IN CNR IOM TRIESTE, ITALY

MOKE INVESTIGATIONS

Summer Internship Report

By

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Introduction

In this work, I am going to present the main results of the scientific activity in which I was involved during my summer internship at CNR-IOM in Trieste (Italy) during the period, May 16, 2019 to August 10, 2019.

This report focuses on the magneto-optic Kerr effect (MOKE) investigations done on two set of samples.

The first set of samples regards the optimization of the deposition parameters of CoFeB, in order to obtain a sample with low coercive field and isotropic behavior. The aim is to obtain a soft isotropic ferromagnetic layer, for further implementation into ferroelectric/ferromagnetic heterostructures.

The second set regards a run of experiments with the aim of setting an exchange bias coupling by partially oxidizing the ferromagnetic layer through the substrate deoxidation. Here Fe (10 nm) ferromagnetic layer is deposited on substrate Lithium Niobate (LNZ).

This experimental report is divided into chapters as follows:

- In Chapter 1, I will explain the theoretical background of the experiments;

- In Chapter 2, a brief description of the experimental techniques MBE and MOKE will be presented;

- In Chapter 3, I will give an overview on the two set of experiments performed and the theory behind them;

- In Chapter 4, I will show the MOKE results, the XPS and XRD graphs on the two experiments.

- Chapter 5 concludes the report with a discussion on the obtained results on the two projects and with scope of further studies that can be taken on them.

Chapter 1

Theoretical Background

1.1 Magnetic materials

In nature, we observe several magnetic materials like Iron, lodestone, rare earth magnets etc. The underlying fact behind the magnetism in these materials is the non-zero magnetic moment possessed by their constituent atoms. But in a macroscopic picture that describes these materials, we should consider several factors that determine the stable state and the properties of a material.

Based on the reciprocal orientation of its magnetic moments, a material can be categorized as paramagnetic, diamagnetic, ferromagnetic, antiferromagnetic or ferrimagnetic. Temperature plays an important role on the thermal stability of the magnetic state of the material, together with other intrinsic and extrinsic factors such as the dimension of the material, strain etc.
Let us briefly discuss about each type of magnetic materials.

- **Diamagnetic materials**- When the magnetic moments of the atoms are oriented such that all the moments cancel one another, then this condition lead to diamagnetic materials. The atoms are thought not to interact with each other but show a negative orientation of their magnetic moment to the applied field. The magnetic susceptibility of these materials is negative and independent of temperature.
- **Paramagnetic materials**- For these materials, because of the small susceptibility the spins are randomly orientated at any temperature in absence of an applied magnetic field. On applying a magnetic field, these spins orient in the same direction as that of the field. Magnetic susceptibility (X_m) varies with temperature obeying Curie's law, i.e. it is inversely proportional to temperature.
- **Ferromagnetic materials**- These materials have a large and positive susceptibility, but above a characteristic temperature called T_C (Curie temperature) they behave like paramagnetic materials (Curie-Weiss law). These materials can reach **saturation magnetization (M_S,** see Figure 2.1) i.e. the magnetization value attained when all moments are oriented in the same direction. A net magnetization is present even in the absence of an external field (**remanent magnetization, M_r**), for several values of θ, see Figure 2.1. In the demagnetized state, the magnetic state of the material is divided into small regions called domains. Each domain is spontaneously magnetized to its saturation value and different domains are arranged in such a way that the total magnetization (**M**) in the material is zero. The field applied necessary to achieve zero M, starting from

M= $\mathbf{M_S}$ is termed as **coercive field ($\mathbf{H_C}$,** see Figure 2.1**)**, and corresponds to the half width of the hysteresis loop. Eg: Fe, Co etc.

- **Antiferromagnetic materials**- They have a small positive susceptibility but above temperature T_N (Néel temperature) they become paramagnetic. Below the T_N, the alignment of the moments becomes antiparallel, the lattice of magnetic ions in the crystal then breaks up into two sublattices, designated A and B, having moments more or less opposed. The total magnetic moment is therefore negligible in the case of antiferromagnetic materials. Eg: Mn, Cr etc.
- **Ferrimagnetic materials**- The spin orientation is similar to that of antiferromagnetic materials, but the net magnetic moment is not zero due to the incomplete cancellation of opposite spins. This is due to the fact that they are either composed by two different elements with different magnetic moment, or by the same element with different valences. Eg: Fe_3O_4, $CoFe_2O_4$, etc.

1.2 Magnetic energies: the Stoner Wohlfrath Model

Materials always prefer to minimize their energy state. There are several factors that contribute to the total magnetic energy of the system and thereby determine the stable state and hence its properties.
A simple model that explains the energies that influence a ferromagnetic material is the Stoner Wohlfrath model.

It considers two types of energies, the **anisotropic energy** (E_{anis}) and the **Zeeman energy** (E_Z).

The total energy is therefore defined as:

$$E_{tot} = E_{anis} + E_z$$

The Zeeman energy is the energy associated to the alignment of the spins in the direction of the applied magnetic field **H**.
It is given as:

$$E_z = - V\, \mathbf{M}\cdot\mathbf{H}$$ where V is the volume of the material.

Hence from the equation, the energy is minimum when the magnetization **M** is along **H.**

E_{anis} is the energy due to the magneto-crystalline anisotropy of the material. Any material with a crystalline structure has a preferential direction of orientation of the spins. Hence when the magnetic field is applied in that direction it easily acquires its saturation magnetization.
The anisotropic energy is defined as:

$$E_{anis} = -K_{anis} \cos^2\theta$$

where K_{anis} is a constant at a given volume and θ is the angle between **M** and anisotropy axis (see Figure 2.1).

When θ is 0° or 180°, the magneto crystalline anisotropic energy is at its minimum and therefore the spin orientation prefers to align along this direction. This is called the ***easy axis*** (EA) of magnetization of the material. The remanent magnetization is at its maximum along the easy axis.

At 90°, the anisotropic energy is maximum, thus the stable state is determined by Zeeman energy. Few spins are oriented in this direction thus the remanent magnetization at zero applied field is small (in the ideal model, zero), while a sudden reversal of **M** does not take place and is replaced by a smooth reversal of the magnetization. This axis of the material is called the ***hard axis***.

The other energies that affect the behavior of the material are exchange energy, dipolar energy, etc. Exchange energy affects only the nearest neighbors whereas dipolar energy affects a larger region far from its neighbours (it is a long range interaction). These energies can explain ferromagnetic behavior in absence of an external field.
Exchange energy (E_{ex}) enables the alignment of spins to saturation in a domain of the ferromagnet in the absence of field. On the other hand, the **dipolar energy** (E_{dip}) has a demagnetizing effect on the material. It explains the division of the material into multidomain structure aligned in a demagnetized state.

