

X-RAY CHARACTERIZATION OF BURIED LAYERS AND INTERFACES IN EuO
BASED SPIN-FILTER TUNNEL JUNCTIONS

by

Ezana Negusse

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Physics

MONTANA STATE UNIVERSITY
Bozeman, Montana

April 2008

©COPYRIGHT by

Ezana Negusse

2008

All Rights Reserved

APPROVAL

of a dissertation submitted by

Ezana Negusse

This dissertation has been read by each member of the dissertation committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the Division of Graduate Education.

Dr. Yves U. Idzerda

Approved for the Department of Physics

Dr. William A. Hiscock

Approved for the Division of Graduate Education

Dr. Carl A. Fox

STATEMENT OF PERMISSION TO USE

In presenting this dissertation in partial fulfillment of the requirements for a doctoral degree at Montana State University, I agree that the Library shall make it available to borrowers under the rules of the Library. I further agree that copying of this dissertation is allowable only for scholarly purpose, consistent with “fair use” as prescribed in the U.S. Copyright Law. Requests for extensive copying or reproduction of this dissertation should be referred to Bell & Howell Information and Learning, 300 North Zeeb Road, Ann Arbor, Michigan 48106, to whom I have granted “the exclusive right to reproduce and distribute my dissertation in and from microform along with the non-exclusive right to reproduce and distribute my abstract in any format in whole or in part.”

Ezana Negusse

April 2008

To my beloved parents,
Thanks for being so special

ACKNOWLEDGMENT

First, my deepest gratitude to my advisor and mentor Prof. Yves Idzerda who financed my research, numerous travels to synchrotron facilities, and conferences. Yves, you taught me how to be a good researcher by being one. My thanks also to Dr. Joe Dvorak and Dr. Dario Arena; I could not have done all the scattering measurements without your guidance and help. A heartfelt thanks to my friends and colleagues here at *ilab*: Dr. Keith Gilmore, Johnathon Holroyd, Adam McClure, Dr. Alexandre Lussier and Dr. Damon Resnick. Thanks for all the fun during the MMM and NSLS trips. Also thanks to Prof. Jerry Lapere and Dr. Paul Rugheimer for the stimulating discussions.

Dr. Tiffany Santos from MIT, a gracious colleague and wonderful friend; Tiffany your positive attitude and approach always inspired and motivated me to do more. Thank you for tirelessly making all the EuO samples (a very long wish list). Dr. Jagadeesh Moodera, working with you and Tiffany has been a privilege. Dr. Sanjay Shinde, from Canon-Anelva, thank you for the MgO samples and for being such a wonderful colleague.

Many thanks to the wonderful Physic Department staff Margaret Jarrett, Jeannie Gunderson, Rose Waldon, Glenda Winslow, Sara Barutha, Norm Williams, and Jeremy Gay. To the amazing people at NSLS and ALS, thank you for making my trips memorable. Dr. Marco Liberati and Dr. Elke Arenholtz, thank you for the outstanding XMCD spectra. My thanks to the incredibly resourceful Gary Nintzel at NSLS. Also thanks to Michael Becker and Dr. Brian Larson (the L^AT_EX guy).

Tina Buckingham, a wonderful mom; just a special treasure who was always there for me through tough times and shared the good times. Dr. Robert Van Buskirk, thank you for that first unforgettable trip to Yellowstone National Park. A very special thanks to my family for your support and encouragement throughout my graduate life. Lord, thank you for teaching and sustaining me through my years in Montana. Thank you all.

