the induced easy axis direction of the Co layer) of the samples treated at different annealing temperature. There was no observable shift in the M/H loop for the sample annealed at 250°C but with increasing the temperature to 300°C, there was a shift in the hysteresis loop accompanied
NiMn/Co exchange bias system

by an increase in the $H_c$. Any further increase in the annealing temperature leads to an increase in $H_{ex}$ and $H_c$.

![Magnetization loops of the samples annealed at different temperatures for 30 min.](image)

Figure 5.3.5. Magnetization loops of the samples annealed at different temperatures for 30 min.

Figure 5.3.6 summarizes the variation of $H_{ex}$ and $H_c$ evaluated from the M/H loops of NiMn/Co bilayer as a function of annealing temperature. The $H_{ex}$ increases gradually with increasing the temperature up to 300°C. Upon increasing the annealing temperature from 300°C to 325°C, the $H_{ex}$ increases sharply from 7 Oe to 160 Oe. This change correlates well with the corresponding change in the NiMn (111) lattice spacing. This shows that the formation of antiferromagnetic fct NiMn is responsible for the observed $H_{ex}$ due to the exchange coupling. A maximum $H_{ex}$ of about 255 Oe was observed for the samples annealed at the temperature of 375°C.

The change in the $H_{ex}$ is accompanied by the corresponding increase in the $H_c$. This change in the $H_c$ can be understood as based on the distribution of the anisotropy energy in the AFM layer. In the case of the NiMn with low anisotropy, the magnetization reversal of the Co layer would cause an irreversible dragging of NiMn spins, which would lead to an increase the coercivity. Whereas, in the case of NiMn with high anisotropy energy, the NiMn spins are held in their sublattices and the Co spins decouple upon applying a higher reversal field. The coexistence of both the processes (anisotropy distribution) would lead to the shift of the M/H loop of the Co layer associated with an increase in the $H_c$. Ohldag et al. showed that the interfacial mixing which occurs upon annealing, increases the interfacial uncompensated AFM spins (see section 5.1.1) which are responsible for an increase in the $H_c$ of an exchange bias system. However, it has to be kept in mind that the $H_c$ significantly depends on the microstructure of the Co layer, which may also change upon annealing.
NiMn/Co exchange bias system

Figure 5.3.6. Variation of $H_{ex}$ and $H_c$ as a function of annealing temperature.

An increased $H_{ex}$ is not the only criteria for the spin valve devices because any significant interfacial diffusion upon annealing would deteriorate the device characteristics. The change in the $M_s$ of Co upon annealing gives us a measure of interfacial diffusion across the Co interfaces, which causes magnetically dead layers. The $M_s$ of the samples annealed at different temperatures obtained from the magnetization curves are plotted in Figure 5.3.7 against an increasing annealing temperature. The $M_s$ of the as-prepared sample was found to be lower than that of the bulk Co (1400emu/cc). This reduced $M_s$ can be attributed to the formation of a magnetically dead Co layer of thickness of about 0.6 nm. Presumably, an intermetallic phase is formed during the deposition of Co with the adjacent Ta layer. [175]

Figure 5.3.7. Change in the $M_s$ of Co layer as a function of annealing temperature.
The $M_s$ of the Co layer decreases gradually upon increasing the annealing temperature up to 325°C. Beyond this temperature, there was a steep decrease in the $M_s$ of Co from 1150 emu/cc to 820 emu/cc for the sample annealed at 375°C for 30 min which corresponds to loss of an effective Co layer thickness of about 2 nm. This drastic decrease in the $M_s$ of Co beyond 325°C indicates the occurrence of significant interfacial diffusion of Co with the adjacent layers, which causes an increase of the magnetically dead layer thickness.

The exchange coupling constant, $J_{ex}$, which is a measure of unidirectional anisotropy, was calculated using the following equation [see section 2.2.2]

$$J_{ex} = \mu_0 M_{FM} t_{FM} H_{ex}. \quad (5.15)$$

Figure 5.3.8 shows the change in $J_{ex}$ as a function of the annealing temperature. The exchange coupling energy increases with increasing annealing temperature up to 350°C, following the change in $H_{ex}$. Any further increase in the annealing temperature beyond 350°C does not cause any significant change in the $J_{ex}$.

Therefore, the optimum annealing temperature should be 350°C at which $J_{ex}$ reaches the maximum value. But even at this temperature there is a significant decrease in the $M_s$, so the influence of annealing time at this temperature has been studied.

### 5.3.2 Optimization of annealing time

Samples have been isothermally annealed at 350°C and the corresponding changes in the structural characteristics were studied using XRD.
Figure 5.3.9. Change in the NiMn (111) lattice spacing as a function of the annealing time at 350°C.

Figure 5.3.9 shows the change in $d_{111}^{\text{NiMn}}$ evaluated from the corresponding XRD scans as a function of annealing time. The lattice spacing changes from 2.1145 Å to 2.1055 Å after annealing for 10 min indicating structural transformation of NiMn from fcc to fct phase. A further increase of the annealing time does not cause any significant change of $d_{111}^{\text{NiMn}}$ at this temperature.

Figure 5.3.10. $H_{\text{ex}}$ and $M_s$ of NiMn/Co bilayers as a function of the annealing time at 350 °C.

