A Comprehensive Study of Impact of Growth Conditions on Structural and Magnetic Properties of CZTB Thin Films

by

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A Thesis presented in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Approved June 2015 by the
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August 2015

ABSTRACT

Soft magnetic materials have been studied extensively in the recent past due to their applications in micro-transformers, micro-inductors, spin dependent memories etc. The unique features of these materials are the high frequency operability and high magnetic anisotropy. High uniaxial anisotropy is one of the most important properties for these materials. There are many methods to achieve high anisotropy energy (Hk) which include sputtering with presence of magnetic field, exchange bias and oblique angle sputtering.

This research project focuses on analyzing different growth techniques of thin films of Cobalt, Zirconium Tantalum Boron (CZTB) and the quality of the films resulted. The measurements include magnetic moment measurements using a Vibrating Sample Magnetometer, electrical measurements using 4 point resistivity methods and structural characterization using Scanning Electron Microscopy. Subtle changes in the growth mechanism result in different properties of these films and they are most suited for certain applications.

The growth methods presented in this research are oblique angled sputtering with localized magnetic field and oblique sputtering without presence of magnetic field. The uniaxial anisotropy can be controlled by changing the angle during sputtering. The resulting film of CZTB is tested for magnetic anisotropy and soft magnetism at room temperature by using Lakeshore 7500 Vibrating Sample Magnetometer. The results are presented, analyzed and explained using characterization techniques. Future work includes magnetic field presence during deposition, magnetic devices of this film with giga hertz range operating frequencies.

Dedicated to

My mother and father

ACKNOWLEDGEMENTS

I am thankful to my parents for allowing me to pursue graduate education here in Arizona State University. I sincerely thank Dr. Hongbin Yu for his continued motivation and support all along my masters program. I thank the committee members for their time and opinions on my research, helping me in improving the quality of the work I do. I thank ASU for its awesomeness. This work cannot be completed without the help of Dr. Tingyong Chen and Dr. Nate Newmann. Lastly I thank the almighty for the love and support given in tough times to be able to stand here and present my thesis.

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CHAPTER

1 INTRODUCTION

Motivations

Magnetic materials have gained popularity in the recent past due to wide applications in spintronics, memories, sensors and microwave devices. The key parameters that influence the use of these materials are anisotropy, uniaxial nature, softness to applied field, polarizable nature.

Softness can be attributed to multiple reasons depending on the chemical composition of the material. Spin coupling on multiple layers was considered the most important factor for the softness in epitaxial deposited films. Many combinations of ferromagnetic materials have been explored so far to form efficient ferromagnetic materials with highly soft nature and high uniaxial anisotropy. Widely researched materials include NiFe, CoFe, CoNi, CoZr etc. There are some composite alloys with group V metals in a proportion in the compound. CoZrTa is one such alloy composition.

The characteristics of an ideal soft ferromagnetic material include high anisotropy and softness, high resistivity etc. The reasons for this are explained in this document. CoZrTa is one such composition where the resistivity is much higher compared to films of CoNi, FeCo, and FeNi on a given substrate. Silicon dioxide is used as a substrate which enhances the resistivity but still gives the possibility to make electromagnetic devices out of these films. This research project aims to explore the different growth conditions, their impact on magnetic properties like anisotropy, Coercivity and softness.

Soft magnetic materials have been used in miniature transmission lines, high frequency data transmission, spin dependent memory devices and micro inductors. For these devices to work efficiently, high ferro magnetic resonance frequency is desired. There are multiple ways to increase the ferro magnetic resonance frequency which is proportional to Coercivity Hk and Magnetic Saturation Ms. as Gurvitch et al suggested, the ferro magnetic resonance depends on softness of the magnetic material to the applied field. With a highly soft magnetic material, one can operate the devices made out of these films at giga hertz to tera hertz regions without loss of efficiency. High resistivity is a desired factor for devices operating at high frequencies. That prevents the losses of fields from eddy currents. High Coercivity is another important factor that minimizes the eddy current losses at high frequencies in devices made of magnetic materials. To increase the resistivity, different substrates such as SiO2, n-Si have been experimented so far by researchers. This research project uses Silicon dioxide as the substrate as the resistivity is enhanced and it gives a possibility of making highly efficient miniature electromagnetic devices that can be embedded in the die of a package.

Growth

Growth method is basically divided into epitaxial deposition and sputtered deposition. Epitaxial deposition involves adding multiple layers of different material compositions on top of the existing layers. This has an advantage that the behavior of the device can be precisely controlled by controlling the surface deposition parameters and compositions. Complex ferromagnetic metal alloys can be developed in this method. However the challenges for this method include precise control of thickness and ensuring chemical separation of the layers. This additional epoxy layers in between the desired material compositions can cause an undesired effect in the magnetic performance of the devices made out of the resulting films.

The second method is most widely used and well documented. It involves sputtering the desired composition of materials from different targets onto a single wafer. This method ensures that the thickness and surface roughness are at a minimum as the wafer stage is rotated during deposition. The uniform thickness of the resulting material provides a high quality film that can be used for making high quality devices. Soft magnetic material alloys are formed by combining two or more metals with one metal from the ferromagnetic metals contributing to the polarizable nature. The other metals in the compound support the high anisotropy and softness to applied magnetic field. Many combinations have been experimented with in the last few years with improvements in deposition techniques greatly affecting the quality of the films. Some examples include FeNi, CoNi, and CoZr etc. These materials have variable anisotropic nature and softness depending on their deposition and measurement conditions.

A brief review of recent publications by different authors on soft magnetic materials is presented here. Xiaoqiang et al[1] deposited soft magnetic material compound of FeNi film on Si substrate using oblique sputtering techniques, modulating the anisotropy in the range of 150-300 Oe applied field using different sputtering conditions. The measurements were conducted at room temperature using a Vibrating Sample Magnetometer. Oblique sputtering causing a geometrical hard axis and easy axis is used by the authors. In oblique sputtering methods, the angle is measured with the direction of normal deposition by fixing the wafer and substrate holder during deposition resulting in non-uniform thickness of the target on the substrate. This results in different magnetic properties of the materials as thicknesses and orientation of crystals on the substrate are different for different angles.

Another group from Harvard demonstrated the same effect by oblique sputtering in the presence of magnetic field at around 1200 Oe. This results in polarization of the target particles while being deposited on the substrate. This causes the anisotropy and softness to increase significantly compared to the sputtering conditions without presence of magnetic field.

Recently a group from Harvard worked on combining both methods by having magnetic field present and using oblique angle sputtering techniques. The advantage of the presence of magnetic field is that it acts as another factor for the anisotropy along with the geometrical obliqueness created during sputtering. Almost negligible hysteresis on the easy axis in plane to the applied field was observed in the resulting films.

These works prove the idea behind this project experimentally and theoretically that highly soft and highly anisotropic magnetic materials can be deposited using oblique angle and magnetic field presence during sputtering.

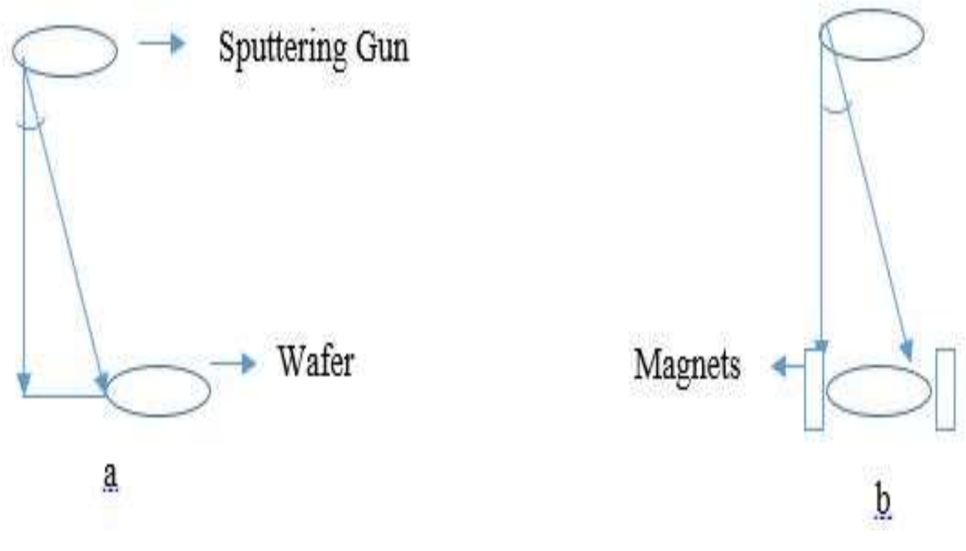

Figure 1 a. Oblique sputtering without magnetic field b. With magnetic field

Effects of growth on device performance

The methods mentioned so far have different impacts on the properties of the films shown. Oblique Sputtering has been shown to result in films with high anisotropy of the orders of 300Oe and the coercivity of 150-200Oe. Saturation fields of about 600 Oe have been shown by these films[2]. Application of external fields enhances the softness even further and the uniaxial anisotropy is in the order of 300 Oe. Saturation fields of about 800 Oe have been shown by these films in the work done by Liangliang Li et al[3]. This project aims at exploring the different growth conditions of the magnetic perm alloy CoZrTa on SiO_2 substrate. Sputtering under oblique angles and oblique sputtering with application of local magnetic fields has been studied.

Effects of these conditions on the anisotropy and softness are studied using VSM. The effects of growth conditions are explained in the later sections.

Scope of this work

Part one of this work focuses on deposition of magnetic materials on silicon substrates using oblique angle sputtering technique. Differences in magnetic behavior of the resulting materials is explained using data collected by measuring the samples with a Lakeshore 7500 VSM. Measurements are done at room temperature and sweeping fields in a range chosen to observe hysteresis of the material along easy and hard axis of the film.

Scanning Electron Microscopy is performed on the resulting films of every growth method and documented. Oblique columns and the orientation of the easy axis along the direction of inclined micro column structures is observed and reported.

Resistivity measurements are done on the sample to observe the effects of varying thickness on the sample with varying angle of deposition. 4 point probe method is used to measure the sheet resistance of the films and then the thickness calculated from the SEM measurements is used to determine the resistivity.

So, this research project is a comprehensive study of the impacts of different growth conditions on the magnetic, electric and structural properties of the thin films of Cobalt Zirconium Tantalum deposited a (111) Silicon Substrate. The results of characterization are explained with reasons attributed to structural and chemical studies of these thin films.

CHAPTER

2 EXPERIMENTAL TOOLS

Tools Used

In this project, the tools used range from deposition, growth, control of thickness to measurement of magnetic, structural and electrical characteristics of the resulting films. The main experimental tools used are:

- Magnetron Sputtering System
- Vibrating Sample Magnetometer
- 4 point probe Resistance measurement system
- Scanning Electron Microscope

We collaborated with Dr. Jiang's group heavily in the growth mechanism. Dr. Nate Newmann and Dr. Tingyong Chen helped us with the measurements of magnetic properties of the films. The challenge was to deposit the films with magnetic fields presence and it required extra efforts to ensure that the fields are in the desired direction with desired strengths. Also the magnets had to be sealed carefully to not impact the quality of the films grown in the clean room. Annealing with the presence of magnetic fields was possible with the help of LECSSS staff and GWC support staff.

Measurements using Scanning Electron Microscopy were done with the help of systems from the LECSSS. Measurements using the Vibrating Sample magnetometer were done in collaboration with Dr. Tingyong Chen's group and Dr. Nate Newmann's group. The following chapter briefly describes the tools used in this project, their experimental set up, conditions used in deposition and measurements of the thin films of CZTB on SiO2 substrates.

Magnetron Sputtering System

The sputtering system used was a Lesker 1 Sputtering system in the ISO Class 4 Clean room in the Engineering Research Center of Arizona State University. The following pictures show the set up and arrangement of the system for the sputtering method of deposition.

Figure 2 Images of sputtering system set up for oblique sputtering method

The image shows the oblique sputtering method set up used for growth of thin films of CZTB on Si substrates. This system is sputter down type of arrangement with 2 DC guns; 1 RF gun, 3” Diameter targets; 4” holder for samples.

Vibrating Sample Magnetometer

A Vibrating Sample Magnetometer is a device to measure the magnetic moment of magnetic materials. It uses two electromagnets that provide the permanent field and two pick up coils measuring the moment of the sample. The Sample is vibrated perpendicular to the direction of the field at a fixed frequency. This is an accurate and convenient way to measure the magnetic moment of materials without causing permanent changes in the structure and alignment of magnetic particles in the material. In this research, thin films of magnetic material thickness 200-300nm on SiO2 substrate of thickness 100um are characterized for magnetic moment using Lakeshore 7500 VSM at room temperature. Lakeshore 7500 VSM has two permanent magnets providing a field and the electromagnet turns can be changed to vary the field during measurement. The pickup coils can measure magnetic moment of the material on the films. A gauss magnetometer monitors the field strengths of the applied field. A holder is placed between the electromagnet coils to align in the direction of the field. This is the in plane measurement position of the sample. The field lines are in plane to the material on the substrate of the film. Now the sample is vibrated at a fixed frequency in a direction perpendicular to the field. This causes the sample to align its particles in the direction of the field and this rapid and constant movement of particles in either direction results in a net moment on the sample. Thus the moment shown by the sample can be measured by the VSM.