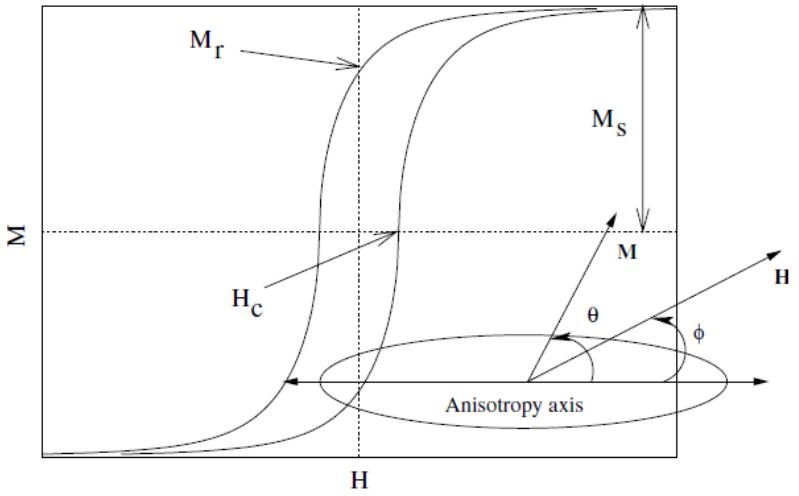

Figure 2.1 – Schematic representation of the plot of hysteresis loop for an arbitrary angle, ϕ, between the magnetic field and the anisotropy axis. In the figure, M_S is the saturation magnetization, M_r is the remanent magnetization and H_C is the coercive field.[1]

Chapter 2

Experimental Setup

The setup used in the experiment is a Ultra High Vacuum (UHV) chamber called the MASK chamber, used to deposit samples via Molecular Beam Epitaxy (MBE) technique. The chamber is maintained at a vacuum of 10^{-10} mbar. MOKE measurements can be done in vacuum using this setup as polarized light can pass through the window openings of the chamber and it get reflected from the sample outside of it. A x-ray photoemission spectroscopy (XPS) setup is also connected to this chamber. Multiple samples can be deposited and stored in the chamber in UHV conditions without capping, and can be taken for MOKE measurements to study their magnetic behavior. The MOKE measurements can also be done in air, by changing the height of the optical table and of the magnet.

2.1 Molecular Beam Epitaxy (MBE)

The deposition of samples takes place at the high temperature evaporation position in the MASK chamber. The MBE technique distinguishes itself from other evaporation crystal-growth methods by employing molecular beams, in a UHV environment. This allows a precise control of composition, growth conditions, high purity etc. In this technique the metals or compounds to be deposited are placed inside a crucible. They are surrounded by a filament, electrically isolated from the crucible. Once the filament current is applied, it heats the materials inside the crucible by thermal radiation. A high voltage is therefore applied on the crucible with respect to the ground. This leads to the ion bombardment from the filament to the crucible by imparting kinetic energy and thus heats it further to a higher temperature. The stage at which the sample is placed is grounded and hence the voltage difference allows the emission of the material in the form of molecular beam to the substrate placed at the stage. This allows layer by layer growth of the material on the substrate and thus a thin film can be efficiently deposited in this chamber using the MBE technique.

In order to evaluate the thickness of the deposited film a **Quartz Crystal Monitor (QCM)**, which is insertable at the position of the deposition stage, is used. It vibrates at a particular frequency, which is dependent on the mass of the quartz itself. As the material is deposited on it, the frequency changes. According to the material deposited, the software associated with it calibrates and calculates the deposited mass. From the mass calculation, it gives the thickness of the film deposited per unit time. This procedure is

done before each deposition in order to calibrate the deposition rate of the used evaporator.

2.2 Magneto Optical Kerr Effect

The Magneto Optical Kerr Effect (MOKE) measurements are taken to study the magnetic behavior of the deposited samples. The MOKE setup associated with the MASK chamber is set in a way that measurements can be taken either while the sample is still in vacuum or with the sample in air. Specifically, the setup of the MASK chamber is a longitudinal MOKE system.

Magneto optical effects are due to the influence of light (an electromagnetic wave) on a magnetized material when it is either transmitted or reflected from it. According to the reciprocal position of the beam light, the sample and the applied magnetic field, the setup can be defined as polar, longitudinal or transverse MOKE. These three configurations are schematically represented here below (Figure 2.1):

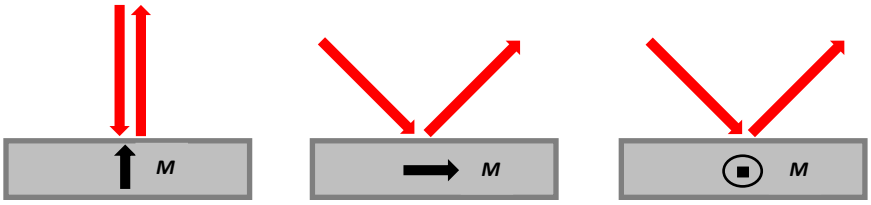

Figure 2.1 – Schemantic representation of polar, longitudinal and transverse MOKE setups

When a plane polarized monochromatic beam with the plane of polarization either parallel (*p*) or perpendicular (*s*) to the plane of incidence is reflected from a magnetic sample under an applied in plane field, it changes its polarization to have both *s* and *p* components, i.e. it becomes elliptically polarized. The major axis of the ellipse is rotated by a small angle with respect to the initial plane of polarization. This rotation is called the **Kerr rotation** and is linearly proportional to the magnetization of the sample. Thus, the measurement of the Kerr signal enables us to study the magnetization of the sample under an in plane magnetic field.

In the case of **longitudinal MOKE (LMOKE)**, the magnetic field is applied along the same plane of the incident light.

Now let us see the setup used to extract these Kerr signals from the magnetized samples.

MOKE Setup

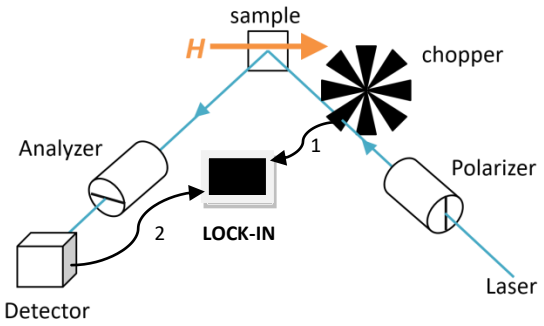

Figure 3.2 - Schematic diagram of longitudinal MOKE setup at CNR-IOM, Trieste, Italy. Label 1 refers to the reference frequency and 2 to the signal detected.

The longitudinal MOKE setup I used during the internship at CNR-IOM, Trieste is schematically represented in Figure 3.2. It is composed by the following elements:

- **LASER:** In the setup we use two different laser sources, with wavelength either blue (405 nm) or red (658 nm), depending on the optimized Kerr signal obtained from the sample.

- **Polarizer**: The polarizer consists of a crystal that acts as an optical filter and allows only a specific polarization to pass through. In our case, the beam of light passing through the polarizer becomes *s* polarized and hits the sample in the vacuum chamber placed at MOKE position through the glass windows or hits the sample in the sample holder when placed in air.

- **Chopper**: It rotates at a particular frequency (789 Hz) and chops the beam from the polarizer into a square wave, before hitting the sample. It helps in cutting off the noise signals of frequencies below its own frequency for eg: signals coming from background lights.