The corresponding change in the magnetic characteristics including $H_{\text{ex}}$ and $M_s$ obtained from the magnetization curves are plotted in Figure 5.3.10 as a function of
annealing time. Samples annealed for 3 min showed an observable shift in the M/H loop and the corresponding $H_{ex}$ is 8 Oe. $H_{ex}$ increases further with increasing the annealing time up to 20 min. Any further increase in the annealing time leads to a decrease of $H_{ex}$. However, there is a continuous decrease in the $M_s$ of Co as the annealing time increases indicating undesirable interfacial diffusion.

![Graph](attachment:image.png)

**Figure 5.3.11. Variation of $J_{ex}$ as a function of annealing time at 350C.**

Figure 5.3.11 shows the change in $J_{ex}$ of the annealed samples as function of annealing time. The $J_{ex}$ increases steeply with an increasing annealing time up to 10 min to a value of 0.14 mJ/m$^2$ and reaches a maximum value of 0.19 mJ/m$^2$ after annealing for 20 min. Any further increase of the annealing time beyond 20 min leads to a decrease of $J_{ex}$. Even though $J_{ex}$ increases gradually with increasing annealing time beyond 10 min, the corresponding decrease in $M_s$ of the Co amounts to an additional loss of 1.2 nm of effective ferromagnetic layer, which has to be strictly avoided as it is of the same order as the thicknesses of the functional layers used in the devices.

These results show that $J_{ex}$ upon annealing is determined by the following two competing factors.

1. The microstructural phase transformation from paramagnetic fcc to antiferromagnetic fct phase of NiMn, which increases the $H_{ex}$.
2. Diffusion across the interface, which reduces the $M_s$.

In conclusion, these experimental results show that the observed increase in the $H_{ex}$ upon annealing correlates well with the corresponding observed microstructural phase transformation of NiMn from paramagnetic fcc to antiferromagnetic fct phase. The increase in the $H_{ex}$ is accompanied by the corresponding increase in the $H_c$ and also a
NiMn/Co exchange bias system
decrease in $M_s$ of Co layer due to interdiffusion. The change in the $J_{ex}$ depends upon the antiferromagnetic phase transformation of NiMn leading to $H_{ex}$ and the interfacial diffusion across the Co interfaces. Therefore, the annealing time should be as short as possible and there should be a compromise between the observed $H_{ex}$ and the interfacial diffusion causing a decrease in the $M_s$ of Co.
5.4 Influence of laser irradiation

For the laser irradiation study, the samples of the form Ta(9.3 nm)/Co(8.5 nm)/NiMn(25 nm) were prepared on Si substrate coated with 100 nm Si₃N₄, which acts as a thermal diffusion barrier. As a laser source, Nd:YAG ($\lambda$=1064 nm) Q-Switch multimode laser beam with a top hat profile (refer Appendix B) and with a pulse duration of 9 ns has been used.

![Figure 5.4.1. Model of the layer structure of NiMn/Co bilayers used in laser irradiation experiments.]

5.4.1 Optimization of laser fluence

The samples were irradiated at different laser fluence ranging from 0.06 to 0.21 J/cm² under protective helium atmosphere. The number of pulses was varied as 1, 5, 10 and 20 for different values of laser fluence. The ablation threshold for the sample was found to be 0.23 J/cm².

![Figure 5.4.2. Variation in saturation magnetisation of the Co layer with increasing laser fluence and increasing number of pulses for the Si/SiN(100 nm)/Ta(9.3 nm)/Co(8.5 nm)/NiMn(25 nm) sample.]

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The changes in the saturation magnetization of the Co layer of laser irradiated samples are shown in Figure 5.4.2. There was no change in the $M_s$ of Co up to laser fluence of 0.15 J/cm$^2$ with 1 pulse beyond which the $M_s$ of Co decreased. With increasing the number of laser pulses beyond 0.1 J/cm$^2$, the $M_s$ of Co decreases significantly. This indicates an intermixing of the Co layer with the adjacent layers beyond laser fluence of 0.15 J/cm$^2$ and with increasing number of laser pulses. This shows that the Co/NiMn and Co/Ta interfaces are within the thermal diffusion length during the laser pulse.[see section 5.2.1] Further optimisation of the laser treatment might be achieved by using even shorter laser pulses or by increasing the thickness of the NiMn top layer or by adding an additional cap layer so that the interfaces are not within the thermal diffusion length.

![Figure 5.4.3. The magnetization curves for the samples irradiated with a laser fluence of 0.15 J/cm$^2$ for varying number of pulses.](image)

Figure 5.4.3 shows the magnetization curves for the samples irradiated with laser fluence of 0.15 J/cm$^2$ for different number of laser pulses. High squareness of the hysteresis loop even after irradiating with 1 laser pulse shows that the induced uniaxial anisotropy of Co layer is conserved. But with increasing number of laser pulses the squareness of the hysteresis loop decreases. And there was no observable exchange bias field upon laser irradiation for any number of laser pulses. Similar results have been obtained for all the laser irradiated samples.

To study the change in the layer structure upon laser irradiation SAXR has been performed and the obtained x-ray scans are shown in Figure 5.4.4 along with corresponding simulated curves. The rms surface roughness values of NiMn and the interfacial roughness across the Ta/Co layers are given in the figure. A decrease in the surface roughness of NiMn from 0.49 to 0.23 nm upon laser irradiation at laser fluence of 0.15 J/cm$^2$ has been found, which is associated with an increased number of observable
Kiessig fringes in the reflectivity curve at higher angles. Using this technique, it is not possible to analyse the interfacial roughness across NiMn/Co layers as they have very similar atomic scattering factor. Therefore, in the simulated curves the roughness at NiMn/Co interface was not considered.