The most convenient feature of this VSM is its ability to measure in plane and out of plane magnetic moment of the samples with ease and accuracy. There are different holders for each kind of measurement as shown in the pictures below. One can easily measure the change of moment with the direction of applied field by simply by rotating the head drive from 0-360 degrees.

Figure 3. Rotatable head drive of VSM

Also, the measurements are done at room temperature and temperature can be swept by heating the sample through radiative heating from induction coils. This mode of operation is not set up in our measurements as we intended to observe the effects of growth conditions at room temperature.

Figure 4 VSM set up with sample inserted and gauss meter enabled

4 Point Probe Resistance Measurement

4 point probe resistance measurement system was used for the sheet resistance measurements of thin films of CZTB on SiO_2 substrates. The wafer dimensions of 4 inchX4 inch made it possible to measure the variation of sheet resistance with thickness and the angle of sputtering. It can be seen here in the following pictures that the setup is fairly simple and easy to measure the sheet resistance of a film of minimum dimensions of 1inX1inch.

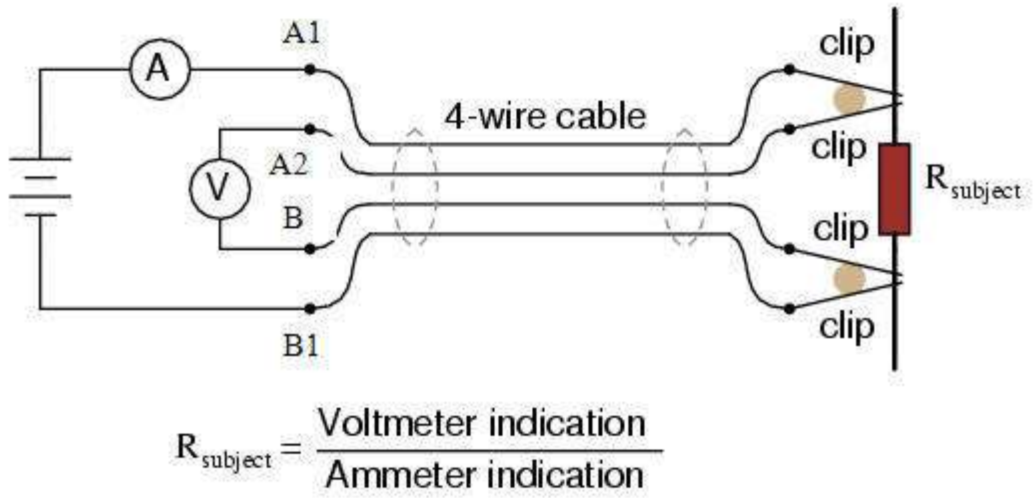

Figure 5 Schematic of 4 point resistance measurement. source: sciencebuddies.org

Scanning electron microscope

A Hitachi S-4700-II Scanning Electron Microscope was used to characterize the thin films for their structural properties. The resolution of the tools is 100nm and the thickness of the magnetic material CZTB deposited varies from 100-300nm across different deposition conditions. So this was the perfect system to observe the structural properties of the materials and their changes with annealing.

As seen in the images below, the samples are mounted on the ceramic slab and then they are observed through the scanning electron microscope on a cross section geometry angle.

This view gives the possibility to observe the structures that stand out of plane to the surface of the samples' substrate. The resolution is varied in order to understand the density and relative dimensions of the structures to the substrate itself.

The samples are again scanned under the microscope after annealing them. This completes the structural studies part of this thesis and helps better understand the reasons behind certain interesting properties shown by these materials under different magnetic and electrical conditions. Also, the impact of magnetic fields during the sputtering conditions on the structural properties of the magnetic materials will be better understood by this study. The following is a brief summary of the setup and conditions used to characterize the thin films of CZTB on 111 SiO2 substrate.

Figure 6. Hitachi S-4700-II FESEM measurement system. Courtesy: asu.edu

CHAPTER

3 GROWTH

Background

Soft magnetic materials have become widely used in magnetic spin based memory devices, tunable filters, microwave frequency micro antennas, high frequency on chip inductors.

Recently a group from UCLA [4] demonstrated giga hertz frequency operation of antennas made using these materials. CZTB is a perm alloy in this category. It is widely used in inductors with high resonant frequency requirements. With on chip inductors being used in the latest semiconductor packages, this material promises to be an efficient soft magnetic material that can be used in the future developments. Growth of the CZTB thin films can be done in multiple ways. The method of oblique sputtering has been demonstrated to cause a geometrically aligned easy axis on the film by Wang[5] et al. In this research, reactive magnetron sputtering has been chosen as the method to grow the films. The reasons being precise control of angle and convenience to cause change in angles of the obliqueness during deposition. Characterization of the films has been done in both optical and magnetic means using Scanning Electron Microscopy and Vibrating Sample Magnetometer respectively. Oblique columns resulting from the oblique sputtering can be identified in the optical method of characterization. The dimensions of the columns relative to the thickness of the sample can be understood from these characterizations.

Magnetic hysteresis can be observed from the magnetic moment measurements. Saturation fields are well documented for each sample deposited in different methods. The softness and the uniaxial anisotropy of the materials resulting can be understood from these measurements. In this research, thin films with different thicknesses and different magnetic moments with unique anisotropy properties are observed and documented.

Oblique sputtering without presence of magnetic field

In this method, reactive magnetron sputtering is the mechanism used for growth of thin films of CZTB on SiO2 (111) substrate. Vacuum is maintained at a pressure of 4 atm.

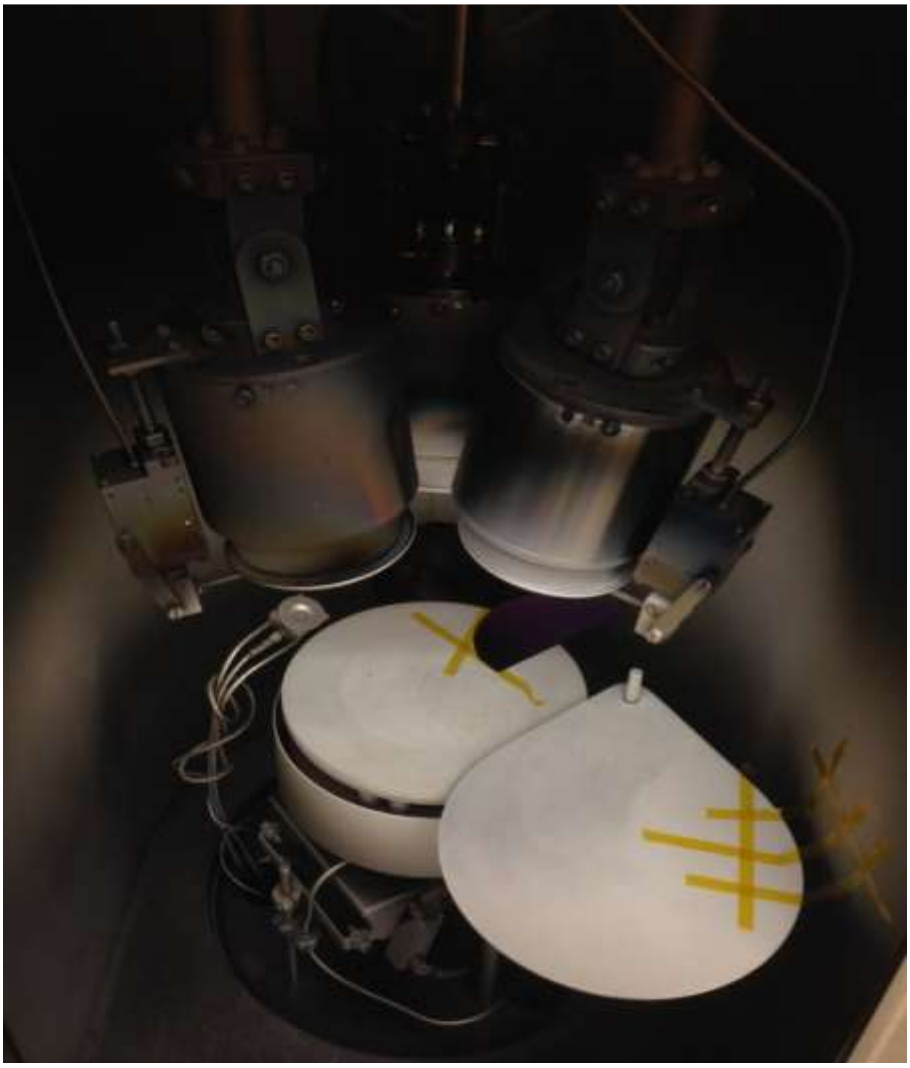

Figure 7 Sputtering system set up for oblique sputtering without magnetic field

In this method, the wafer is placed at a distance from the center of the sputtering gun with the shutter left open. The sample is not rotated to maintain the gradient during sputtering. The dimensions of the wafer are 4 inch X 4 inch. When the angle needs to be increased, the wafer is pushed further apart from the center of the sputtering gun. The materials from the target are thus supposed to fall on the wafer at an oblique angle unlike the regular sputtering. The differences between oblique sputtering and regular sputtering with respect to resulting film properties are given in this table.

Table 1 Differences in regular and oblique methods of sputtering

	Regular sputtering	Oblique Sputtering
Thickness	Uniform	Gradient
Material deposition	Layered	Columns inclined at the desired angle
Optical characterization	Normal	Cross section
Magnetic properties	No definite easy axis determined during sputtering	Easy Axis aligns to the direction of the oblique angle
Resistivity	Uniform sheet thickness across the surface results in uniform sheet resistance	Non uniform thickness of the materials across the surface result in sheet resistance

The oblique angle of sputtering assists in aligning the easy axis of the film with the geometrical angle of sputtering. It becomes really easy to identify the axes of magnetism and thus makes fabrication of devices on this film much efficient.

Oblique Sputtering with presence of localized magnetic field

Figure 8. Sputtering with presence of magnetic field during sputtering

Application of field during sputtering has been demonstrated by Pedra et al[4] in their work on Cobalt Zirconium films. They were able to incline the stage in sputtering at a desired angle and apply a field of 1200 Oe across the wafer. They were able to observe the easy and hard axis distinction with much ease once they apply the field. A residual magnetism of about 20 Oe was observed. Taking their work as a basis, we tried to work on growing films without the inclined wedge and applied field. The angles are changed by calculating the distance from the center of the gun that would give a desired angle of deposition on a certain part of the wafer.

Using those calculations, the stage was moved to certain locations in the chamber to meet the requirements. This resulted in creating the angle during sputtering relatively with less effort than using the inclined wedge.

To be able to set up a magnetic field during sputtering, the magnets are placed on either side of a set of glass slides acting as a local stage. They are then sealed using carbon tapes to that location on the stage of the sputtering system. Also, the magnets are insulated from the sputtering plasma by using copper tapes.

Once the distances are calculated, the above mentioned set up is made to create a local magnetic fields with strengths up to 0.07-0.1T i.e. up to 1000 Oe. This resulted in a uniform distribution of field across the surface of the film unlike the previous work where the field at the center was about 1200 Oe but gradually increased on either side of the center.

This experiment was done to achieve a better aligned easy axis and softer magnetic film. The images show the setup of the magnetic fields and the glass slides used as a local stage to bring up the film in between those magnets. Now with the fields and the rotation off, the samples are grown in the sputtering chamber.

To control the thickness of the samples grown in the chamber the following methods are employed. Since, magnetic material is being deposited and there are magnets that attract the material towards them, this makes the localized magnetic field more efficient in terms of the material density around the local stages created. Also, one of the depositions had an angle of 0 requirement i.e. the local stage directly under the sputtering gun. This initially was not perceived as a problem to parallel depositions at other angles like 45 or 60. But due to the same phenomenon of magnetic attraction forces drawing the plasma towards them, the 0 degree angle localized stage had more material deposited compared to the 45 degree one. To avoid this in future depositions, we used alternate magnetic field directions and precise calculations to place the localized stages so that we get a uniform thickness on similar locations of multiple samples that were being deposited in a single run.

Now the stages are set and a wafer of 1in X 1in was placed on the local stages. The conditions used in this run were a temperature of 30C, pressure of 5X10-2 Pa, Atmosphere of Ar gas at atm pressure as shown in these figures.