- **Sample**: The sample is placed on the sample holder with help of silver paste and is kept at the MOKE position of the MASK chamber. The plane of the sample is perpendicular to the plane of incidence. The sample is rotated to different angles from 0° to 360° in step size of a chosen value (in our case 15°). This allows studying the magnetic response as a function of the planar angle between the crystalline structure of the sample and the applied magnetic field. This kind of measurement is known as ***rotational MOKE***.

- **Analyzer**: The polarized beam of light is reflected from the sample and goes to the analyzer. The analyzer is a second crystal, identical to the polarized, with its polarization placed at crossed condition (90°) with respect to the polarizer, plus a little offset. This allows us to filter the signal coming from the laser and let pass only the small contribution due to the magnetic signal of the sample.

- Detector: The detector used is a photodiode whose sensitivity is maximized around the wavelength of interest. In the used MOKE setup, two detectors are available, one centered around the blue wavelength and a second one around the red one. This helps in reducing the noise signal coming from different wavelengths.

- Lock-in amplifier: It receives the frequency from the chopper as input signal and collects from the detector only the signals of frequency of the chopper (see Figure 3.2). It helps in reducing the noises from all other frequencies.

- Software: The signal obtained is connected to the computer and a software is used to control the magnet and the lock-in amplifier during the hysteresis loop. The field is varied from a positive value, which is chosen to be large enough to attain saturation magnetization, to the negative of the same value with small steps, whose distance is chosen to allow understanding the hysteresis loop trends. Once the loop is finished, a datasheet containing the magnetic field intensity and the lock-in amplifier signal is produced, allowing treating the data.

- Origin Lab: The Origin lab software is used to plot the measured hysteresis loops and doing data treatment. In particular, by calculating the remanent magnetization and the coercive field of the sample for all rotational angles, it is possible to plot the so-called ***polar plots***, which allow to easily understand the in plane anisotropy of the sample.

Chapter 3

The Project Plans

3.1 The $Co_{60}Fe_{20}B_{20}$ Project

Aim: The aim of the project is to develop a ferromagnetic layer that is isotropic and has the lowest possible coercive field.

Task: Amorphous CoFeB samples were deposited on MgO (001) substrate at different conditions and optimized samples were taken for further studies.

Theory: The total energy of a magnetic material is contributed by the exchange energy, the dipolar energy, the anisotropic energy and the Zeeman energy (as mentioned in chapter 1).

$$E_{tot} = E_{ex} + E_{dip} + E_{anis} + E_z$$

An external contribution can influence the system if the energy contributions of the above given factors is small compared to that from the external one. According to the Stoner-Wohlfrath model, the two energies that make major contribution to the energy of the system are the anisotropic energy and the Zeeman energy. If the energy contribution of the anisotropic term can be reduced by making the sample isotropic, then the system is mostly influenced by the external applied field (Zeeman contribution). In this case, the energy barrier between the two stable states is small, allowing a small applied field to induce the magnetization reversal of the system, thus giving a small coercive field.

In this project, we aim to deposit thin films of amorphous CoFeB in different deposition conditions and to verify its magnetic response, with the goal of having an isotropic behavior -with low coercive field.

3.1.1 Amorphous $Co_{60}Fe_{20}B_{20}$

The amorphous $Co_{60}Fe_{20}B_{20}$ is used because the presence of boron makes it pinning free (i.e. the defects are not pinned) and therefore reduces the energy barrier between the stable states, which implies a reduction of H_C. The amorphous nature makes the compound isotropic because no crystallographic order is present in it. Most of the deposited samples had a thickness of 5nm, as the future applications require an optimized thickness of 5nm for observing desired changes. We also used a thickness of 20nm, as it is the minimum thickness that enables us to carry out XRD measurements.

The samples are always capped before exposure to air with 2-3 nm of Au or with MgO to avoid sample oxidation.

3.1.2. MgO (001) substrate

MgO is a very stable substrate. It is non-magnetic and does not interact with the magnetic properties of the thin film deposited on it. Amorphous CoFeB is deposited on MgO (001) plane. The (001) plane is preferred as it is easier to cut the substrate along this plane.

3.2 The Exchange Bias Project

Aim: The aim of this project is to observe exchange bias coupling in an isotropic ferromagnetic sample. It is expected to be achieved by the formation of an antiferromagnetic layer at the interface due to oxygen migration from the substrate upon annealing under an applied magnetic field[2].

Task: Amorphous Fe was deposited on Lithium Niobate (LNZ) substrate and the sample was annealed under an applied field. The annealing and the cooling conditions were optimized to observe the exchange bias shift.

Theory: Exchange bias is a unidirectional anisotropy created on the magnetic response of a ferromagnetic layer, due to the effect of an interfacial coupling with an antiferromagnetic layer in contact with it. The Exchange bias phenomenon takes place via a procedure shown in Figure 3.1. The sample is heated at a temperature which is lower than the Curie temperuature T_C (i.e. the ferromagnetic layer is still magnetic) but high enough to make the antiferromagnetic layer loose its magnetic order (i.e. at temperature above T_N). Usually for polycrystalline structures, the antiferromagnetic material loose its magnetic order at a temperature called blocking temperature (T_B) which is below the bulk T_N of the material. After heating the system is cooled down under an applied setting field, which creates an interfacial coupling once the antiferromagnetic layer regains its magnetic order. This coupling adds a unidirectional anisotropy to the energy of the system, responsible of the shift of the hysteresis loop along the direction of the applied setting field.

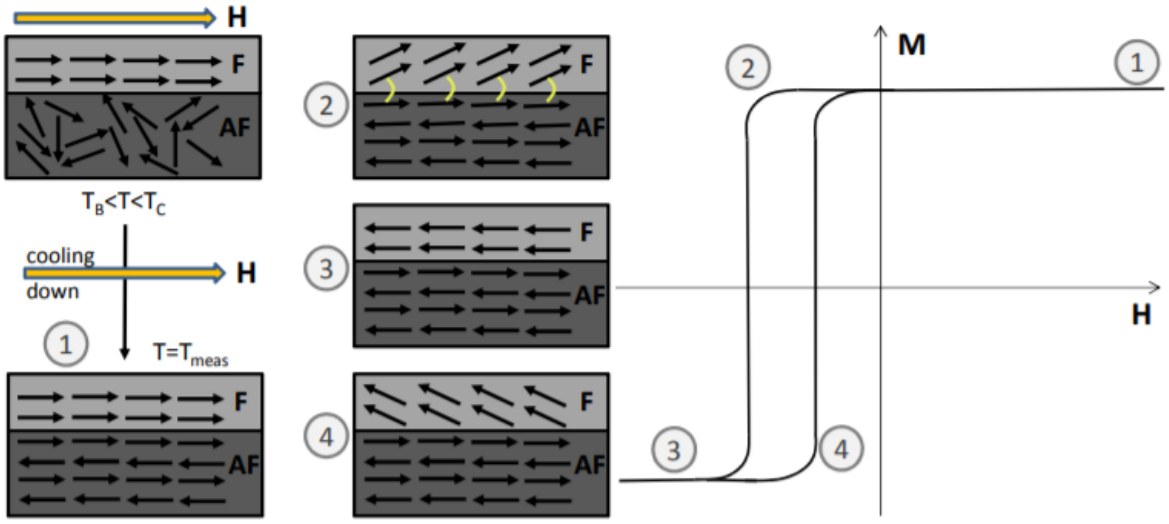

Figure 3.1 - Schematic diagram of exchange bias phenomena[3].