![Graph showing reflectivity curve with experimental and simulated data](image)

**Figure 5.4.4.** SAXR scans (open circles) of as-prepared and laser irradiated sample. The solid curves are the corresponding fits obtained using REFSIM. The $\sigma_{\text{NiMn}}$ and $\sigma_{\text{Co/Ta}}$ denote the corresponding rms roughness values of the NiMn surface and Co/Ta interface, respectively.[176]

Interfacial roughness and interdiffusion are indistinguishable in the SAXR measurements. The increase of the roughness value of the Co/Ta interfaces is only of the order of one monolayer. Therefore, even if this increase is due to interdiffusion this would not lead to a significant reduction of the measured $M_s$ of the Co layer in agreement with the results presented in Figure 5.4.2.

![AFM images](image)

**Figure 5.4.5.** AFM images of the as-prepared and the laser irradiated (0.15 J/cm$^2$) samples.
To characterize the surface roughness of laser irradiated sample, AFM studies were carried out and the corresponding images are shown in Figure 5.4.5. The estimated rms surface roughness decreases from 0.91 nm (as-prepared) to 0.42 nm upon laser irradiation (0.15 J/cm²). This decrease in the surface roughness of NiMn upon laser irradiation is similar to the earlier findings from the SAXR scans. The change in the surface roughness upon laser irradiation could be due to the significant grain growth upon melting of the surface layer of NiMn. The absence of any significantly changes at the Co/Ta interface as observed in SAXR suggests that only a few sub-surface layers of NiMn must have been molten. This argument is also supported by the fact that the melting point of the equiatomic NiMn (1050°C) is significantly lower than that of the pure Co (1500°C).\(^{107}\) Moreover, it should also be noted that the estimated diffusion length of Mn in to the bulk Co is insignificant upon laser irradiation even at the temperature close to the melting point of NiMn [refer section 5.2.2].

![Figure 5.4.6. Scanning electron microscopy images of the laser irradiated samples treated at laser fluence of (left) 0.17 J/cm² and (right) 0.19 J/cm².](image)

The change in the surface topography was characterized using SEM. Upon irradiating the sample at higher laser fluence of 0.17 J/cm², there is a significant change in the film topography with the formation of small holes as observed in SEM image (Figure 5.4.6). Increasing the laser fluence to 0.19 J/cm² leads to the formation of a crater like topography, which must be due to the expulsion of the molten material upon extremely fast melting and cooling process accompanied by dewetting process.\(^{177}\). These results show that the optimal laser fluence for irradiating the samples without destroying the layer structure is 0.15 J/cm². Any further increase would be detrimental and has to be avoided.

### 5.4.2 Characterization of the Microstructure

Figure 5.4.7 (a) shows the x-ray scattering curves of the as-prepared and the laser irradiated (0.15 J/cm²) sample. For the laser irradiated sample, there exists a shift in both NiMn (111) and Co (111) peaks to higher 2θ values. Figure 5.4.7 (b) summarizes the
NiMn (111) and Co (111) peak shifts upon laser irradiation as a function of laser fluence. As the peak shifts of Co and NiMn correlate well, the peak shift in NiMn need not be just due to fcc to fct phase transformation but could also be due to tensile stress induced in the sample upon laser irradiation.

![Graph showing peak shifts](image)

**Figure 5.4.7.** (a) XRD scans of as-prepared and laser irradiated Si/SiN(100 nm)/Ta(9.3 nm)/Co(8.5 nm)/NiMn(25 nm) sample. (b) The change in the NiMn (111) and Co (111) peak positions as a function of the laser fluence.\[^{[176]}\]

In order to investigate a possible fcc to fct phase transformation of NiMn upon laser irradiation, the (220) Bragg peaks have been studied in detail by performing XRD in an asymmetric geometry. The latter involves tilting the sample holder to a value
corresponding to the angle between the (111) and (220) plane. For a cubic structure, the angle $\phi$ between two lattice planes $(h_1,k_1,l_1)$ and $(h_2,k_2,l_2)$ is given by,

$$
\cos \phi = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \sqrt{h_2^2 + k_2^2 + l_2^2}}
$$

The estimated value of the angle between (111) and (220) lattice planes is 35.26°. Since the samples possess a strong (111) texture, tilting the sample holder to a constant angle of 35.26° enhances the intensity of the (220) Bragg peaks significantly. The observed x-ray scans for the sample before and after annealing are shown in Figure 5.4.8. Both the as-prepared and the laser irradiated samples exhibit a NiMn fcc (022) peak. The structural phase transformation in NiMn can be characterized by the splitting of NiMn fcc (022) peak to NiMn fct (220) and fct (022) peaks. As there was no such change, we can conclude that there is no fcc to fct phase transformation in the NiMn upon laser irradiation.

The absence of the fcc to fct phase transformation upon laser irradiation can be attributed to the low value (700°C) of the order-disorder transformation temperature [see Figure 5.1.1] of NiMn which is most likely lower than the peak temperature during the laser irradiation. The extremely fast cooling rate after each laser pulse can lead to a quenching of the disordered high-temperature fcc phase down to room temperature. The observed NiMn (111) peak shift can only be attributed to an increase of the tensile stress.
in the irradiated sample. The decrease in the FWHM of NiMn (022) reflections (Figure 5.4.8) indicates grain growth in the NiMn layer upon laser irradiation. The corresponding values of the grain size estimated using the Scherrer formula (Eq (3.19)) are 5.2 nm and 8.5 nm for the as-prepared and the laser irradiated samples, respectively. This also shows that the increase in the tensile stress upon laser irradiation must be due to the annihilation of grain boundaries or in other words, a reduction in the defect density.\textsuperscript{(178)} A very high cooling rate averts any possible strain relaxation and this leads to the tensile stress in the film.