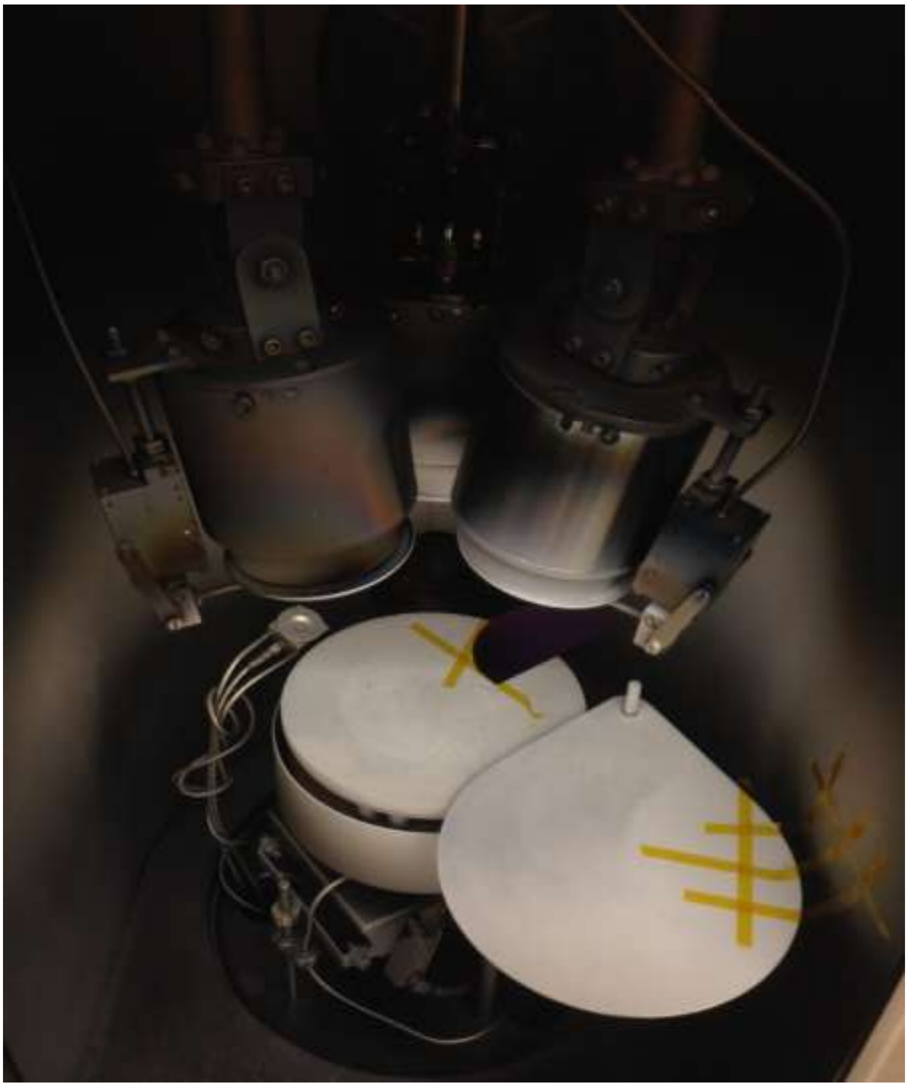

Figure 9 Set up of sputtering for oblique sputtering without field

4 different runs were done as part of the growth related studies. They are as follows.

Run1. Oblique sputtering without the presence of magnetic field. A whole wafer with one side is put at the far edge of the stage.

In Lesker 1 (Kurt J. Company) sputtering system, a thin adhesive layer of Cr of 20nm is deposited on a Si wafer coated with SiO_2. The applied power is 200W and deposition rate is 2.2 A/s. Then 200 nm of CO/B/Zr/Ta is deposited. The applied power is 200W and deposition rate is 1.4 A/s. The Base pressure for this run is 7e-7 Torr. With Argon flow, the sputter capman pressure is 3mTorr. Resulting films had an oblique angle calculated as from 0 to 60 degree across the 4inX4in wafer.

Run2. Oblique sputtering with presence of localized magnetic field. The magnetic direction is orthogonal to the near to far direction. One is put under the gun (~0 degree). The other is put at the far edge of the stage (~60 degree). In Lesker 1 (Kurt J. Company) sputtering system, a thin adhesive layer of Cr of 5nm is deposited on a Si wafer coated with SiO_2. The applied power is 100W and deposition rate is 0.6 A/s. Then 300 nm of CO/B/Zr/Ta is deposited. The applied power is 250W and deposition rate is 0.9 A/s. The Base pressure for this run is 1e-6 Torr. With Argon flow, the sputter capman pressure is 3mTorr.

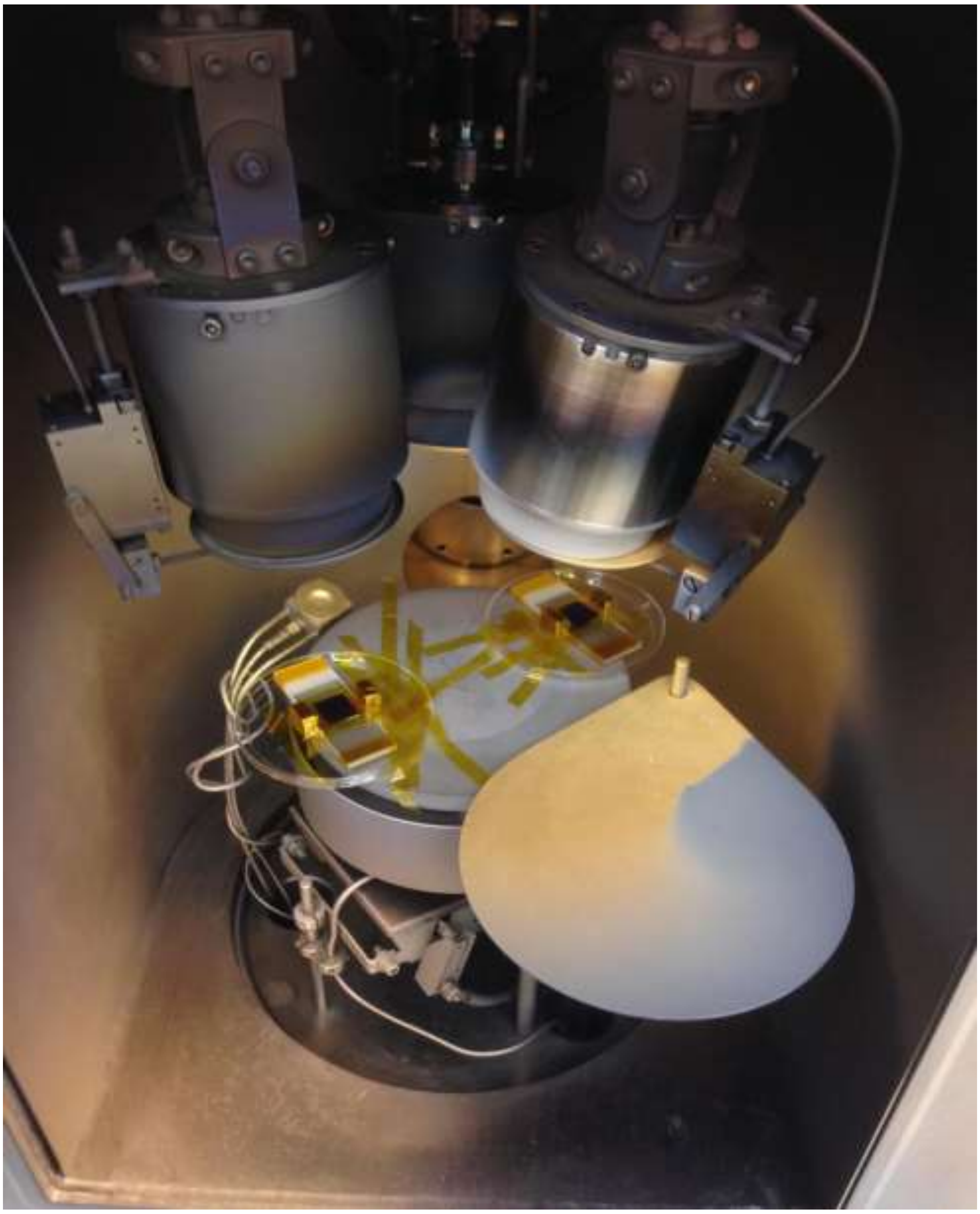

Figure 10 Sputtering with magnetic field along easy axis direction

Resulting films had an oblique angle sputtering of 0 degree and 30 degree.

Run 3: Oblique sputtering with presence of localized magnetic field

Figure 11 Sputtering with field in easy axis direction angles of 30-60 degrees
The magnetic direction is parallel to the near to far direction. One is at the center of the stage (~25 degree). The other is put at the far edge of the stage (~60 degree).

In Lesker 1 (Kurt J. Company) sputtering system, a thin adhesive layer of Cr of 5nm is deposited on a Si wafer coated with SiO2. The applied power is 100W and deposition rate is 0.6 A/s. Then 300 nm of CO/B/Zr/Ta is deposited. The applied power is 200W and deposition rate is 1.1 A/s. The Base pressure for this run is 1e-6 Torr. With Argon flow, the sputter capman pressure is 3mTorr.Resulting films had an oblique angle sputtering of 45 and 60 degree.

Run 4: Oblique sputtering without presence of magnetic fields

The middle of the wafer is at the far edge of the stage (40~75 degree).

In Lesker 1 (Kurt J. Company) sputtering system, a thin adhesive layer of Cr of 5nm is deposited on a Si wafer coated with SiO2. The applied power is 100W and deposition rate is 0.6 A/s. Then 300 nm of CO/B/Zr/Ta is deposited. The applied power is 200W and deposition rate is 1.1 A/s. The Base pressure for this run is 1.2e-6 Torr. With Argon flow, the sputter capman pressure is 3mTorr. Resulting films had an oblique angle sputtering of 45-75 degrees on a 4 in X 2 in wafer.

Figure 12 Sputtering without magnetic fields in angles of 45-75 degrees

Figure 13. Sample run 4. 45-75 degree angle

Table 2 Deposition runs, conditions and results

Property\Run	**1**	**2**	**3**	**4**	**5**
Angles	**0-60**	**0,60**	**30,60**	**45-75**	**20-70**
Magnetic field direction	**None**	**Normal to near-far angle**	**Parallel to near-far angle**	**None**	**None**
Notations used	**1-0,1-30,1-45,1-60**	**2-0,2-60**	**3-30,3-60**	**4-45,4-55,4-75**	**5-60**

CHAPTER

4 CHARACTERIZATION

Measurements using 4 point probe method

A 4 point probe method is the most easiest and reliable method of measuring the sheet resistance of a given sample. So it was used to measure the sheet resistance of the small 4mmx4mm samples cleaved from the wafer precisely at locations that give certain angles.

So the samples taken at 0, 30, 45, 61 and 71 degree to the sputtering gun are characterized for electrical resistance using this 4 point probe method. The thickness of the material on the films gradually decreases with the distance from the sputtering gun. But for the 4mmX4mm samples, the variation is quite minimum and neglected. This assumption makes it easier to calculate the resistivity provided a thickness is known. SEM measurements done prior to this give the thickness of the films and then they are measured for electrical sheet resistance. The instrument used was FPP-5000-4 point probe method. The following sheet resistances were observed.

Table 3 Resistivity measurements of deposition run 1

Sample\Property	Sheet Resistance per □	Resistivity in Ωcm
1-0	0.422	0.422
1-30	0.506	0.506
1-45	0.611	0.611
1-50	0.894	0.894
0-60	1.031	1.031

The measurement is done in a cleanroom environment to minimize the contamination from other particles. The following are the results of the measurements.

Table 4 Resistivity measurements of deposition run 2

Sample\Property	Sheet Resistance per □	Resistivity in Ωcm
2-0	0.546	0.422
2-60	0.622	0.506

Table 5 Resistivity measurements of deposition run 4

Sample\Property	Sheet Resistance per □	Resistivity in Ωcm
4-45	1.431	0.422
4-55	22.8	0.506
4-60	40.7	0.611
4-65	99.4	0.894
4-75	105.1	1.031

Table 6 Resistivity measurements of deposition run 5

Sample\Property	Sheet Resistance/ □	Resistivity in Ωcm
5-20	20.5	0.422
5-30	29.6	0.506
5-45	62.0	0.611
5-60	118	0.894
5-70	95.2	1.031

Measurements using VSM

In this project, the goal is to make a softer and a sample with more uniaxial anisotropy. Oblique sputtering with and without magnetic field is done to make different thin films of CZTB on SiO2. Each film has a different thickness and samples cleaved from each of the wafers are characterized for in plane uniaxial anisotropy and hysteresis properties.

The method chosen for the analysis of anisotropy and the softness is as follows. The magnetic moment of the material follows a hysteresis pattern when the field is swept to and from a fixed reference level. So, different ranges are selected for different samples based on their saturation magnetization. For some samples it was close to 800 Oe whereas for others it went up to 2400 Oe. Once the saturation fields are identified, sweeping the field up to that range on either side of the Y-axis i.e. the moment axis will give us a clear graph showing the softness of the material and the hysteresis along a chosen magnetic axis direction.

Similarly, the process is repeated for the other axis direction and graphs are documented. Comparing both axes results on a single graph gives the anisotropy values of the material on the thin film and a much better understanding of the softness of the materials to the applied field.

Figure 3 VSM characterization of the sample

The following are the results from Lakeshore 7500 VSM measuring the magnetic moment of samples with varying field applied.