TABLE OF CONTENTS

1. INTRODUCTION	1
Magnetic Devices and Applications	4
Magnetoresistance in Multilayer Structures	7
Interfaces: Chemical and Magnetic	10
Interface Magnetism	13
Spin-dependent Tunneling (SDT)	15
Dissertation Overview	16
2. TUNNELING JUNCTIONS AND SPIN-DEPENDENT TUNNELING	19
Introduction	19
Magnetic Tunneling Junction	20
Spin Filtering with Ferromagnetic Insulator	24
3. X-RAY CHARACTERIZATION OF BURIED INTERFACES AND LAYERS	26
Synchrotron Characterization Techniques	26
Interface Sensitivity with Magnetic Contrast	27
Experimental Chamber	28
Reflectivity: XRS and XRMS	29
Scattering Setup	30
Types of Scattering Measurements	33
Summary	37
4. SPIN-FILTER TUNNEL JUNCTION WITH EuO BARRIER	39
Introduction	39
EuO: a Novel Oxide	40
Sample Fabrication and Characterization	41
Wedge (Stair-step) Samples	42
Tunnel Barrier Quality and Oxides Present	43
Oxides of Europium	44
Choice of Electrode	44
Angle-dependent XAS and Eu ₂ O ₃	47
Oxide Layer Thickness	49
Direct Investigation of Buried Interfaces	51
Magnetic Characterization of Ultrathin EuO Films	55
Summary	61
5. CONCLUSION AND OUTLOOK	63

TABLE OF CONTENTS – CONTINUED

APPENDICES	66
APPENDIX A: Magnetic Characterization of CoFe(B)/MgO Interfaces	67
APPENDIX B: Magnetoresistance Based Exchange Bias Sensor	79
APPENDIX C: Extracting Fraction of EuO and Eu ₂ O ₃ from XAS Spectra	90
REFERENCES	97

LIST OF TABLES

Table		Page
4.1	Fraction of Eu_2O_3 and roughness parameters for EuO films with different electrodes.	47
4.2	RMS roughness values at the top and bottom interfaces for 10 Å EuO film. .	54

LIST OF FIGURES

Figure		Page
1-1	A generic multilayer magnetic device, the basis for tunnel junctions and other magnetic structures.	2
1-2	Magnetic hard disk drive (HDD) with a TMR read-head.	5
1-3	Cross-point configuration MRAM with MTJ memory elements.	6
1-4	Resistance versus temperature of pure Ni metal.	8
1-5	Illustration of a magnetic interface and parameters used to describe the topology.	11
2-1	High (low) resistance configurations due to applied magnetic field that give rise to magnetoresistance.	21
2-2	Spin-dependent tunneling in F/I/F tunneling junction.	22
2-3	Complete magnetic tunnel junction with MgO barrier and CoFeB electrodes.	24
2-4	Schematic of spin filtering effect with EuO barrier below T_C	25
3-1	XMCD spectra at the europium $M_{4,5}$ -edges of a 20 Å EuO film.	31
3-2	Configuration of the scattering chamber at beamline U4B, NSLS.	32
3-3	Momentum transfer vector $\mathbf{q}$ and its components.	34
3-4	Specular ($\omega = \theta$) scan at Fe L_3 with the XRMS signal.	36
3-5	Typical sample rocking scan showing the specular and diffuse components.	37
4-1	Basic structure of the EuO samples.	42
4-2	XAS signature peaks of EuO and Eu_2O_3	45

LIST OF FIGURES – CONTINUED

Figure	Page
4-3 XAS spectra of EuO films with different electrodes.	46
4-4 Relative fraction of europium oxides as function of sample angle for 80 Å thick EuO sample.	48
4-5 Thickness dependence of fraction of EuO and Eu ₂ O ₃	50
4-6 XAS spectra at Cu L _{2,3} show the bottom Cu electrode is metallic.	53
4-7 Rocking scans, performed at different energies, to examine the roughness of the buried interfaces.	54
4-8 XMCD spectra of 20 Å EuO films capped with Al and Y.	56
4-9 Relative fraction of europium oxides as function of sample angle for 10 Å thick EuO film.	57
4-10 XMCD spectra for EuO wedge with thicknesses ranging from 10 – 60 Å.	58
4-11 EuO fraction and XMCD signal for yttrium capped EuO wedge.	59
4-12 Magnetization versus temperature and thickness dependence of T _C	60
A-1 Abridged MTJ structure of the CoFe(B)/MgO samples used in the study.	69
A-2 XAS spectra of the CoFe(B) electrodes at Fe and Co L _{2,3} edges.	72
A-3 Rocking scans at Co L ₃ edge for samples with CoFeB electrodes.	73
A-4 Specular (bulk) hysteresis loops at Co and Fe L ₃ edges showing the effect of boron addition and annealing.	75
A-5 Bulk and interface hysteresis loops for the as-grown and annealed samples with CoFeB electrodes.	76