![Graph showing X-ray rocking curve scans for NiMn (111) peak of as-prepared and laser irradiated sample.](image)

*Figure 5.4.9. X-ray rocking curve scans for NiMn (111) peak of as-prepared and laser irradiated sample.*\textsuperscript{(176)}

Figure 5.4.9 shows the rocking curves of the as-prepared and the laser treated samples. The FWHM of the as-prepared and the laser irradiated (laser fluence of 0.15 J/cm\textsuperscript{2}) samples are found to be 5.5\degree and 4.1\degree respectively. The reduction of the FWHM shows a reduction in the mosaicity of NiMn upon laser irradiation. The reason for the increased texture of NiMn can be attributed to preferential grain growth of (111) oriented grains during laser irradiation. A reason for the observed reduction of surface roughness of the NiMn upon laser irradiation (Figure 5.4.4) can now be attributed to the reduced mosaicity of the NiMn due to significant grain growth.

The as-prepared sample and the laser irradiated sample (laser fluence of 0.15 J/cm\textsuperscript{2}) were annealed to investigate the influence of the microstructural change upon laser irradiation on the exchange bias. The heat treatment was carried out in a vacuum better than 10\textsuperscript{-6} mbar for 10 min at different temperatures. During annealing an external field of 1000 Oe was applied along the induced easy axis direction of magnetization of the Co layer.
5.4.3 Magnetic and structural characteristics (post annealing)

![Graph showing magnetization measurements](image)

Figure 5.4.10. Magnetization measurements of as-prepared (solid line) and laser irradiated (dashed line) samples after post annealing treatment at 300°C, 325°C and 350°C for 10 min.\(^{[176]}\)

From Figure 5.4.10, we observe that post annealing at 300°C does not give rise to any observable shift in the hysteresis loop of Co. Upon increasing the annealing temperature to 325°C, there was an observable shift in the hysteresis loops for both the as-prepared and the laser irradiated samples. With further increasing the temperature to 350°C, an increasing shift in the hysteresis loops was observed.

Table 5.1. Magnetic characteristics of post annealed as-prepared and laser irradiated (0.15 J/cm\(^2\)) NiMn/Co bilayers.

<table>
<thead>
<tr>
<th>Annealing temperature (10 min)</th>
<th>As-prepared</th>
<th>Laser irradiated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(H_c) (Oe)</td>
<td>(H_{ex}) (Oe)</td>
</tr>
<tr>
<td>300</td>
<td>31</td>
<td>0</td>
</tr>
<tr>
<td>325</td>
<td>41</td>
<td>8</td>
</tr>
<tr>
<td>350</td>
<td>90</td>
<td>127</td>
</tr>
</tbody>
</table>
The corresponding values of the $H_{ex}$ and $H_c$ are given in Table 5.1. The increase in $H_{ex}$ can be attributed to an increased exchange coupling energy across the NiMn/Co interface. The calculated values of $J_{ex}$ of the as-prepared and the laser irradiated samples annealed at 350°C for 10 min were found to be $0.12\pm0.02$ mJ/m$^2$ and $0.21\pm0.02$ mJ/m$^2$, respectively.

![Graph showing XRD scans of NiMn peak](image)

*Figure 5.4.11. XRD scans of showing NiMn peak in the as-prepared and the laser irradiated samples annealed at 300°C, 325°C and 350°C for 10 min.*
Figure 5.4.11 shows the corresponding x-ray scans of as-prepared and laser irradiated samples treated at different temperatures. The samples have been tilted as described earlier to enhance the intensity of the (220) Bragg peaks. In the case of both the as-prepared and the laser irradiated samples annealed at 300°C, there was no observable Bragg peak corresponding to L1\textsubscript{0} ordered fct phase of NiMn. This shows that NiMn was in paramagnetic fcc phase. This correlates well with the absence of $H_{ex}$ for the corresponding samples. The fct (022) and fct (220) peaks first appear for the sample annealed at 325°C for 10 min, and their intensity increases after annealing at 350°C for 10 min. This shows that the onset of L1\textsubscript{0} ordering of NiMn under these annealing conditions occurs between 300°C and 325°C irrespective of the laser irradiation.

### 5.4.4 Degree of ordering

The increased exchange bias observed in the laser irradiated sample upon annealing compared with that of the as-prepared sample might also be due to an increased L1\textsubscript{0} ordering in the laser irradiated sample. Moreover, recently D. Halley et al reported that chemical ordering of an epitaxial film can be influenced by the internal stresses in the film.\textsuperscript{179} To investigate the change in the L1\textsubscript{0} ordering, both the laser irradiated and the as-prepared samples were isothermally annealed at 350°C.