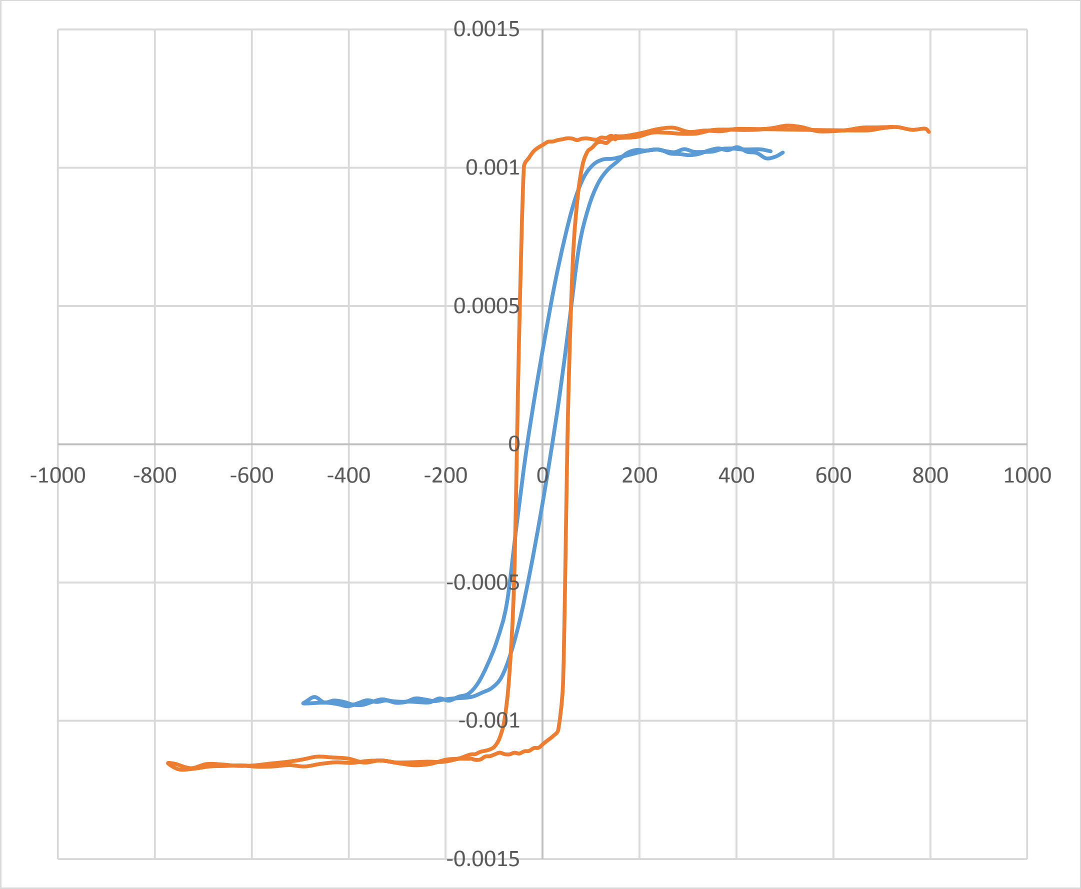

Figure 4 VSM measurement of sample 1-60. Refer to table 2

The above graph shows the magnetic moment for an obliquely sputtered sample at an angle of 60 degrees with the Sputtering gun. Inferences can be made from the graph that the saturation magnetic field of 255 Oe is present for the sample. The easy axis graph represented by color orange and the hard axis graph by color blue have different saturation field strengths.

The following is another result of the same deposition run.

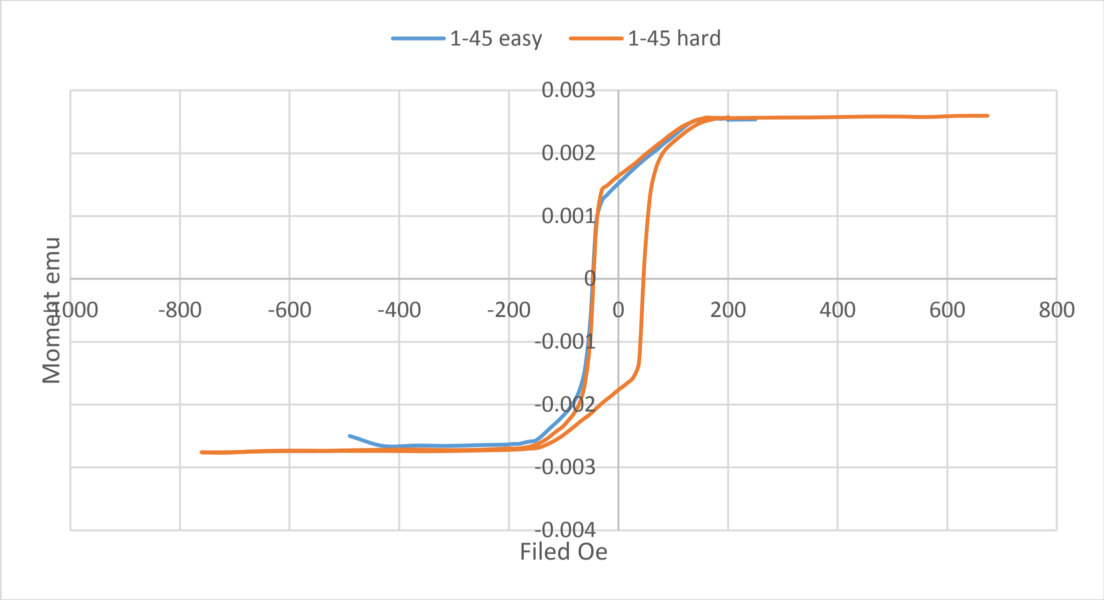

Figure 5 VSM measurement of sample 1-45

The above graph shows the magnetic moment variation with applied filed in a sample deposited at 45 degree angle to the sputtering gun. This result does not show a clear anisotropy but the saturation fields of 200 Oe are maintained constant from the previous result. The following results are for the film deposited at 30 degree angle in the same deposition run.

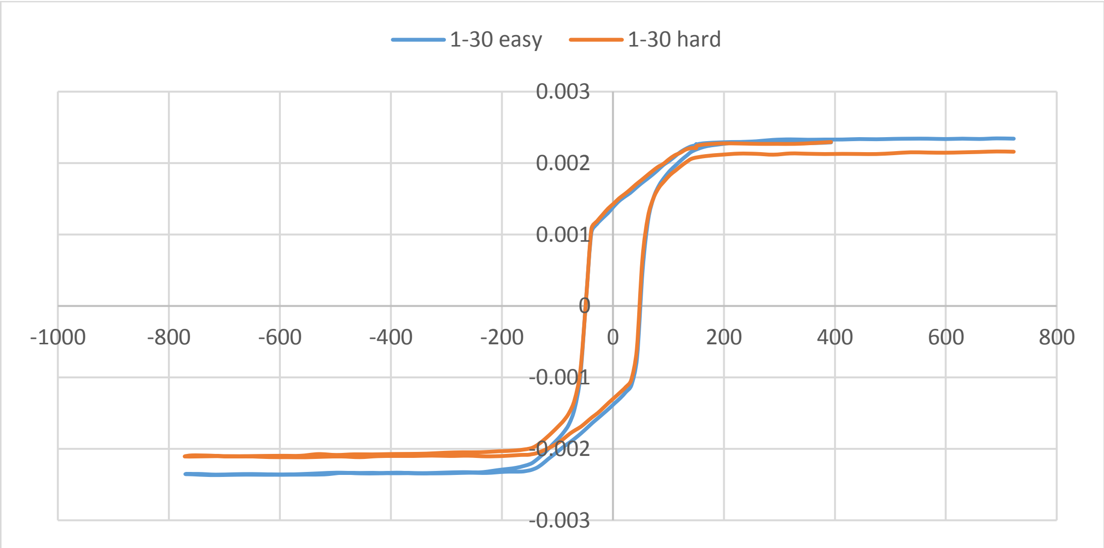

Figure 6 VSM measurements of sample 1-30

The above graph shows the Ms of easy and hard axis is not much different. The coercivity is same for both easy and hard axis. Also, the anisotropy is very minimal. This shows that this angle of deposition is not desired for high anisotropy and soft magnetic film extraction methods.

The following discussion is on the effects of magnetic field presence during deposition. During the second sputtering run, magnets were placed across the film to create local magnetic fields of strength 0.07 T so that the effects of field can be studied. There were two possible options to explore. The scenario where the field is parallel to the oblique angle created and another where the field is perpendicular to the oblique angle created due to placing the sample at an offset distance on the stage from directly below the center of the sputtering gun. The VSM measurements revealed the following observations.

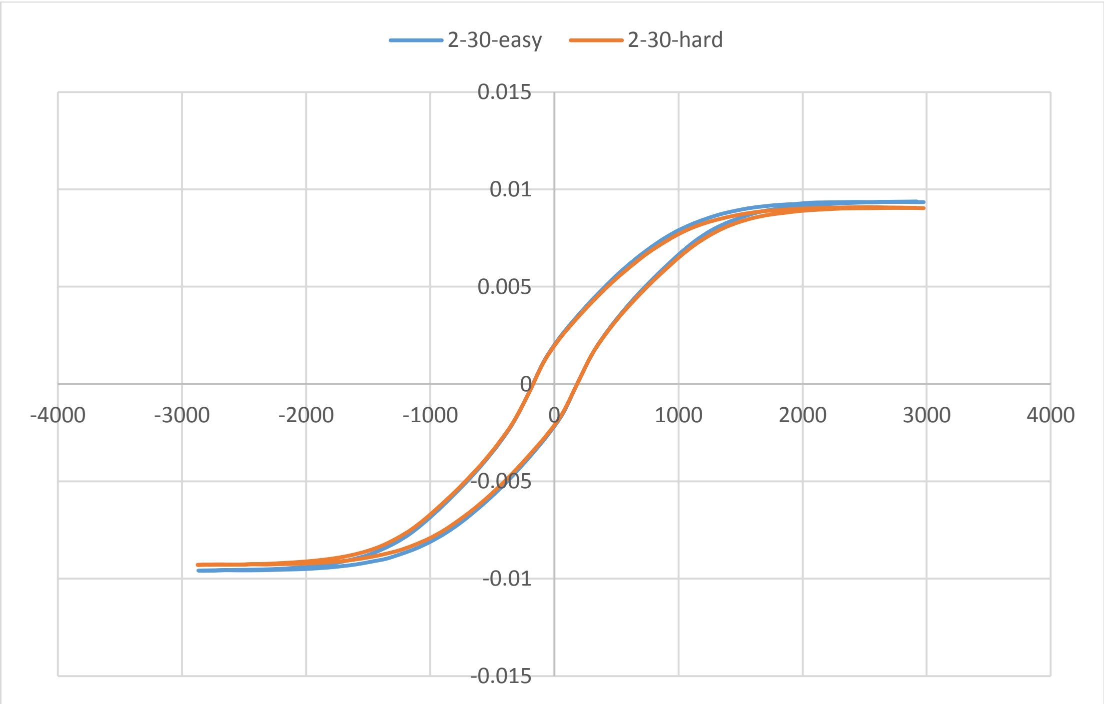

Figure 7 VSM measurements of sample 2-0. Refer table 2 for notations

The saturation magnetism is at 1700 Oe. This is due to the fact that the applied field induces an opposing stress to the geometrically induced angular stress. This sample is deposited directly under the sputtering gun so that no angle is created by the oblique sputtering.

The following result is of the sample deposited with magnetic field perpendicular to the direction of obliqueness in the same deposition run as above.

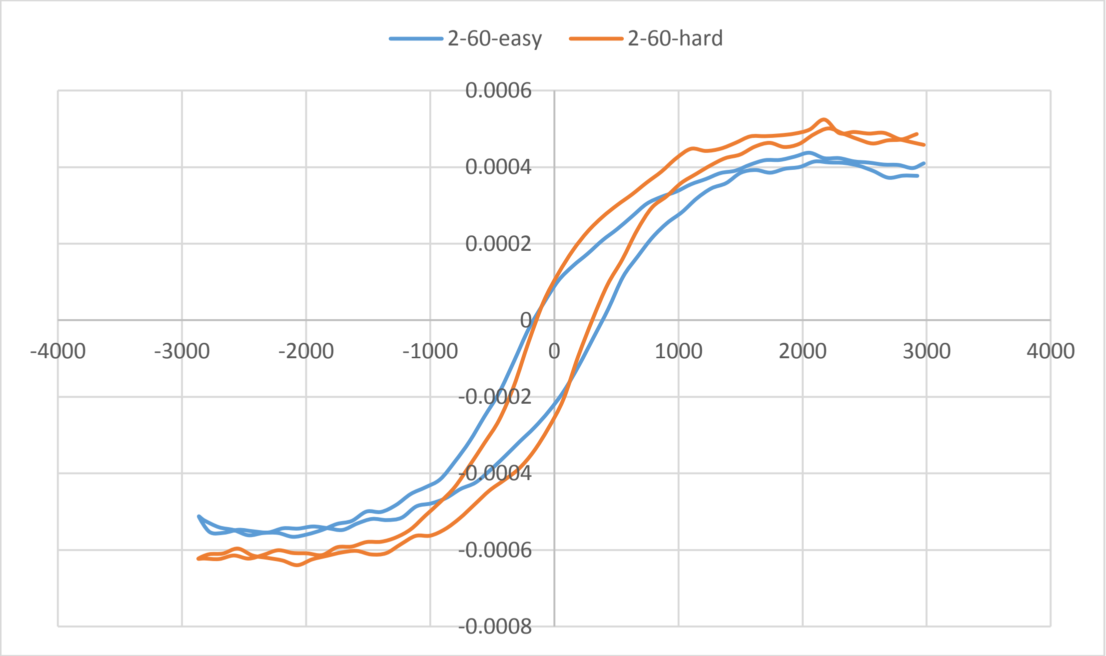

Figure 8 VSM measurements of sample 2-60

So, the structure of the material on the thin film is not an oblique column or stripe structure that induces the soft magnetism in the film. The forces of magnetic field in the direction perpendicular to the obliqueness created by the deposition.