LIST OF FIGURES – CONTINUED

Figure		Page
A-6	Hysteresis loops for the bulk and interfacial moments for samples with CoFe electrodes.	77
B-1	Exchange bias process	81
B-2	Measurement principle at zero operational field.	83
B-3	Modeling of the MR response with two offset Gaussian curves and the corresponding Δ MR spectra.	86
B-4	Sensitivity is improved by performing the measurement at $H_{OP} \neq 0$	87
B-5	Dependence of operation range and sensitivity on with of MR response. . .	88
C-1	Comparison of XAS standards for EuO and Eu_2O_3 spectra against published spectra.	92
C-2	Decomposition of XAS spectrum at the $M_{4,5}$ edges of europium.	95

ACRONYMS

AFM	Atomic Force Microscopy
CMR	Colossal Magnetoresistance
ESMH	Element Specific Magnetic Hysteresis loop
EuO	Europium Oxide
Gbps	Giga bits per square inch
GMR	Giant Magnetoresistance
MFM	Magnetic Force Microscopy
MgO	Magnesium Oxide
MR	Magnetoresistance
MTJ	Magnetic Tunneling Junction
PCAR	Point Contact Andreev Reflectivity
PPMS	Physical Properties Measurement System
QCM	Quartz Crystal Microbalance
TMR	Tunneling Magnetoresistance
XAS	X-ray Absorption Spectroscopy
XMCD	X-ray Magnetic Circular Dichroism
XRMS	X-ray Resonant Magnetic Scattering
XRS	X-ray Resonant Scattering

ABSTRACT

Spin filtering tunnel junctions provide a convenient method for controlling and manipulating the spin of electrons in spintronic devices. In a tunnel junction, the tunneling current depends exponentially on the thickness of the tunneling barrier. Ultrathin (~ 20 Å) barriers are highly desirable because they lower the junction resistance. In addition to the barrier thickness, the spin filtering efficiency of the junction depends on the tunneling barrier's magnetic properties and the nature of the barrier-electrode interfaces. EuO's high T_C (69 K) and large exchange splitting ($2\Delta E = 0.54$ eV) in the conduction band make it a material of choice for achieving a spin-polarized tunneling current. We examined the properties of ultrathin EuO films of different thicknesses with different electrodes. The chemical and magnetic characterization of buried layers and buried interfaces was done using interface sensitive x-ray techniques with element specificity and magnetic contrast. Of the many materials studied, we found that yttrium overlayers are the best electrodes to protect the EuO barrier and prevent formation of Eu_2O_3 , a stable nonmagnetic oxide, at the top (EuO-electrode) interface. We examined the electrode-EuO interfaces of EuO films with Cu bottom electrode deposited on Cr/Cu buffer layer. We found that the roughness of the top and bottom interfaces (above and below the EuO layer) is random and nonconformal in nature. EuO films grown on Cr/Cu buffer layer have smoother top interfaces compared to those deposited directly on Si substrate or Al bottom electrode. Moreover, compared to the Cr/Cu or Cu/EuO interfaces, the top (EuO-electrode) interface is smoother. Here we present results from chemical and magnetic characterization of ultrathin EuO film and the impact of reduced barrier thickness on the magnetic properties of the ferromagnetic tunneling barrier.