In the L1\textsubscript{0} ordered NiMn, let us assume that the correct atom positions assigned for the Ni and Mn in the crystal lattice be $\alpha$ and $\beta$ respectively. Then the order parameter $S$ can be expressed as follows\textsuperscript{180}

\begin{equation}
S = r_\alpha + r_\beta - 1 = r_\alpha - w_\beta - w_\alpha
\end{equation}

where, $r_\alpha$ and $r_\beta$ are the fraction of $\alpha$ and $\beta$ sites occupied by the right atom and $w_\alpha$ and $w_\beta$ are the fraction of $\alpha$ and $\beta$ sites occupied by the wrong atom, respectively. For NiMn with complete order and with stoichiometric composition, the order parameter $S$ equals unity. Any deviation from the complete order would lead to $S$ less than 1, and for complete randomness $S$ equals zero.

The order parameter $S$ can be accurately determined from the lattice parameters $c$ and $a$ using the formula\textsuperscript{181}

\begin{equation}
S^2 = \frac{1-(c/a)}{1-(c/a)_{eq}}
\end{equation}

where, $c/a$ is the ratio of $c$ to $a$ axis lattice parameter which amounts to $(c/a)_{eq}=0.945$\textsuperscript{182} for the fully ordered L1\textsubscript{0} phase of NiMn. In order to determine the order parameter, the lattice parameters $c$ and $a$ have been determined precisely from XRD scans. For a
tetragonal lattice structure, the lattice spacing can be related to the miller indices \((h,k,l)\) and the lattice parameter \((a\) and \(c)\) as

\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{c^2} + \frac{l^2}{c^2}
\]

Combining this equation with Bragg’s condition (Eq. (3.10)) yields

\[
\sin^2 \theta = A(h^2 + k^2) + B l^2
\]

where, \(A\) and \(B\) are \(\lambda/4a^2\) and \(\lambda/4c^2\), respectively.

Using NiMn fct (111), (022) and (220) peak positions obtained from XRD scans, the coefficients \(A\) and \(B\) and hence the lattice parameters were determined by least square fitting. \([183]\) By substituting the lattice parameters in the Eq (5.18), the order parameter \(S\) for both as-prepared and laser irradiated sample upon annealing was calculated and the corresponding results are shown in Figure 5.4.12. The order parameter increases with increasing annealing temperature. However, there was no significant difference in the order parameters between the laser irradiated and the as-prepared samples upon annealing.

![Graph showing order parameter vs. duration of annealing](image)

*Figure 5.4.12. Order parameter calculated from XRD scans of as-prepared and laser irradiated samples after isothermal annealing at 350°C.*

The magnetic measurements of the corresponding samples (Figure 5.4.13) reveal that the exchange bias field of the laser irradiated samples are larger than those of the as-prepared samples. The observed increase in the exchange bias field for the laser irradiated samples cannot be explained by different degrees of ordering but only by the increased grain size and an improved NiMn (111) texture upon laser irradiation (see section 5.1.2)
These experimental results conclude that laser irradiation at 0.15 J/cm\(^2\) leads to a significant change in the microstructure of NiMn without deteriorating the layer structure. The laser irradiated samples showed an increased exchange bias field after post annealing treatment compared to that of the as-prepared samples. The degree of ordering and the onset of the phase transformation of the samples are found to be the same irrespective of the laser irradiation.

Figure 5.4.13. Variation of exchange bias field of as-prepared and the laser irradiated samples as function of annealing time at 350°C.
5.5 Conclusions

Isothermal annealing experiments on the influence of annealing time and temperature showed that the paramagnetic fcc to antiferromagnetic fct phase transformation of NiMn upon annealing results in an observable $H_{ex}$. The exchange bias field was found to increase with increasing annealing temperature. At the same time, annealing at an elevated temperature causes a reduction in $M_s$ of the Co layer due to the formation of dead magnetic layers by interfacial diffusion. The change in the $J_{ex}$ upon annealing was found to be correlated with the phase transformation of NiMn from fcc to fct phase. As a result, $J_{ex}$ increases with increasing annealing temperature and annealing time and it reaches maximum for certain annealing conditions beyond which it decreases due to the increased interfacial diffusion. This shows the necessity for an optimized annealing condition that would result in a maximum $H_{ex}$ without significant change in the $M_s$ of the Co layer, which affect the device characteristics. The conventional annealing experiments showed that annealing at 350°C for 10 min leads to an increased exchange bias field without any increased interdiffusion across the interfaces, which would be detrimental.

Upon laser irradiation, a significant increase in both the (111) texture and the lateral grain size of the NiMn was observed. The resulting microstructural changes involving a reduced mosaicity cause a reduction in the rms surface roughness of NiMn. The laser irradiation does not lead to any observable fcc to fct structural phase transformation of NiMn. This must be due to the low (compared to the peak temperature during irradiation) order-disorder transformation temperature of the equiatomic NiMn resulting in quenching of the high temperature disordered fcc phase upon irradiation.

After subsequent annealing at 350°C for 10 min, the laser irradiated samples showed a higher exchange bias field of 207 Oe compared to that of the as-prepared samples of 127 Oe. A maximum $J_{ex}$ of 0.21 mJ/cm² was observed in the laser irradiated samples. This value was higher than the maximum value obtained upon conventional annealing at any temperature and for any period of time. Onset of fcc to fct phase transformation of NiMn in both the laser irradiated and the as-prepared samples occurs between 300°C and 350°C. The degree of ordering was found to be the same irrespective of the laser irradiation. The observed increase in the exchange bias field of the laser irradiated samples has been attributed to the change in the microstructure of the NiMn layer upon laser irradiation. Therefore, the laser irradiation provides an alternative way to optimize the unidirectional anisotropy of NiMn based exchange bias systems by avoiding an undesirable interdiffusion of the individual layers.
NiMn/Co exchange bias system
6 Summary and Outlook

The purpose of this thesis work was to tailor the effective magnetic anisotropy determining the preferred orientation of the magnetization in the magnetic thin films and MLs. This has been achieved by optimizing the magnetoelastic and unidirectional anisotropy energy contributions associated with the system.