The following result is of the sample 3-30 from the VSM.

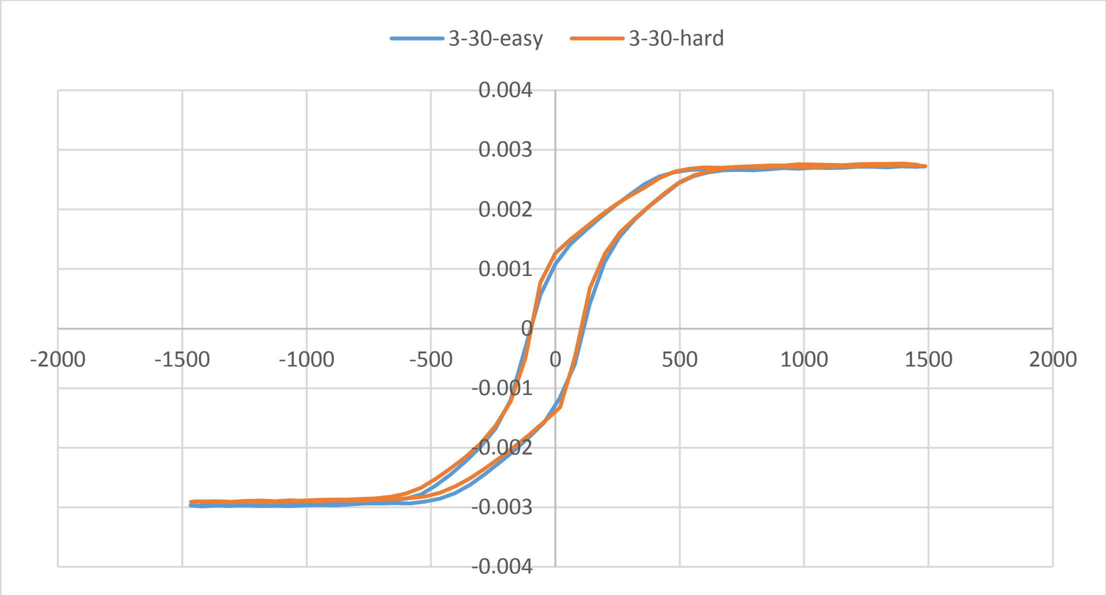

Figure 20. VSM measurements of sample 3-30.

As the above graph shows, the saturation magnetism of the sample is 700 Oe, much lesser than the sample 2-60. The reason is that this sample had magnetic field across the sample in the direction of the oblique angle created by the sputtering set up shown in Figure 2.3**.**

The following result is of the sample 3-60 deposited at a much oblique angle of 60 degree in the same run as above.

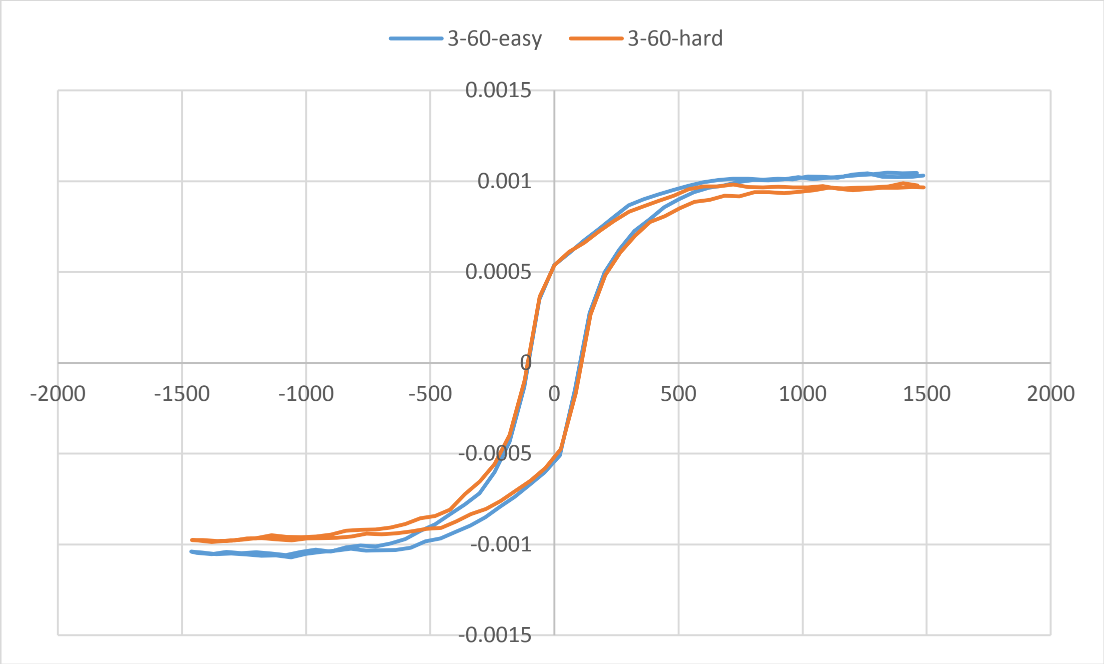

Figure 21. VSM measurement of sample 3-60

The above result is of sample 3-60. In this run the magnetic field is across the sample aligned to the oblique angle created during the sputtering. The saturation magnetism of 650 Oe is seen here. The reasons are that the angle of sputtering is larger than the previous sample which reduces the magnetic hardness of the material. There is no clear easy axis on this sample and the reasons are discussed in the analysis section.

The following result is from the sample 4-45. This deposition had the oblique angle ranging from 45 to 75 degrees with the sputtering gun. There has been no magnetic field applied during the deposition. The saturation magnetism of about 350 Oe is observed from the VSM measurements. There is a mixed axis phenomenon in this sample with no clear easy and hard axis. This result confirms our expectation that the angle of sputtering needs to be more than 55 degrees in this arrangement to see any anisotropy clearly.

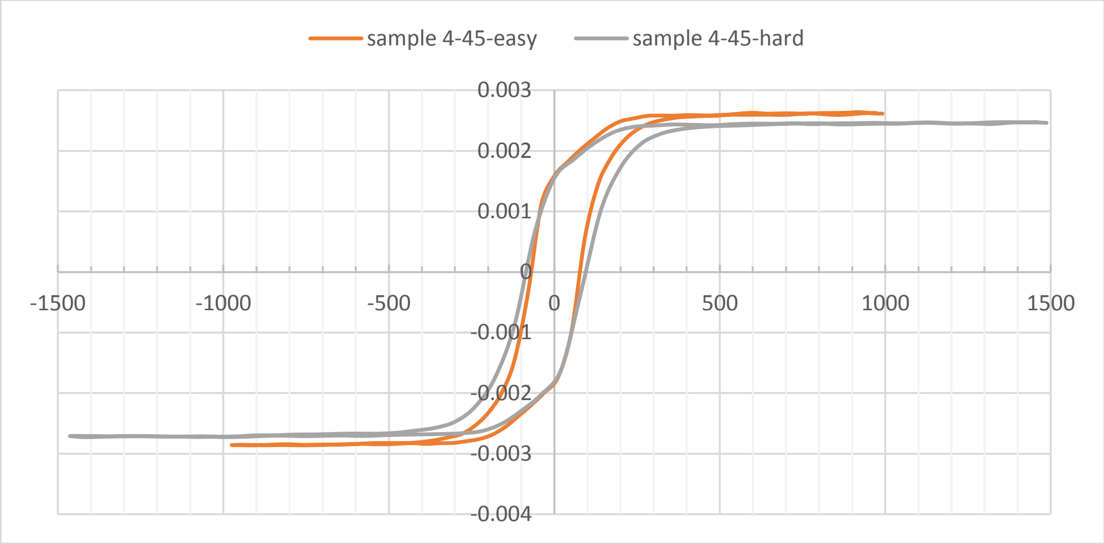

Figure 22. VSM measurement of sample 4-45

The following graph is the result of VSM measurements of sample 4-2 deposited in the same run as above and at an angle 55 degrees.

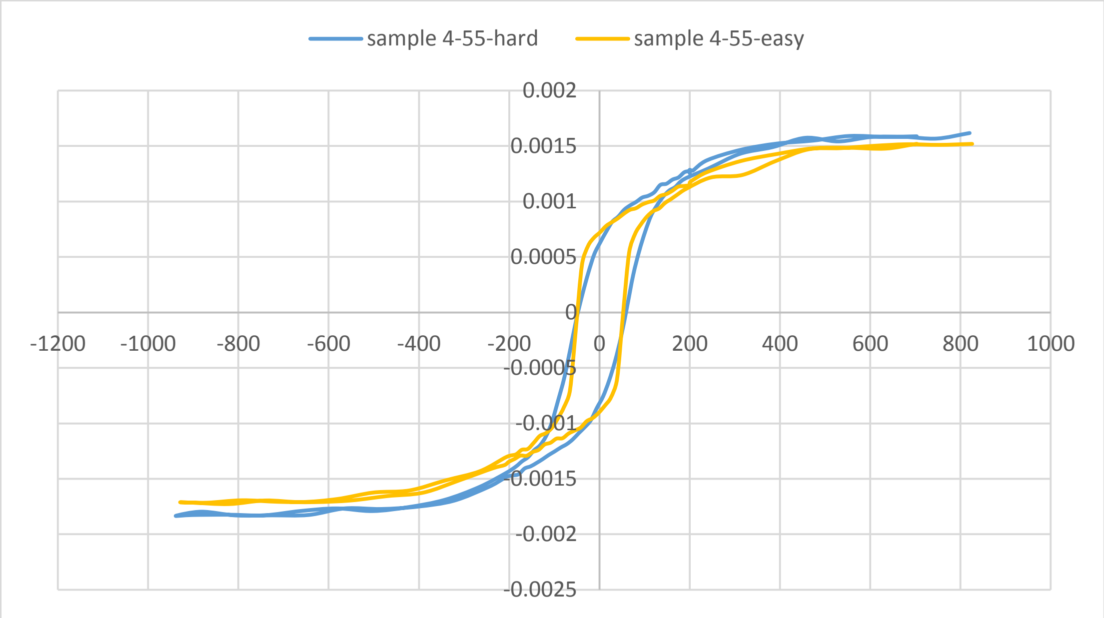

Figure 9. VSM measurement of sample 4-55

As seen in the above graph, the easy and hard axis of magnetism show different saturation fields showing uni axial anisotropy. The saturation fields of 400 Oe are shown here by the sample. This is an indication that the softness of the material at this angle is much higher than at 45 degree angle.

The following is the VSM measurement result of the sample 4-60. This sample is deposited during the same run as the above sample, with no magnetic field applied. The angle of obliqueness with the sputtering gun is 60 degrees.

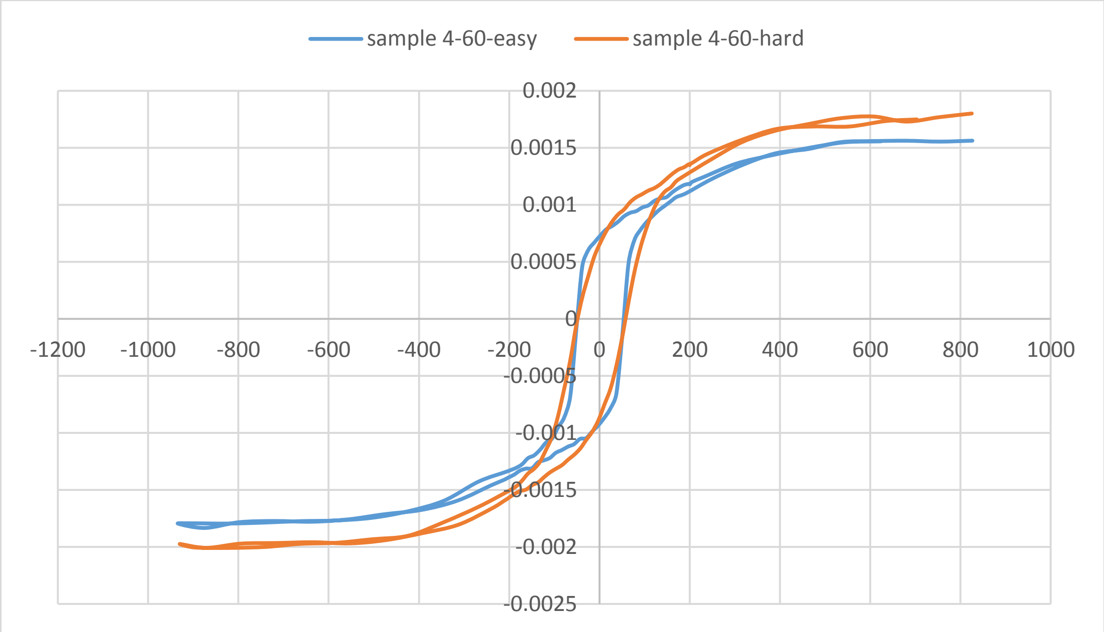

Figure 10. VSM measurement of sample 4-60

The graph shows the saturation fields of 600 Oe in the easy axis orientation and about 800 Oe in the hard axis orientation. The anisotropy though not much higher than the 55 degree obliquely sputtered sample, it is considerable.