CHAPTER 1

INTRODUCTION

Magnetism is full of interesting dichotomies [1]. Many things in magnetism seem so obvious, yet their complexity confounds even the experts and veterans of the field. One such phenomenon, discovered over 40 year ago but only recently used for applications in information processing and storage technology, is *spin-dependent transport*. One method that has been successfully used to control and manipulate spin transport is using devices made of multilayer magnetic structures [2, 3]. Stacking thin layers of magnetic, nonmagnetic, metallic or insulator layers, however, gives rise to structures with magnetic properties different from the constituent layers. These properties, which are sometimes unique and interesting, arise due to the complex interactions that take place at the interfaces but affect the whole structure. Exchange bias and spin-dependent tunneling are two such examples. Phenomenological models have been used, with varying degree of accuracy and success, to describe properties, such as exchange bias by Meiklejohn and Bean [4] and spin-dependent tunneling in magnetic tunnel junctions by Jullière [3].

The understanding of these interface based properties and the appropriate use of them has opened and is still opening many more fascinating applications. As in other systems, interface sensitive probes are essential for studying the buried layers and buried interfaces, and nondestructive tools are a must in the study of interface magnetism where having the whole structure intact is crucial.

In magnetism, one of the most exciting areas of active research is the study of the complex interactions at the interfaces, which give rise to exotic properties such as exchange bias and spin-dependent electron transport. Often, interfacial properties such as chemical

and magnetic roughness are viewed as detrimental to device operation and performance. Complete elimination of interfacial roughness, however, is not possible, and ideal interfaces may not always be desirable. Understanding interface properties is essential to utilize interfacial roughness as a means to engineer the properties and functionality of multilayer structures.

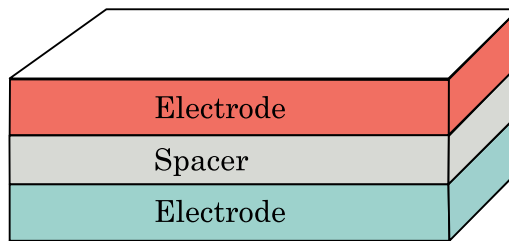


Figure 1-1: A generic multilayer magnetic device composed of magnetic and nonmagnetic layers. If a non-magnetic oxide spacer layer, such as MgO , is sandwiched between two ferromagnetic layers, then the trilayer is a magnetic tunnel junction. Replacing the spacer layer (tunneling barrier) with a ferromagnetic semiconductor, such as EuO , would make the structure a spin-filter tunnel junction.

A generic multilayer magnetic device is shown in Fig 1-1. The essential components are the spacer and the electrodes, creating a basic trilayer structure. Depending on the properties of the materials used and the desired functionality, the structure can be turned into many devices. Devices that have this trilayer structure include some of the most commonly used magnetic devices, such as giant magnetoresistance (GMR), magnetic tunnel junctions (TMR), and spin-filter tunnel junctions. Other structures such as synthetic anti-ferromagnet (SAF) also use this basic trilayer configuration. The main difference between them is the material used as the spacer, whether it is magnetic or nonmagnetic, an insulator or semiconductor. It is the same with the choice of the electrodes used; whether they are magnetic conductors or nonmagnetic metals determines the nature of the devices. For instance, in GMR structures, the spacer is a nonmagnetic metal, such as Cu with magnetic

electrodes such as Fe, Co, or their alloys. In TMR structures, where the main process involved is tunneling across a barrier, the spacer is an insulator such as Al_2O_3 , MgO , or TiO_2 , with ferromagnetic electrodes made of Fe or Co. Just by switching to a semiconductor ferromagnetic barrier, such as EuO , and using nonmagnetic electrodes, the trilayer tunneling structure becomes a spin filter tunneling junction. By adding different layers, the properties and functionality of the basic structure can be enhanced or tailored to provide the desired response.

However, there are several things that are common to all systems. These can be subdivided as bulk and interface properties. The study of the bulk properties is related to materials issues such structural, chemical, magnetic, electric, and mechanical material properties. However, the main focus of this study is on the interfaces between the different layers of the multilayer structure. They have a profound effects on the overall magnetic, chemical, and spin transport properties of the entire multilayer devices. These properties include oxidation, interfacial roughness (both chemical and magnetic), alloying, and segregation, and diffusion of constituent elements.