First part of this thesis work addresses the optimization of the effective magnetic anisotropy of thin films and MLs by applying a persistent in-plane biaxial stress. A novel method of applying an in-plane biaxial stress has been proposed that involves deposition of the functional layers on the Ta substrate that are then loaded with hydrogen. This method of applying stress has been successfully demonstrated on Ni and Co\textsubscript{50}Fe\textsubscript{50} thin films and Co/Pd MLs. The strains in the functional layers are varied by varying the hydrogen concentration in the Ta substrate. In the case of Co/Pd MLs, a maximum in-plane strain of about 1.22\% has been induced, and this value is significantly larger than the maximum amount of strain induced in Ni and Co\textsubscript{50}Fe\textsubscript{50} thin films. The reason for the difference is most likely the limited strength of the films. A high in-plane strain transfer to the Co/Pd MLs shows that they have higher yield strength, which could be due to the hindrance for the dislocations to pass through the entire ML structure.

A complete strain transfer from Ta substrate to Co/Pd MLs has been observed in the single phase α-TaH phase region. XRD measurements revealed an inhomogeneous strain in the Co/Pd MLs that has been attributed to the coexistence of tantalum hydrides with different crystal structure at higher hydrogen concentration. This shows that one limitation of our method of applying stress is that a homogeneous strain in the functional layers can be achieved only in the single phase α-TaH region. In situ XRD scans during hydrogen loading revealed that the hydrogen diffuses into the Co/Pd ML prior to the loading of the Ta substrate. Upon exposing the sample to pure Ar or air the hydrogen diffuses out of the Co/Pd ML but remains in the Ta substrate leading to a persistent in-plane strain in the Co/Pd MLs.

The applied biaxial stress induces an additional anisotropy component perpendicular to the sample surface, which influences the $K_{\text{eff}}$ of the sample. In case of Ni, the $K_{\text{eff}}$ changes by 40\%, whereas for Co\textsubscript{50}Fe\textsubscript{50} it changes only by 15\% showing that the $K_{\text{eff}}$ can be significantly influenced for the samples with high $\lambda$ and low $M_s$. In the case of Co/Pd MLs, the stress induced anisotropy significantly influences the coercivity and squareness of the hysteresis loop. In case of [Pd(0.98 nm)/Co(0.26 nm)]\textsubscript{30} MLs, $H_c$ increases from 1.36 kOe in the as-prepared state to 2.14 kOe upon applying a biaxial stress of 2.1 GPa. The corresponding increase in the $K_{\text{eff}}$ amounts to $\approx$100\%. Analyzing the $K_{\text{eff}}$ data in terms of a simple micromagnetic model yields a magnetostriction constant that is in good agreement with the literature value. This agreement proves that the increase in $K_{\text{eff}}$ upon applying
Summary

Biaxial stress is primarily due to the stress induced perpendicular anisotropy. Since Co/Pd ML is a potential candidate for the ultra high-density perpendicular storage media, this method would provide an additional degree of freedom to optimize the effective magnetic anisotropy of Co/Pd MLs and hence the magnetic properties. Moreover, this method of applying stress can be applied to a wide variety of systems to study the stress induced magnetic anisotropy in ultrathin films, as it does not require actual solubility of hydrogen in the functional layers. Since the yield strength of thin films increases with decreasing films thickness or grain size, larger magnetoelastic anisotropy contributions may be achieved in the nanostructured materials with grain sizes in the range of a few nanometers. Therefore, as an outlook it would be interesting to study the influence of the biaxial stress induced anisotropy on the nanostructured thin films and MLs.

Second part of the thesis is focussed on the optimization of unidirectional anisotropy associated with the NiMn/Co bilayer system by pulsed laser irradiation. Conventional isothermal annealing experiments showed that the paramagnetic fcc to antiferromagnetic fct phase transformation of NiMn causes an observable $H_{ex}$ in the Co layer. The $H_{ex}$ increases with increasing annealing temperature but the $M_s$ of the Co layer decreases due to the formation of magnetically dead layers caused by interfacial diffusion. The $J_{ex}$ associated with the microstructural changes in the NiMn layer was estimated from the measured $H_{ex}$ and $M_s$ of the Co layer. With increasing annealing temperature and annealing time the $J_{ex}$ increases and reaches a maximum for certain annealing conditions beyond which it decreases due to the increased interfacial diffusion. The $J_{ex}$ was found to be dependent on two competing factors namely, the microstructural phase transformation from paramagnetic fcc to antiferromagnetic fct phase of NiMn that increases the $H_{ex}$ and the diffusion across the interface that reduces the $M_s$. The conventional annealing experiments showed that annealing at 350°C for 10 min leads to an increased exchange bias field without any increased interdiffusion across the interfaces, which would be detrimental.