3.2.1 Amorphous Iron

Amorphous Fe is used as the ferromagnetic layer in the project as the FeO, produced during the substrate deoxidation, is antiferromagnetic. FeO has a T_N of 198 K and T_C of 570 K. Hence, as desired the sample can be annealed under a magnetic field to a temperature above T_N and below T_C to observe the exchange bias coupling.

3.2.2 Lithium Niobate [$LiNbO_3$] (LNZ) (0001)

It is a well-known ferroelectric (ABO_3 type, see Figure 3.2) and has a hexagonal crystal structure. In Lithium Niobate z-cut (LNZ), the substrate is cut perpendicular to the crystallographic axis parallel to the z direction. It is a very unstable oxide. The compound have strong tendency to be off stoichiometric due to the presence of defects. Therefore, at higher temperature, deoxidation of the compound takes place which helps in oxidizing the ferromagnetic (Fe) layer deposited on it and creates an antiferromagnetic layer at the interface.

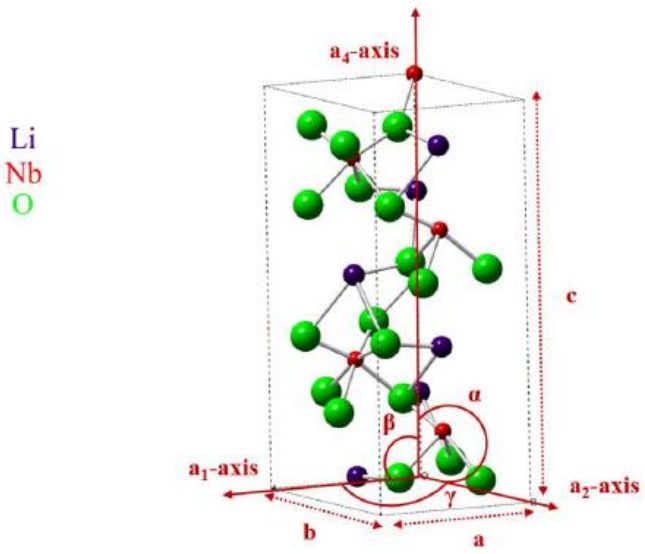

Figure 3.2- Hexagonal unit cell of $LiNbO_3$ ferroelectric. $\alpha = \beta = 90°$, $\gamma=120°$, in the hexagonal coordinate system. In the orthogonal system z-axis is parallel to the a_4 axis shown in the figure.[4]

Chapter 4

Experimental Results

4.1 The CoFeB Project

Several samples of CoFeB were deposited in the MASK chamber at different conditions and MOKE measurements were taken to understand their magnetic behavior. Few of the important observations made during MOKE measurements on these samples are listed below.

4.1.1 The Effect of angle of deposition

(a) Sample 1: MASK042 As grown

Deposition conditions:

1. Temperature : Room Temperature(RT)
2. Substrate : MgO (001)
3. Evaporation rate: 1.88 Å/min
4. **Position : At an angle not perpendicular to the substrate**
5. Thickness : 20.4 nm
6. Capping : 3 nm Au

MOKE measurements:

(i) Temperature : RT
(ii) Measurement angles : 320°(1-10) to 200°
(iii) Magnetic response : Anisotropic
(iv) Coercive Field : 100 Oe

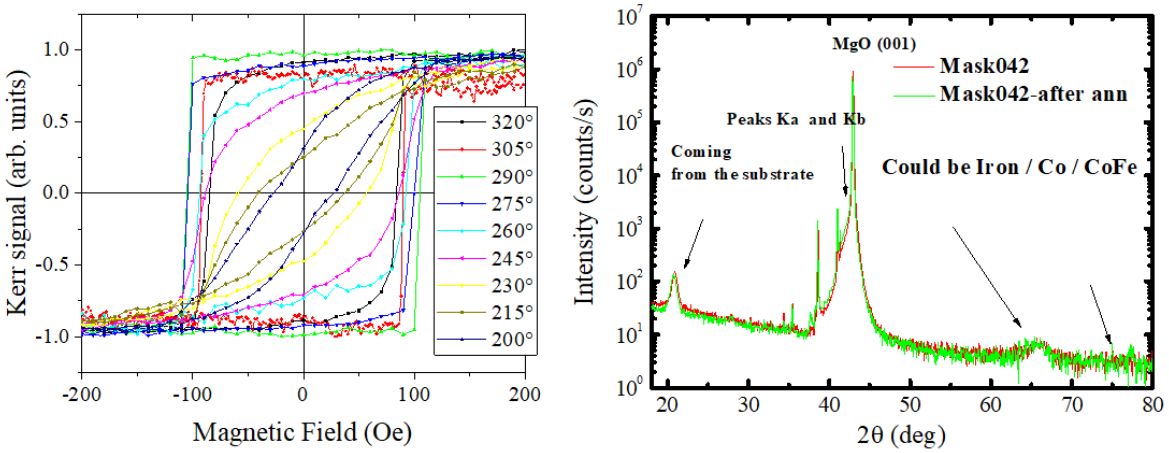

Figure 4.1: (a) MOKE measurements made on MASK042 as grown sample for 320°-200° angles in steps of 15° at RT; **(b):** XRD measurements on MASK042.

The MOKE results show that MASK042 has relatively large coercive field (compared to literature values, see ref.[5]) and it is anisotropic, contrary to what is desired. The XRD measurements show only the presence of substrate peaks and confirm that CoFeB is still amorphous.

The position of the substrate at an angle with respect to the evaporator was suspected to be the reason for the measured anisotropy. Therefore, the position of the CoFeB evaporator inside the MASK chamber was substituted in order to allow depositions normal to the sample substrate. All the following samples have been deposited with this new setup.

(b) Sample 2: MASK044 As grown

Deposition conditions:

(i) Temperature : Room Temperature(RT)
(ii) Substrate : MgO (001)
(iii) Evaporation rate: 1.81 Å/min
(iv) **Position : Perpendicular to the substrate**
(v) Thickness : 5.3nm
(vi) Capping : 2nm Au

MOKE measurements:

(i) Temperature : RT
(ii) Measurement angles : 320° to 200°
(iii) Magnetic response : Isotropic
(iv) Coercive field : 50 Oe

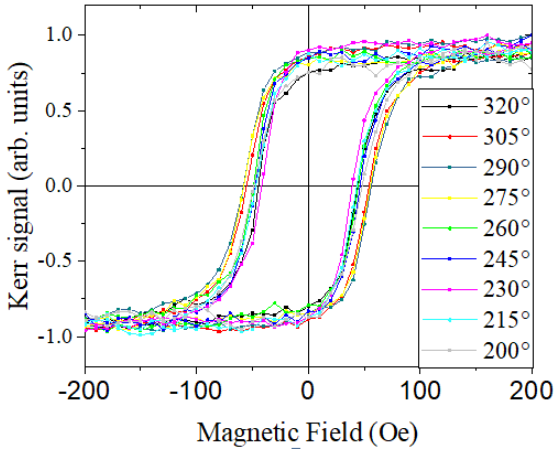

Figure 4.2 - MOKE measurements done on MASK044 as grown sample at RT.