The following is a VSM measurement of the sample 5-60.

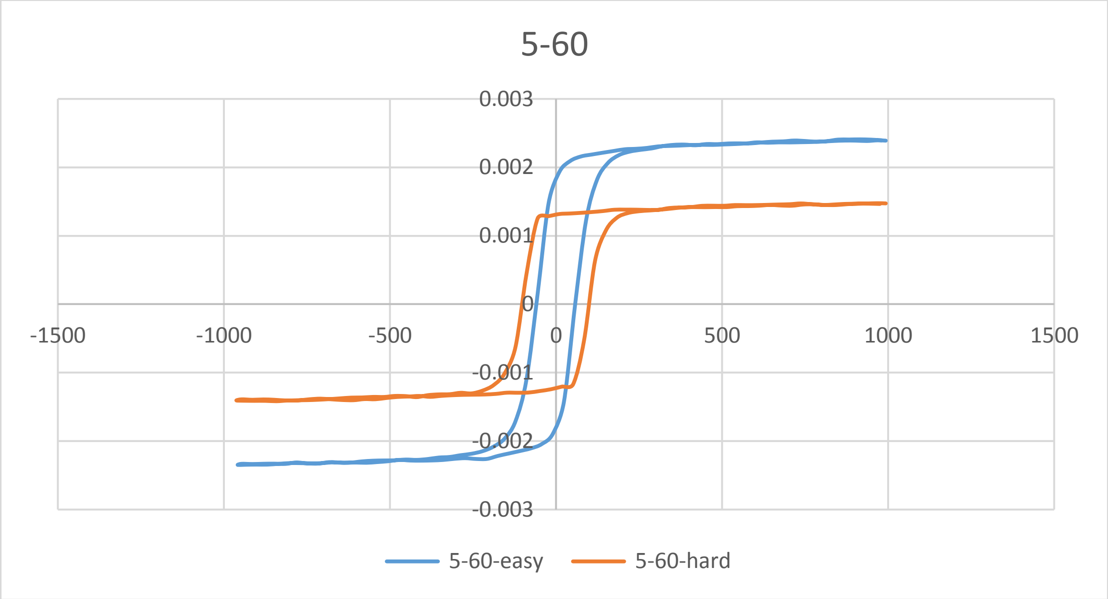

Figure 11 VSM measurement of sample 5-60

The clear easy and hard axis can be observed and the anisotropy is much higher in this sample than the previous deposition runs.

Structural Characterization

The structural characterization of the samples is done to study the effects of growth on the structure of CZTB thin film. The thickness of the films and changes in the structure with applied field during deposition, post deposition annealing can be studied clearly.

SEM can also be used to measure the thickness of the sample using cross section geometry observations. So the method used to analyze these films for structural properties is done on cross section geometry.

The SEM image below shown is the sample 2-0. In this run magnetic field perpendicular to the near-far axis.

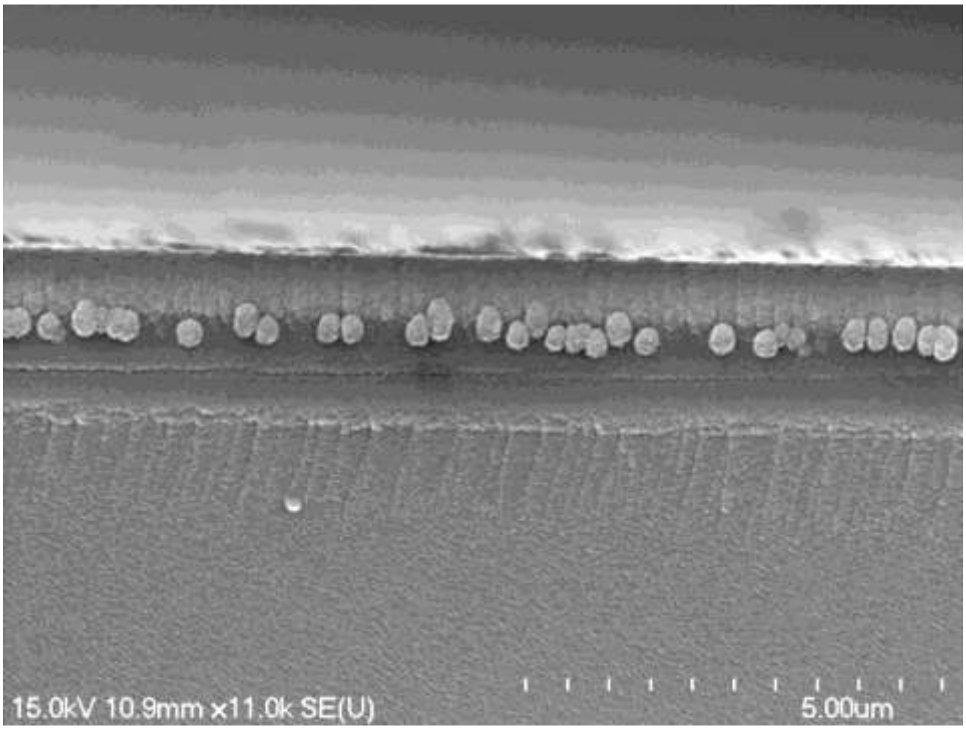

Figure 12. SEM image to oblique columns in sample 2-0

The following SEM image is of the sample 2-60.

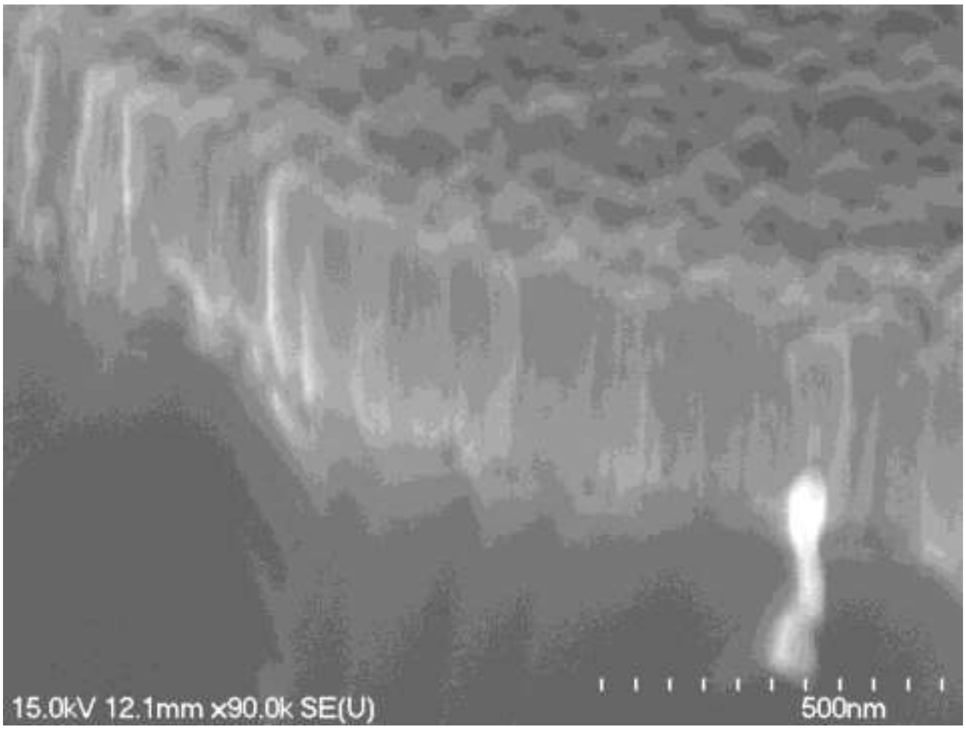

Figure 13. SEM of sample 2-60. Columns normal to surface of film

The following is the SEM image of the sample 3-60. During this deposition, magnetic field was applied along near-far direction and obliqueness of columns increased as a result of the magnetic field. Field was applied along the easy-far axes and the oblique column structure is visibly clear.

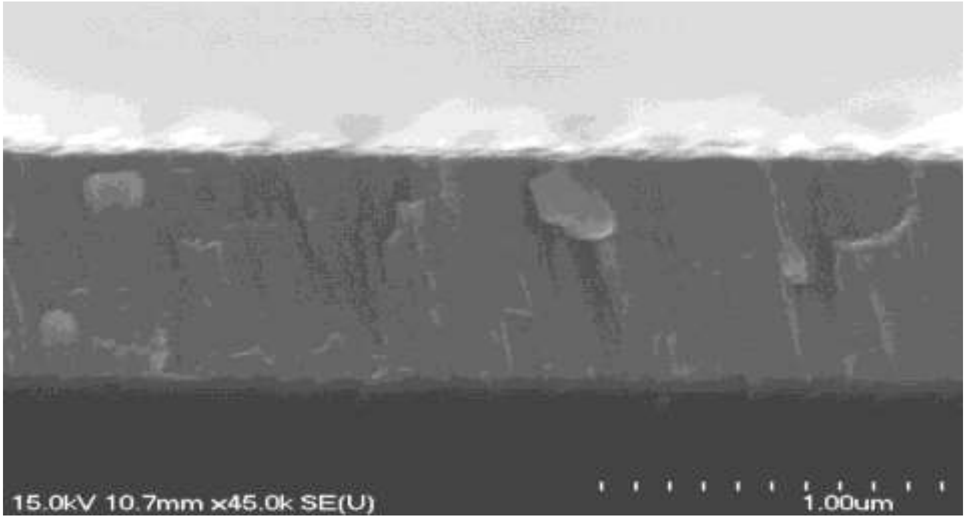

Figure 14 SEM image of the sample 3-60.

The following is the SEM image of the sample 4-75. No magnetic field was applied during sputtering and angles ranged from 45-75 degrees.

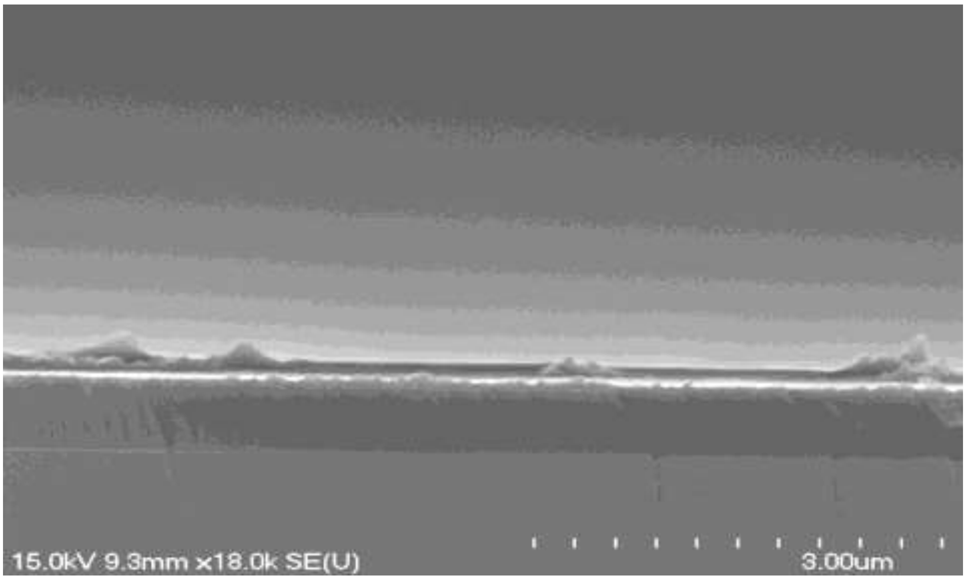

Figure 15 SEM image of sample 4-75.

EDAX analysis was done on the samples to examine the composition of the sample. These are the results of the sample.