Pulsed laser irradiation causes a significant increase in both the texture and the grain size of the NiMn. The optimum laser fluence to influence the microstructure of NiMn without significantly influencing the interfaces was found to be 0.15 J/cm². The laser irradiation does not lead to any observable fcc to fct structural phase transformation of NiMn. The absence of structural phase transformation has been attributed to the low order-disorder transformation temperature of NiMn resulting in quenching of the high temperature disordered fcc phase upon irradiation. After subsequent conventional annealing, the laser irradiated samples showed about ≈100% increase in the $H_{ex}$ compared to that of the as-prepared samples. A maximum $J_{ex}$ of 0.21 mJ/cm² was observed in the laser irradiated samples. This value was higher than the maximum value of $J_{ex}$ obtained upon conventional annealing at any temperature and for any period of time.
Onset of fcc to fct phase transformation temperature and the degree of ordering were found to be the same irrespective of the laser irradiation. The observed increase in the exchange bias field of the laser irradiated samples has been attributed to the change in the texture and the grain size of the NiMn layer upon laser irradiation. Therefore, the laser irradiation provides an alternative way to optimize the unidirectional anisotropy and hence the resulting $H_{ex}$ of NiMn based exchange bias systems by avoiding an undesirable interdiffusion across the individual layers.

As an outlook, it would be interesting to study systematically the correlation between the microstructure and the unidirectional anisotropy related to the interfacial coupling in NiMn/Co based exchange bias system. This can be carried out by studying the dependency of the blocking temperature of the exchange bias system on the corresponding microstructural characteristics. Moreover, the configuration of the interfacial spins at NiMn/Co bilayer is unresolved. Therefore, it would be interesting to study the interfacial spin structure using x-ray magnetic circular dichroism measurements. With respect to utilization of pulsed laser irradiation, further improvements may be achieved by optimising the thermal diffusion length by using ultra short pulsed laser irradiation (in picosecond regime). This may assist to influence the microstructure of the selected layer without affecting the interfaces.
7 Appendix

A. Magnetoelastic anisotropy in a biaxial stress state

The magneto elastic anisotropy of a cubic system can be written as,

$$E_{me}^{cubic} = -\frac{3}{2} \lambda \left( \sigma_1 \alpha_1^2 + \sigma_2 \alpha_2^2 + \sigma_3 \alpha_3^2 \right) \quad (A-1)$$

where, $\alpha_1$, $\alpha_2$, $\alpha_3$ are the direction cosines ($\alpha_i = \cos \theta_i$) relating the direction of magnetization with the strain along the crystallographic axes as shown in Figure A-1(left). Note that the sign of this equation is negative; in order to describe $E_{me}$ in terms of directional cosines.

According to above equation, application of an in-plane biaxial tensile stress to the functional layer with $\lambda<0$ would induce a uniaxial anisotropy in the direction normal to the sample plane as shown in Figure A-1 (right).

In the case of biaxial stress state, $\sigma_1 = \sigma_2 = \sigma$, $\sigma_3 = 0$, then the Eq. (A-1) takes the form,

$$E_{me}^{cubic} = -\frac{3}{2} \lambda \alpha_1^2 \sigma \quad (A-2)$$

Using the relation $\alpha_1^2 + \alpha_2^2 + \alpha_3^2 = 1$, the above equation can be written as,

$$E_{me}^{cubic} = -\frac{3}{2} \lambda \left( 1 - \alpha_3^2 \right) \quad (A-3)$$

$$E_{me}^{cubic} = -\frac{3}{2} \sigma \lambda \sin^2 \theta_3 \quad (A-4)$$

Figure A-1. (left) Geometrical representation of direction cosines relating the magnetization direction with the crystal axes. (right) Schematic representation of the induced uniaxial anisotropy due to an in-plane biaxial tensile stress.
B. Q-switch multimode laser

Q-switch

The process of Q-switching causes a very high peak power laser pulse by building a population inversion and the emission of laser in a short time scale of the order of ns. One of the ways to achieve this is by introducing an electro-optic element in the laser cavity. It basically consists of a polarizer, a λ/4 wave plate, and a Pockels cell as shown in Figure B-1 (left). The latter alters the polarization of the incoming light when subjected to an electric field.

The basic function of an electro-optic Q-switch is as follows. The polarizer vertically polarizes the light entering the Q-switch and with no voltage applied to the Pockels cell, it does not affect the polarization of the light. The λ/4 wave plate converts the linearly polarized light to a circularly polarized light. As the polarized light reflects back by the optical reflector, the λ/4 wave plate converts it to a horizontally polarized light. The latter does not transmit through the polarizer and thus build a population inversion. By applying a voltage to the Pockels cell, the polarization retardation caused by the λ/4 wave plate gets cancelled. This allows the transmission of a very high energy laser pulse through the polarizer.

![Schematic representation of an electro-optic Q-switch](image)

Figure B-1. (left) Schematic representation of an electro-optic Q-switch. (right) Top hat laser beam profile resulting from the superposition of multiple resonator modes.