As suspected before, the anisotropic behavior of the sample was due to the position of the substrate at an angle with respect to the evaporator. MASK044 as grown sample magnetic measurements show that the new position of the evaporator has corrected it. Together with the isotropic behavior, also the coercive field is reduced compared to MASK042.

H_C is desired to be as small as possible. New samples were deposited at various conditions to find the lowest possible coercive field.

Firstly, the effect of deposition temperature in the coercive field was studied.

4.1.2 Temperature effect

(a) Sample 3: MASK048 As grown

Deposition conditions:

(i) **Temperature : 78 K**
(ii) Substrate : MgO (001)
(iii) Evaporation rate: 2 Å/min
(iv) Position : Perpendicular to the substrate
(v) Thickness : 5nm
(vi) Capping : 2.5nm Au

MOKE measurements:

(i) Temperature : RT
(ii) Measurement angles : 320° to 200°
(iii) Magnetic response : Isotropic
(iv) Coercive field : 290 Oe

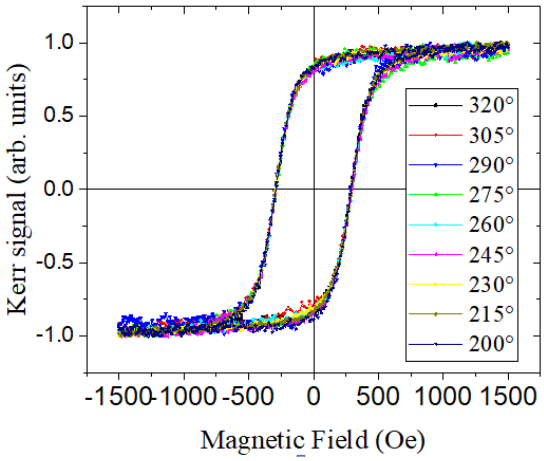

Figure 4.3 - MOKE measurements taken on MASK049 as grown sample at RT

The measurements presented in Figure 4.3 show that the deposition at a lower temperature (78 K) increases the coercive field tremendously than before. It is due to the fact that at low temperature the molecules do not have enough energy to get deposited on the substrate layer by layer, hence defects are formed. The presence of defects increases the energy barrier and H_C is increased. It was concluded that deposition at low temperature was the wrong direction for the desired value of the coercive field. Therefore, further samples were deposited only a room temperatures.

The additional parameter for optimizing the magnetic properties was the annealing of the sample.

4.1.3 Annealing effect

(a) Sample 4: MASK050 As grown

Deposition conditions:

(i) Temperature : RT
(ii) Substrate : MgO (001)
(iii) Evaporation rate: 2 Å/min
(iv) Position : Perpendicular to the substrate.
(v) Thickness : 5nm
(vi) Capping : 2.5nm Au

MOKE measurements:

(i) Temperature : RT

(ii) Measurement angles : 320°, 290° and 275°

(iii) Magnetic response : Isotropic

(iv) Coercive field : 6 mT

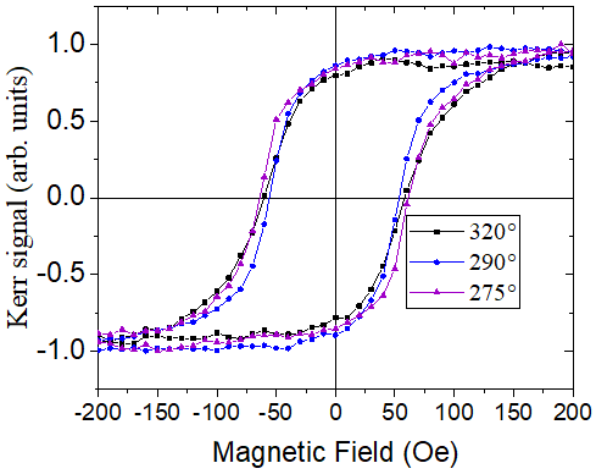

Figure 4.4 - MOKE measurements done on MASK 050 as grown sample on 320°, 290° and 275° angles at RT

Annealing conditions:

(i) Temperature : 500°C

(ii) Time : 1 hour

MOKE measurements:

(i) Temperature : RT

(ii) Measurement angles : 365°- 170°

(iii) **Magnetic response : Slightly anisotropic**

(iv) **Coercive field : 40- 60 Oe**

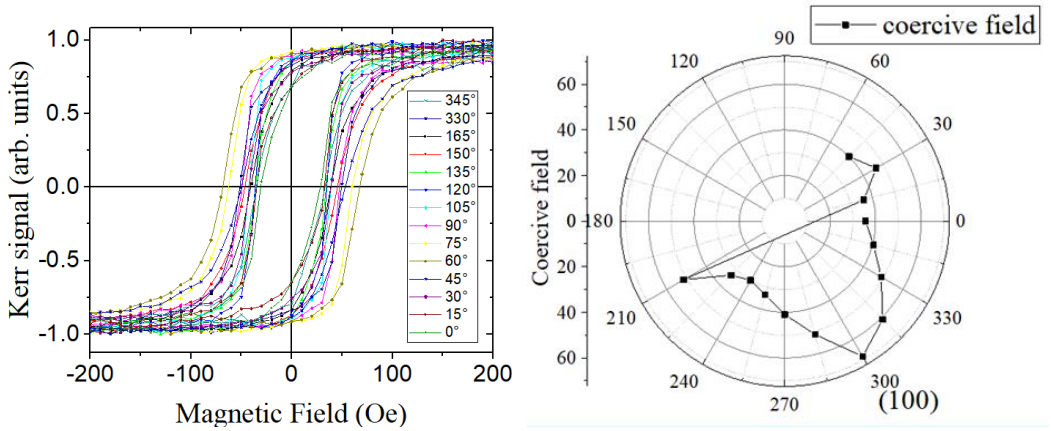

Figure 4.5 - (a) MOKE measurements done on MASK 050 after the annealing, at RT. (b) Polar plot on the coercive field of MASK050 annealed sample, 0° in the plot refers to 120° in the hysteresis loop.

The annealing done on the sample gives a slight anisotropy in the magnetic response (see Figure 4.5), which was not present before the annealing (see Figure 4.4).

Thus, we conclude that as grown samples give more isotropic response and are the most suited for our project.

4.1.4 CONCLUSIONS

Table 4.1 summarizes the list of deposited and characterized CoFeB samples, with the main features listed.