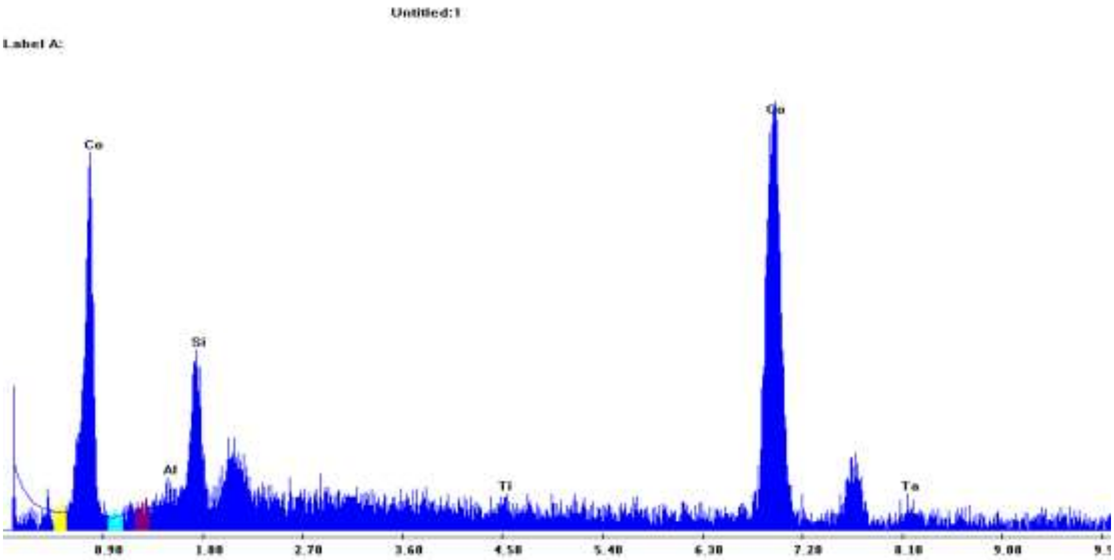

Figure 30 EDAX measurements of CZTB sample

The thin films were deposited using a CZTB target with 68% of Cobalt, 24% of Zirconium, 5% of Tantalum and 3% Boron. The substrate used is 100 orientation SiO2. So the presence of Si can be seen in the results as well.

CHAPTER

5 ANALYSIS OF THE CHARACTERIZATION RESULTS

The following chapter is on the analysis of the results obtained from VSM, Resistivity and SEM measurements of the samples discussed in the previous chapters. The key aspects of discussion are Saturation Magnetization (M_S), Coercivity, Structural properties leading to the observed results, Resistivity measurements supporting to explain the results.

Impact of oblique angle on the magnetic hardness of the materials

Magnetic materials are said to be soft when the dipole moments of the materials align without much effort in the direction of the applied field to minimize their total energy. Magnetic domains can be used to explain the reason a ferromagnetic material has a considerable net moment whereas Diamagnetic and Paramagnetic materials do not show the same behavior. The saturation magnetization of the soft magnetic materials will be as small as 50 Oe while for a hard magnetic material, it will be in the range of 100s-1000s of Oe. A given ferromagnetic material has two axes of magnetization, easy and hard axes. If a field is applied in the easy axis direction, the material particles align to that field easily and saturates at a smaller applied field, where as in the hard axis direction, it takes application of stronger fields to saturate the magnetic moment.

The following graph is a study of impact of oblique angle on the hard axes saturation fields (M_H).

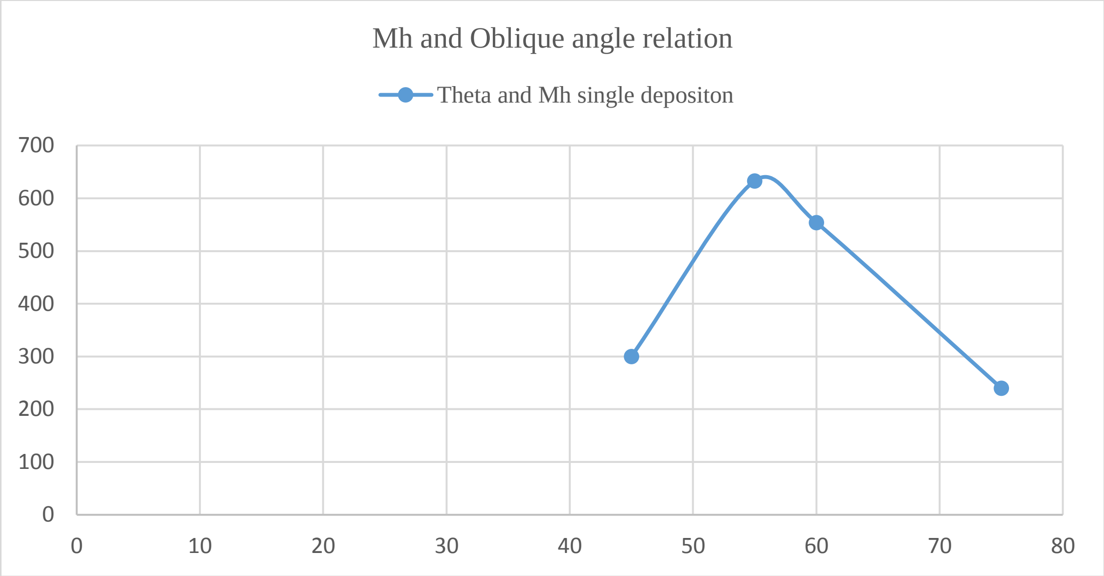

Figure 31. Relation between angle and Saturation on Hard axis direction

In the above graph, the samples are analyzed for saturation magnetization in the hard axis direction. All these samples are deposited in the same run and can thus be compared for analysis. This result is in accordance with a similar analysis performed by Wang et al[5] in their work on oblique sputtering. The optimum angle is decided based on the anisotropy energy which depends on the difference in saturation magnetization fields of hard axis and easy axis direction. So ideally, we would want hard axis saturation to be in the order of 1000s of Oe and easy axis in 100s of Oe to get a highly anisotropic magnetic film.

The following is a graph of the analysis performed on hard axis saturations of samples sputtered obliquely in presence of magnetic field.

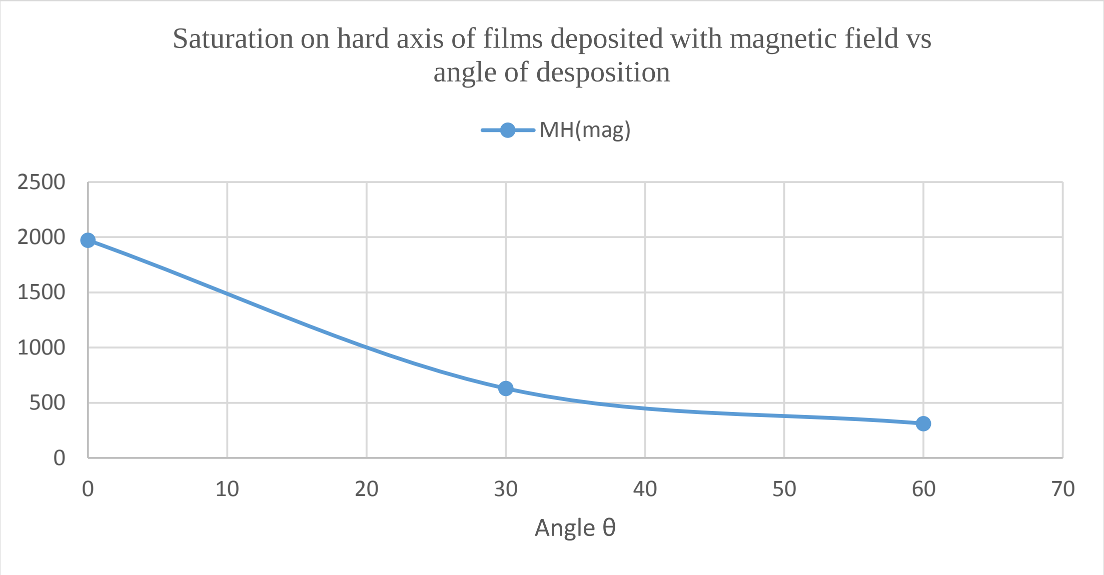

Figure 32. Dependence of saturation field strength on oblique angle of film.

Impact of oblique angle on the anisotropy of the film

Magnetic anisotropy can be defined as the difference in magnetization of the material when field is applied across multiple directions along the surface of the thin film. Here in our project, the films deposited are expected to have in plane magnetic moment. To verify the claim, here is the result of a VSM measurement of the sample 2-0 with an out of plane field applied.

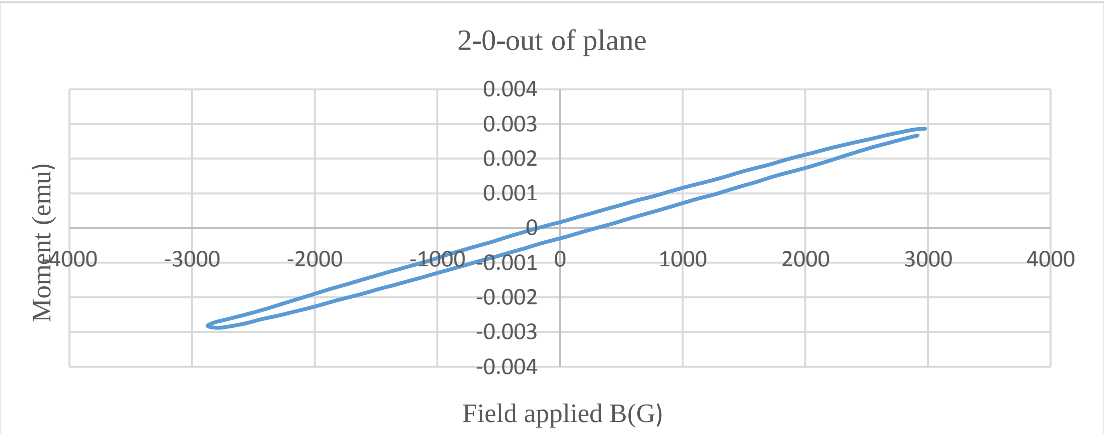

Figure 33. Out of plane field applied CZTB of sample 2-0.

The behavior shows a simple paramagnetic characteristic feature of a linear response to the applied field. This proved the assumption that the moment for these samples is in plane with the surface of the material.

The following analysis is on anisotropy of the CZTB thin film deposited on Si substrate using methods described in this document above. H_K is the notation used for the anisotropy field. Here are the graphs that best describe the H_K values of the samples. An introduction to the calculation of H_K.

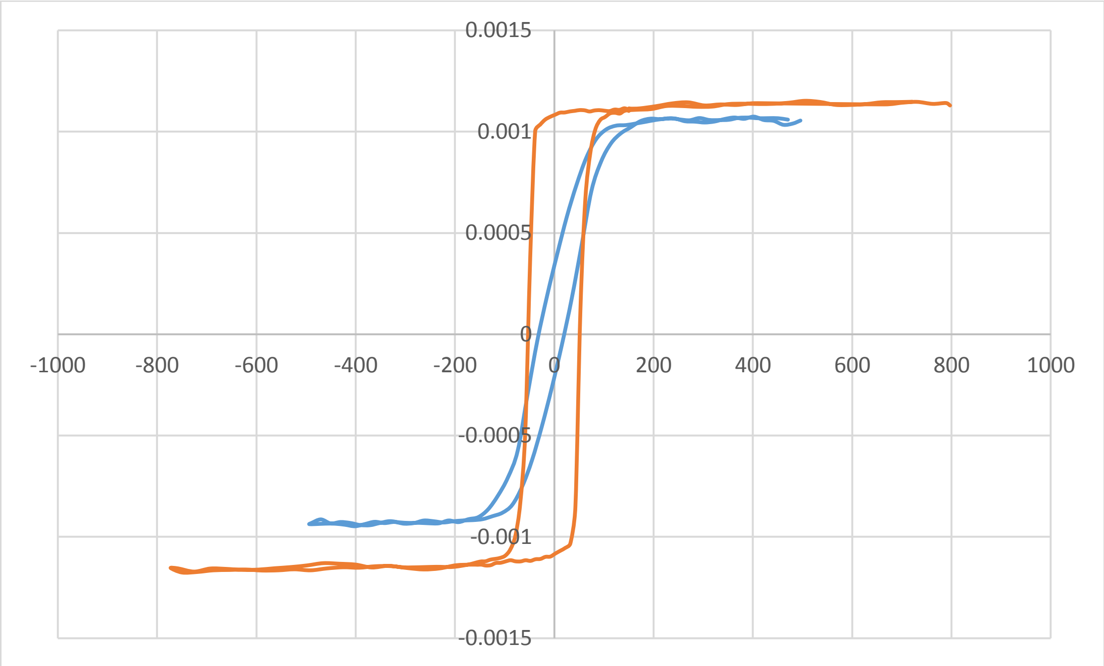

Figure 16. Sample 1-60 VSM measurement results

In this graph, the saturation field for the thin film when field is applied in the hard axis direction is 213.44 Oe and in the easy axis direction is 122.44 Oe. The difference is 91 Oe. Usually the mean of this difference can be considered to give an understanding of the Hk values. Which is 45 Oe.

This calculation is performed on all the samples considered in this project and the resulting anisotropies are compared in this analysis.