Resonator modes

A resonator containing parabolic mirror results in a mode with Gaussian beam profile, where the optical intensity distribution is defined by a Gaussian function. Depending upon the optics in the resonator, it can also have higher order modes called as TEM_{pl} modes. The optical intensity distribution of such a mode has \( p \) number of radial nodes and \( l \) number of angular nodes. The superposition of these multiple resonator modes results in a top hat profile having a constant intensity within the given beam radius as shown in Figure B-1 (right).
C. **List of abbreviations and symbols**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Antiferromagnetic layer; atomic force microscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-ray analysis</td>
</tr>
<tr>
<td>FM</td>
<td>Ferromagnetic layer</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>ML</td>
<td>Multilayer</td>
</tr>
<tr>
<td>PMA</td>
<td>Perpendicular magnetic anisotropy</td>
</tr>
<tr>
<td>SAXR</td>
<td>Small angle x-ray reflectometry</td>
</tr>
<tr>
<td>SFD</td>
<td>Switching field distribution</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>$a$</td>
<td>Lattice parameter; absorption coefficient</td>
</tr>
<tr>
<td>$A$</td>
<td>Amplitude; absorptivity; exchange stiffness constant</td>
</tr>
<tr>
<td>$c$</td>
<td>Atomic fraction of hydrogen; lattice parameter</td>
</tr>
<tr>
<td>$c_p$</td>
<td>Specific heat</td>
</tr>
<tr>
<td>$d$</td>
<td>Interplanar lattice spacing; domain width</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>$E$</td>
<td>Young’s modulus; electric field</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>$f_{sw}$</td>
<td>Domain wall energy density</td>
</tr>
<tr>
<td>$F$</td>
<td>Laser fluence</td>
</tr>
<tr>
<td>$g$</td>
<td>Geometric factor</td>
</tr>
<tr>
<td>$H$</td>
<td>Magnetic field, Heaviside function</td>
</tr>
<tr>
<td>$H_c$</td>
<td>Coercive field</td>
</tr>
<tr>
<td>$H_d$</td>
<td>Demagnetizing field</td>
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<td>$H_{ex}$</td>
<td>Exchange bias field</td>
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<tr>
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<td>Saturation field</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>Heat of formation</td>
</tr>
<tr>
<td>$I_0$</td>
<td>Intensity</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$J_{ex}$</td>
<td>Exchange coupling</td>
</tr>
<tr>
<td>$k$</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>$l_d$</td>
<td>Diffusion length</td>
</tr>
<tr>
<td>$l_{th}$</td>
<td>Thermal diffusion length</td>
</tr>
<tr>
<td>$K_{eff}$</td>
<td>Effective magnetic anisotropy</td>
</tr>
<tr>
<td>$K_d$</td>
<td>Shape anisotropy</td>
</tr>
<tr>
<td>$K_{mc}$</td>
<td>Magnetocrystalline anisotropy</td>
</tr>
<tr>
<td>$K_{me}$</td>
<td>Magnetoelastic anisotropy</td>
</tr>
<tr>
<td>$K_s$</td>
<td>Surface/interface anisotropy</td>
</tr>
<tr>
<td>$M$</td>
<td>Magnetization</td>
</tr>
<tr>
<td>$M_r$</td>
<td>Remanent magnetization</td>
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<tr>
<td>$M_s$</td>
<td>Saturation magnetization</td>
</tr>
<tr>
<td>$n$</td>
<td>Refractive index</td>
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<tr>
<td>$N_D$</td>
<td>Demagnetizing tensor</td>
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<tr>
<td>$P$</td>
<td>Pressure</td>
</tr>
<tr>
<td>$Q$</td>
<td>Energy per unit volume</td>
</tr>
<tr>
<td>$Q_a$</td>
<td>Energy per unit area</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant; reflectivity; radius of laser beam</td>
</tr>
<tr>
<td>$S$</td>
<td>Order parameter</td>
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<tr>
<td>$S^*$</td>
<td>Squareness of the hysteresis loop</td>
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<tr>
<td>$\Delta S$</td>
<td>Entropy of formation</td>
</tr>
<tr>
<td>$t$</td>
<td>Thickness; time</td>
</tr>
<tr>
<td>$t_g$</td>
<td>Grain size</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
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<tr>
<td>$T_0$</td>
<td>Room temperature</td>
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<tr>
<td>$T_C$</td>
<td>Curie temperature</td>
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<tr>
<td>$T_N$</td>
<td>Néel temperature</td>
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<tr>
<td>$V_m$</td>
<td>Mean atomic volume</td>
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<tr>
<td>$\Omega$</td>
<td>Partial molar volume</td>
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<tr>
<td>Symbol</td>
<td>Definition</td>
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<td>--------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>$z$</td>
<td>Depth</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Thermal diffusivity</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Strain</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Imaginary part of the refractive index</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Magnetic moment; chemical potential</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>Magnetic permeability of vacuum</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Magnetostriction constant; wavelength</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stress</td>
</tr>
<tr>
<td>$\chi_{irr}$</td>
<td>Irreversible susceptibility</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Laser pulse duration</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson’s ratio</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Frequency</td>
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D. **Units conversion table for common magnetic quantities**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>CGS</th>
<th>SI</th>
<th>CGS to SI conversion factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic field, $H$</td>
<td>Oersted (Oe)</td>
<td>A/m</td>
<td>$10^3/4\pi$</td>
</tr>
<tr>
<td>Magnetization, $M$</td>
<td>emu/cc</td>
<td>A/m</td>
<td>$10^3$</td>
</tr>
<tr>
<td>Magnetic moment, $m$</td>
<td>emu</td>
<td>Am$^2$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>Permeability, $\mu$</td>
<td>dimensionless</td>
<td>H/m</td>
<td>$4\pi \times 10^{-7}$</td>
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</tbody>
</table>
8 References


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References


References


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Publications


Conference contributions


5. Effect of pulsed laser irradiation on the structural and magnetic properties of NiMn/Co exchange bias system, 52nd Magnetism and Magnetic Materials Conference, Tampa, Florida, Nov. 5 – 9, 2007.


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