Sample name	Sample	Perpendicu-larity	Substrate	Thickness (nm)	Evaporation rate(A/min)	T d (K)	Annealed (Sample/ Substrate)	Coercive field(Oe)	Anisotropy
MASK-042	CoFeB	No	MgO	20	1.8	RT	No	100	Yes
MASK-042	CoFeB	No	MgO	20	1.8	RT	Yes (sample)	50	Yes
MASK-044	CoFeB	Yes	MgO	5	2.0	RT	No	50	No
MASK-046	CoFeB	Yes	MgO	5	2.0	RT	Yes (substrate)	40	No (s*)
MASK-048	CoFeB	Yes	MgO	5	2.1	80	No	290	No (s*)
MASK-049	CoFeB	Yes	MgO	20	9.5	RT	No	100	Yes
MASK-045	CoFeB	Yes	LNZ	5	2.0	RT	No	35-55	No (s*)
MASK-050	CoFeB	Yes	MgO	5	2.0	RT	No	60	No
MASK-050	CoFeB	Yes	MgO	5	2.0	RT	Yes (sample)	30-60	No (s*)

Table 4.1 - List of samples that were deposited and the different parameters that affects the coercive field and anisotropy of the samples. (*slight anisotropy)

From the MOKE measurements made above we can draw the following conclusions on the CoFeB sample:

1. Deposition perpendicular to the substrate yield to an isotropic magnetic response.

2. Deposition at high temperature yields to a reduction of the coercive field.

Annealing induces slight anisotropy and hence is detrimental on the CoFeB samples. As grown samples are more fit for the experiment.

4.2 The Exchange Bias Project

Amorphous Fe/LNZ samples were deposited and annealed at different temperatures under magnetic field, expecting the deoxidation of the substrate and formation of an antiferromagnetic interface and hence, the setting of an exchange bias coupling.

The MOKE results obtained on the samples after each annealing are shown below.

4.2.1 Sample 1: MASK043 – Au(3nm)/Fe(10nm)/LNZ

MOKE before annealing:

(i) Temperature : RT
(ii) Magnetic response : Isotropic
(iii) Coercive field : 60 Oe

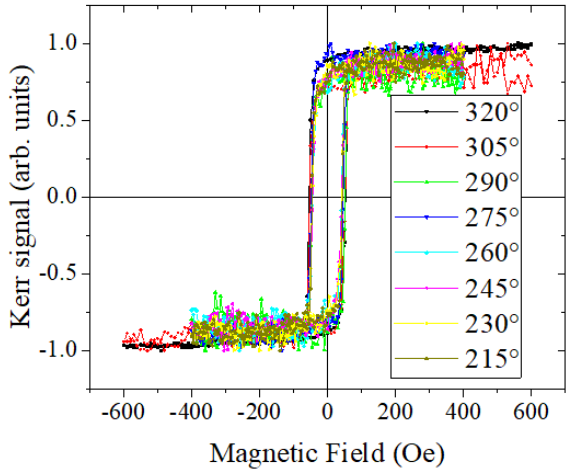

Figure 4.6: MOKE measurements done on MASK 043 as grown sample on 320°- 215° angles at RT

Annealing conditions:

(i) Temperature : ~800°C
(ii) Time : 1 hr
(iii) Cooling field : 200mT
(iv) T_{stop} : RT
(v) Magnetic response : No signal

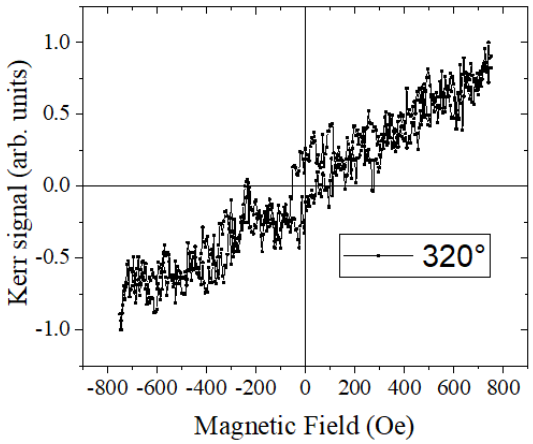

Figure 4.7: MOKE measurements done on MASK 043 annealed sample along the easy axis at 80K.

The results show that high temperature annealing has destroyed the magnetic properties of the sample (Figure 4.7). The hysteresis loop does not show any feature of ferromagnetic behavior, even at 80 K. This means that the annealing temperature was too high and damaged the whole Fe layer.

A new sample was therefore deposited and annealed in steps of increasing temperature to ensure the non-destruction of the magnetic properties.

4.2.2 Sample 2: MASK047 – Fe(10nm)/LNZ

MOKE before annealing:

(i) Temperature : RT
(ii) Magnetic response : Isotropic
(iii) Coercive field : 60 Oe

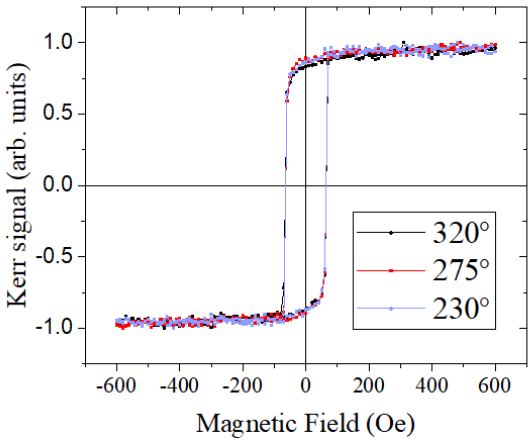

Figure 4.8: MOKE measurements done on MASK 047 as grown sample on 320°, 275° and 230° angles at RT.

First Annealing:

(i) Temperature : ~500°C
(ii) Time : 1 hr
(iii) Cooling field : 3500 Oe
(iv) T_{stop} : 330K
(v) Magnetic response : Isotropic
(vi) Coercive field : 850 Oe

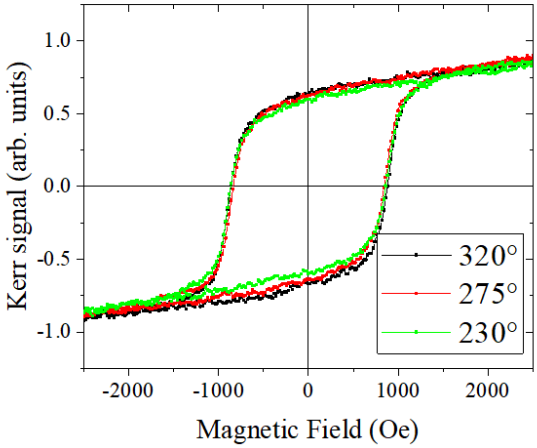

Figure 4.9: MOKE measurements done on MASK 047 sample on 320°, 275° and 230° angles at RT after the first annealing at 500°C.