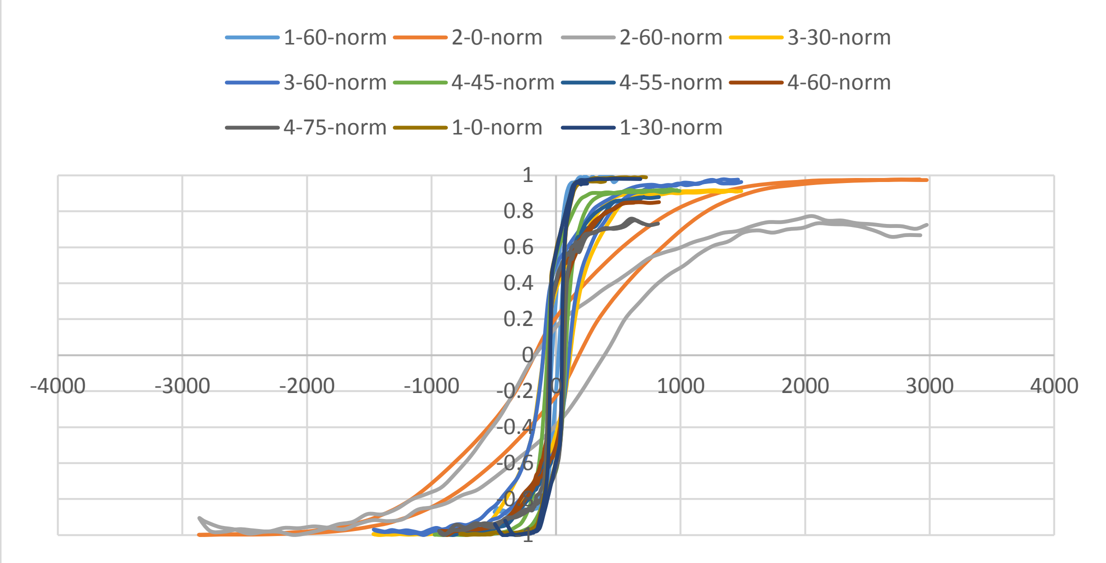

Figure 17 Normalized easy axis VSM measurements of all samples deposited

The following is a graph of normalized moment in hard axis direction of samples deposited.

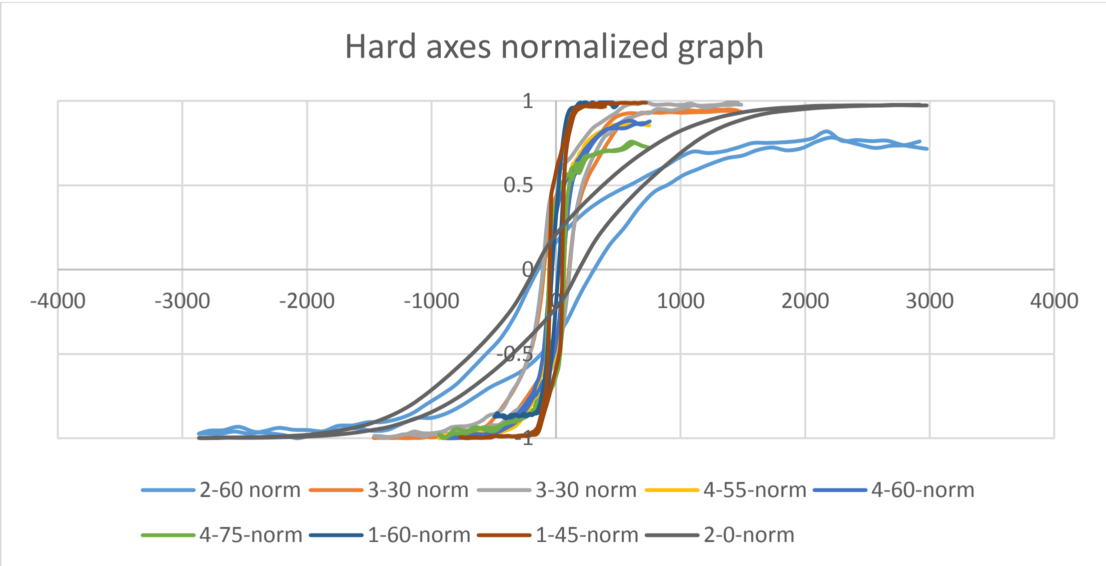

Figure 18 Hard axis magnetic moment normalized of all samples.

On analysis of these graphs, some conclusions on the effects of oblique angle on anisotropy can be made. With increase of angle in the range of 45-60 degrees without application of external magnetic field during deposition, the anisotropy effectively increases and there will be a maximum angle at which this behavior is reversed and anisotropy decreases with increase of angle. So the results discussed above prove this observation.

Reasons for magnetic anisotropy of CZTB films deposited by oblique sputtering

The results from structural characterization using SEM has been discussed in the above chapter. The sample 1-60 has oblique columns aligned with the geometric angle created from the sputtering method.

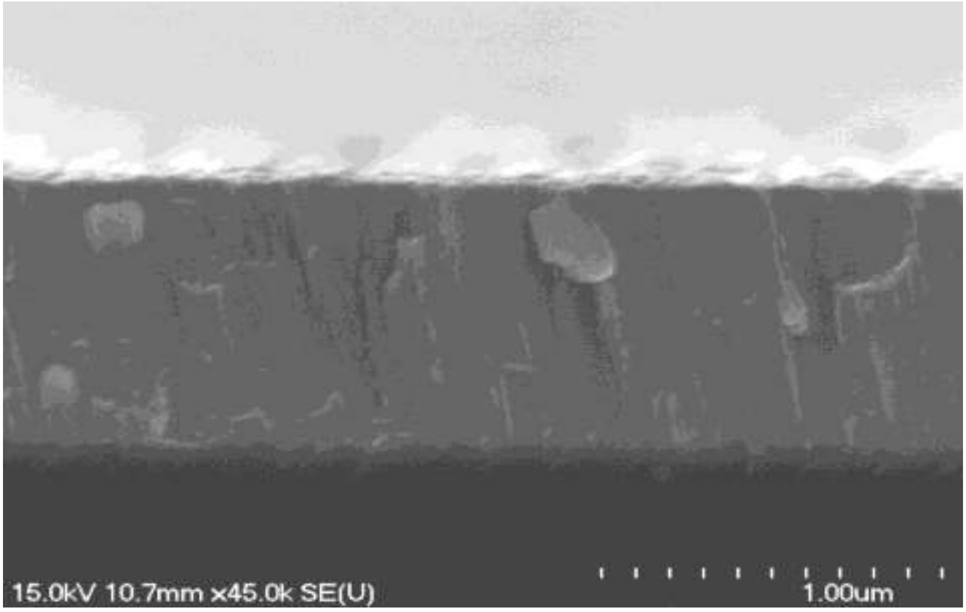

Figure 19 SEM image of CZTB sample 3-60

The image above shows the oblique columns created by the oblique sputtering method. These columns align themselves to the applied field causing a net moment in the film. So when the applied field is along the easy axis direction, these columns align to the field and the material saturates at weaker magnetic field. Conversely, if the field applied is along the direction perpendicular to these columns, the saturation occurs at stronger fields.

Also, the existence of columns on the film depends on the thickness of the material. Thicker deposition of the material CZTB results in the formation of stripe domains, as shown in the SEM image below.

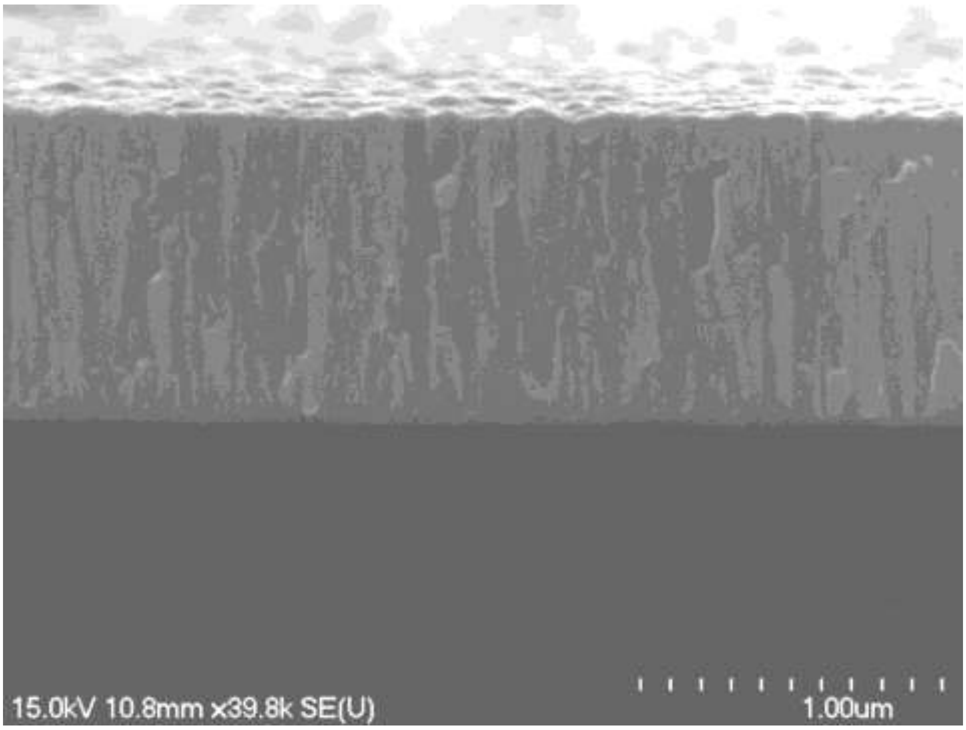

Figure 20 SEM image of Sample 2-0

Stripe domains have been mentioned as reasons for hindering the uniaxial anisotropy among thin films by Wang et al[5] and they were observed for films deposited at smaller angles. We observed a similar behavior among films deposited at smaller angles.

Bubble structures have been reported by Wang et al[5] on the films deposited at higher angles and which show large perpendicular uniaxial anisotropy as exhibited by the samples 1-60, 4-60 and 5-60. The following is a SEM image of the sample 3-60

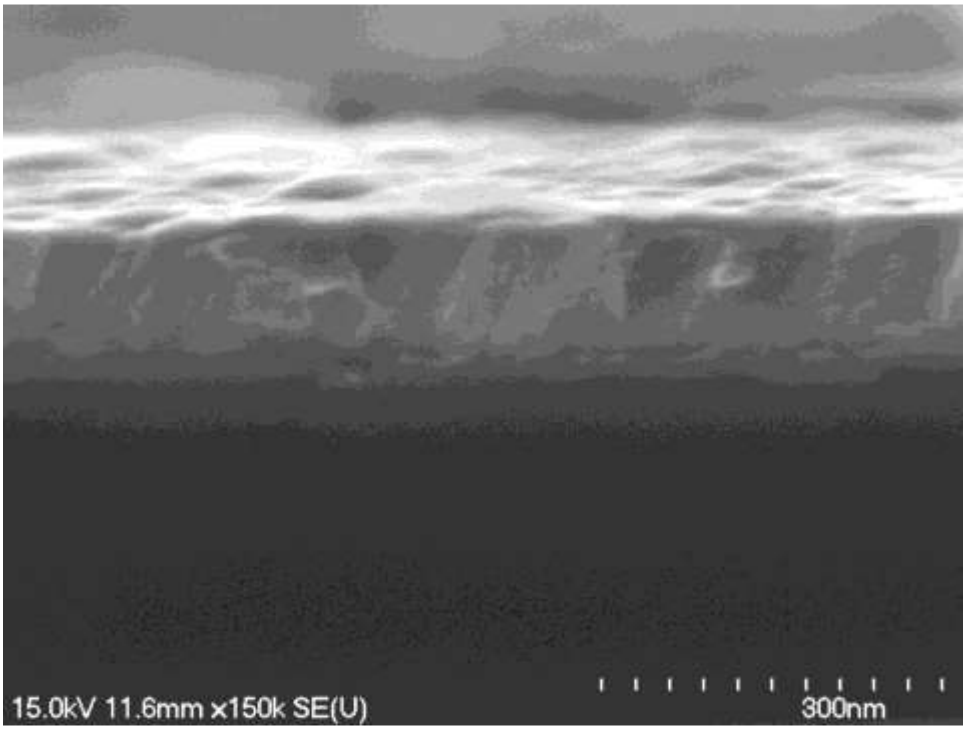

Figure 21 SEM image of sample 3-60 with bubble structures on surface

This analysis completes the structural analysis of the thin films of CZTB for their magnetic uni axial anisotropy.

CHAPTER

6 CONCLUSION

In this work, magnetic material CZTB thin films have been deposited using oblique sputtering with and without presence of magnetic fields during the deposition. The resulting films have been measured for magnetic moments on Lakeshore 7500 VSM in easy and hard magnetic axis directions. To study the reasons for such behavior, structural and composite analysis were done on the thin films using Hitachi S-4700-II SEM and EDAX systems. Resistivity measurements were done on these films to explain certain characteristics that make these CZTB thin films efficient for applications in spin based memory devices and magnetic switches that operate at high 4-5 GHz frequency ranges. This completes the study of effects of growth techniques on the characteristics of CZTB thin films.

In future, our group plans to extend this research in optimizing the growth and deposition techniques mentioned in this work. Devices that use the magnetic spin polarization and high uniaxial anisotropy can be developed using this CZTB material which has high resistivity and magnetic moment. The opportunities to expand on this research is enormous as this material can be deposited efficiently resulting in high quality films that can have devices made out of them.

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