The first annealing done on MASK-047 shows that the coercive field has increased tremendously, the magnetization value is unsaturated even for a field value of 2000 Oe and the exchange bias shift is absent (see Figure 4.9). From the observations it was suspected that an antiferromagnetic interface, above the T_N is formed, hence the unsaturation. A model that could explain the observations is that the deoxidation of the substrate oxidized the Fe layer at the interface and an antiferromagnetic (above T_N) Fe_xO_{1-x} was formed, as desired. The absence of the exchange bias shift was attributed to the turning off of the magnetic field before the supposed blocking temperature.
For this reason a second annealing was done under field, removing the setting field at a lower temperature to verify if this would have led to the setting of the exchange bias.

Second annealing:

(i) Temperature : ~300°C

(ii) Time : 1 hr
(iii) Cooling field : 200mT
(iv) T_{stop} : 310K
(v) Magnetic response : Isotropic
(vi) Coercive field : 440 Oe

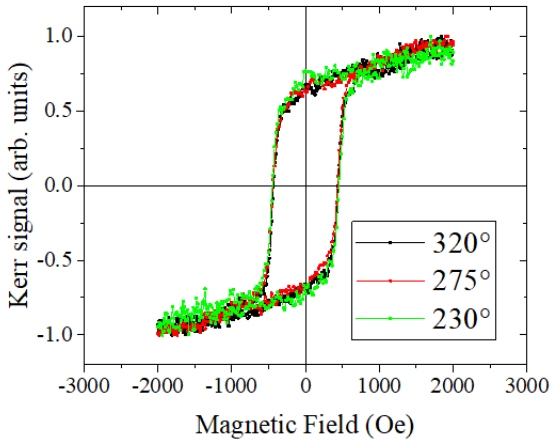

Figure 4.10 - MOKE measurements done on MASK 047 at 320°, 275° and 230° angles at RT after the second annealing.

The second annealing shows a considerable reduction of the coercive field to approximately half of the value of the first annealing (see Figure 4.10), keeping the unsaturation of the magnetization value the same. Exchange bias is still absent.
In order to try forcing the setting of the exchange bias coupling, we played with the parameters of annealing temperature, T_{stop} and the cooling field. As a result, a third annealing was done with the same parameters except for the cooling field, which was increased to 5000 Oe, and the temperature measurement, set at 78 K. Still, no exchange bias was observed, as shown in Figure 4.11. Hence the influence of the cooling field in the absence of exchange bias was rejected.
Another model was proposed building up on the first one that due to the instability of the substrate Lithium Niobate, migration of compounds Li, Nb, oxygen are also possible. These compounds that were possibly formed during the previous annealing could have now diffused in the sample. The diffusion could have considerably reduced the defects that were formed, thereby reducing the coercive field. The unsaturation of magnetization could also be possibly due to the compounds of Li and Nb formed which behave as paramagnetic materials in the presence of a high magnetic field. The suspicion of the presence of an antiferromagnetic interface is weakened due to the explanation of the unsaturation, large coercive field and the absence of exchange bias by the new model.

Third annealing:
(i) Temperature : ~300°C
(ii) Time : 1 hr

(iii) Cooling field : 5000 Oe
(iv) T_{stop} : 78K
(v) Magnetic response : Isotropic
(vi) Coercive field : 720 Oe

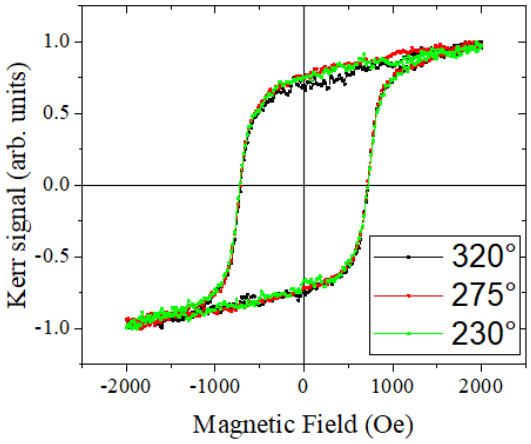

Figure 4.11 - MOKE measurements done on MASK 047 at 320°, 275° and 230° angles at 78K after the third annealing.

In the third annealing, we observe an increase in the coercive field, the presence of magnetization unsaturation and the absence of exchange bias shift (see Figure 4.11). The increase in coercive field was due to measurements taken at low temperature, where the thermal energy is less and energy required for magnetization reversal given by the external applied field is more. Our existing model can explain the unsaturation in the magnetization value. The absence of exchange bias shifts leaves the following possibilities:

i. An antiferromagnetic interface is absent.
ii. The blocking temperature of the antiferromagnetic layer is below 78K
iii. The substrate has an unclean surface that disallows the coupling between the ferromagnetic and the antiferromagnetic layer.

The next step was taken to check for the presence of an antiferromagnetic layer. The sample was annealed again until the magnetic properties were destroyed, as it happened with the first sample shown in Figure 4.7. According to our first model, a complete oxidation of the whole ferromagnetic layer should take place. The magnetically "destroyed" sample was taken for element specific X-ray Photoemission Spectroscopy (XPS) measurements (probe only 1 nm thickness) to check for the presence of antiferromagnetic iron oxides.

Fourth Annealing:

(i) Temperature : ~650°C
(ii) Time : 1 hr
(iii) Cooling field : 5000 Oe

(iv) T_{stop} : 280K
(v) Magnetic response : No signal

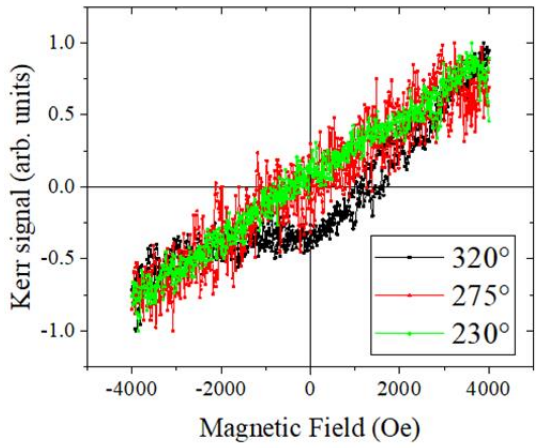

Figure 4.12 - MOKE measurements done on MASK 047 sample on 320°, 275° and 230° angles at 280K after the fourth annealing.

The fourth annealing shows that the magnetic properties of the sample have been destroyed as desired (Figure 4.12). XPS measurements were carried out to further understand the chemistry of the sample at the surface.

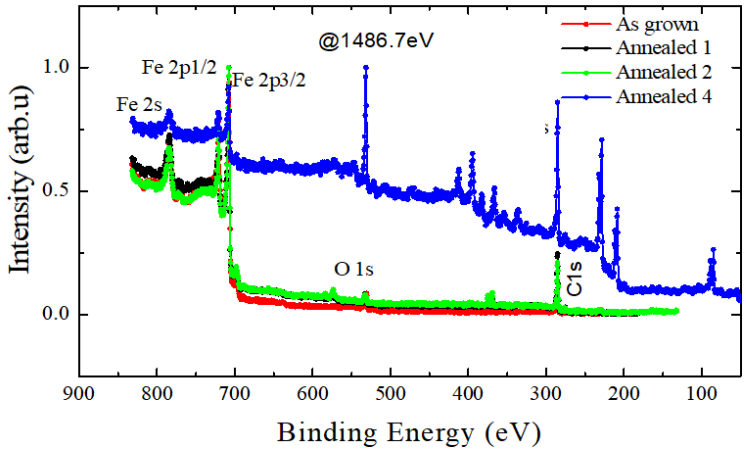

Figure 4.13 - XPS measurements done on MASK 047 during the different steps of annealing.

Without going into a detailed analysis of the spectra, Figure 4.13 shows that after the fourth annealing the XPS spectrum presents several more peaks compared to the spectra measured in the previous steps. Indeed, we can observe peaks due to Nb, Li, and oxygen. Other impurity peaks like that of C, O, CO, etc were also present. This is a sign of a great contamination of the Fe surface upon LNZ annealing, with not only O migration, but also with the migration of the other elements constituting the substrate.

4.2.3 CONCLUSIONS

1. Our studies on amorphous Fe/LNZ samples show the LNZ is unstable and can form compounds of Nb, Li and oxygen under annealing.
2. We suspect that the exchange bias shifts were not observed as the T_b of Fe is below 80K (our system can measure only down to 80K).
3. New samples of Amorphous Ni were deposited on LNZ and annealed under field as T_B of Ni is above 80K. This sample is under study.

Note:

The Ni/LNZ samples that is understudy is chosen because the T_N of NiO (antiferromagnetic material) that will be formed is 525K, hence the T_B is expected to be above 80 K. The literature value of the exchange bias shift due to Ni/NiO interfacial coupling is 16 Oe^2.

The electromagnet used in our MOKE setup, i.e. with the magnetic core in the solenoid, is less sensitive to the measurement of exchange bias shift as small as 16 Oe (literature value). But we found that the electromagnet without the magnetic core is more sensitive (by a factor of 10) to the field measurements. The calibration data taken on the electromagnet with and without the magnetic core are shown below (see Figure 4.14). It shows that the coercive field of the electromagnet without the magnetic coil is close to zero and hence can be sensitive to measurements with accuracy of the order of 1 Oe. This will enable us to observe the expected exchange bias shift in the Ni/LNZ samples.

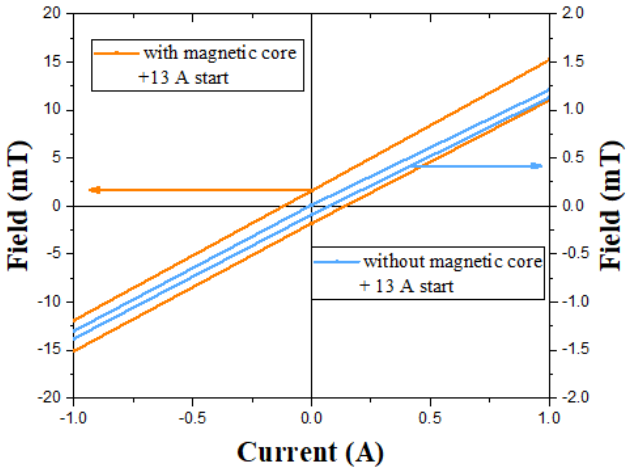

Figure 4.14- Calibration graph of the electromagnet with and without the magnetic core. The Y axis of the data without the core (on the right side) is a factor of 10 less compared to the one with the core (left side).

Chapter 5

Summary and Future scope of the work

5.1. The CoFeB project

5.1.1. Summary

In our CoFeB project, we managed to reach our goal of depositing samples with a low coercive field and an isotropic magnetic response. Here are listed the optimized deposition conditions and the resulting magnetic response:

Optimized Conditions:

(i) Angle of deposition perpendicular to the substrate.
(ii) Deposition at room temperature.
(iii) As grown samples.

Response of the sample under optimized conditions:

(i) Magnetic response: Isotropic
(ii) Coercive field : 50 Oe

Thus, we were able to deposit a soft isotropic ferromagnetic layer that could find further use in ferroelectric/ferromagnetic heterostructures.

5.1.2. Future scope

This set of measurements and calibrations on CoFeB deposition via MBE in the MASK chamber will allow the group of CNR-IOM in Trieste to exploit trustfully this material for more complicated systems, such as multiferroic heterostructures, i.e. systems coupling a ferromagnetic and a ferroelectric/ferroelastic material, or patterned systems. In these cases, the presence of a ferromagnetic material with low coercive field and isotropic response is ideal for observing modifications of the magnetic response through an external parameter, such as voltage-induced strain, charge accumulation or shape effects.

5.2. The Exchange Bias Project

5.2.1. Summary

In this project, we observed that the exchange bias coupling was absent in our sample under different conditions of annealing. This was possibly due to the absence of an antiferromagnetic interface. The successfully observed, by combining MOKE and XPS measurements, that the LNZ substrates are very unstable at high temperatures, and tend to loose oxygen, which migrates and couples with the metallic layer on top of it. Nonetheless, the annealing temperature has to be chosen carefully, since a too high or too long annealing leads to a release of not only oxygen, but also Li, Nb and their compounds towards the sample surface.

5.2.2. Future scope

Despite the difficulty in setting the exchange bias coupling, the trials in inducing a field cooling coupling via oxygen migration led to a calibration of the annealing setup in the MASK chamber, in presence of a magnetic field. This is, by itself, an improvement in the performances of the chamber, which opens the way to other possible experiments involving exchange bias or thermally induced oxygen migration.

Regarding the studied exchange bias project, the study is now focused on Ni/LNZ sample. In this case, the oxygen migration is expected to create an interfacial antiferromagnetic NiO layer, and therefore allow setting an exchange bias coupling.

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Sandra Santhosh

2/10/2019.

BIBLIOGRAPHY

1. Tannous C, Gieraltowski J. The Stoner – Wohlfarth model of ferromagnetism The Stoner – Wohlfarth model of ferromagnetism C Tannous and J Gieraltowski. 2008. doi:10.1088/0143-0807/29/3/008
2. Lukaszew RA, Mitra M, Zhang Z, Yeadon M. P HYSICAL J OURNAL B Exchange bias on epitaxial Ni films due to ultrathin NiO layer. 2005;184:181-184. doi:10.1140/epjb/e2005-00183-6
3. Giovanni M Vinai. Scalability and improvement of exchange bias properties for Thermally Assisted MRAM To cite this version : HAL Id : tel-01558898 Scalability and improvement of exchange bias properties for Thermally Assisted MRAM. 2017.
4. Polewczyk V. Growth of hybrid piezoelectric / magnetostrictive systems for magnetic devices based on surface acoustic wave resonators To cite this version : HAL Id : tel-01882229 soutenance et mis à disposition de l ' ensemble de la Contact : ddoc-theses-contact@univ-. 2018.
5. Teixeira JM, Silva RFA, Ventura J, et al. Domain imaging , MOKE and magnetoresistance studies of CoFeB films for MRAM applications. 2006;126:180-186. doi:10.1016/j.mseb.2005.09.031