In this work, we studied how the thickness of the EuO barrier and choice of electrode materials affect the chemical and magnetic properties of spin-filter tunneling junctions with an EuO barrier. EuO is chosen because of its potential in magnetoelectronic (spintronic) applications that utilize the electrons' spin degree of freedom (spin-electronics) [5]. A renewed interest in tunneling junctions was largely propelled by remarkable advances on various fronts. These advantages range from highly automated sample fabrication with unprecedented quality and precise structure control to characterization and imaging techniques with unparalleled resolution. Several sophisticated modeling packages are also facilitating the discovery, exploration, and understanding of these complex and complicated systems. Of the available characterization tools, synchrotron based x-ray probes have had a huge impact [6].

X-ray absorption spectroscopy (XAS), its magnetic counterpart x-ray magnetic circular dichroism (XMCD), and x-ray resonant magnetic scattering (XRMS) were all used in this study. These techniques have been successfully utilized to address important issues in magnetism, such as layer switching in structures made of magnetic multilayers [7] and separation of the spin and orbital contributions to the magnetic moment [8]. Using XMCD and XRMS, buried interfaces and hidden layers can be directly probed in an element-specific and layer selective manner with magnetic contrast. Buried interfaces or layers are found beneath other layers composed of different elements, whereas hidden layers are covered by another layer composed of the same element or another magnetic layer [9].

With these nondestructive techniques, roughness parameters of buried interfaces can be quantified, weak interfacial magnetic moments can be measured, the nature of the coupling between interfacial and bulk moments can be characterized, and magnetic ordering at interfaces can be examined [10–12]. Furthermore, XRMS has been employed to *quantify* interfacial chemical and magnetic roughness and selectively measure the magnetic hysteresis of bulk and interfacial atoms [10, 12]. These techniques are thus, ideal tools for direct investigation of interfaces and examining the role of interfacial roughness.

Magnetic Devices and Applications

The two prominent applications of magnetoresistance are magnetic field sensors and magnetic memory elements. By partial replacement of giant magnetoresistance (GMR) read heads and longitudinal media (density less 100 Gbpsi (Gigabits per square inch)) with AlO_x and TiO_2 based magnetic tunneling junction (MTJ) [13] read head systems to perpendicular media (with density between 200 – 500 Gbpsi). For increased sensitivity to changes in the field generated by the storage media, the free and pinned layers are set at perpendicular to each other as shown in Fig. 1-2. Even though HDDs are cheaper and

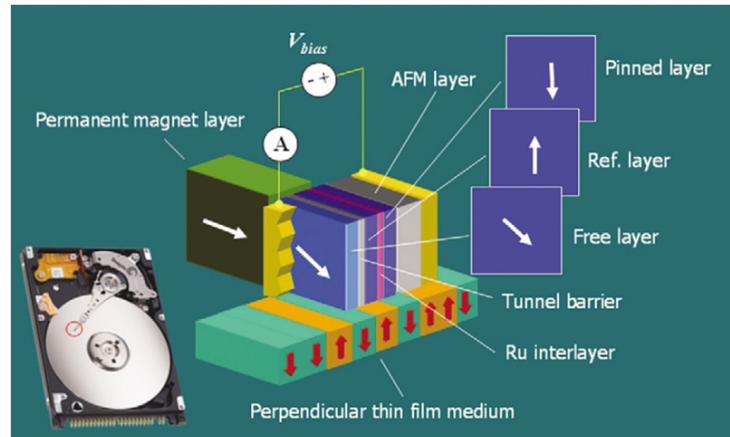


Figure 1-2: Magnetic hard disk drive with a magnetic tunnel junction read-head. The magnetization of the reference layer is anchored to the pinning layer. The read-head can detect the small magnetic field generated by the memory elements in the perpendicular medium. Figure from [13].

have more storage capacity and density, they also have an inherent drawback: access time is very long compared to other memory systems. The second application, where magnetic memory elements are used for random access memory, promises to address this major issue and has the potential to become the universal memory element [13].

Magnetic random access memory (MRAM) [5] is a nonvolatile, ultra-fast memory that uses magnetic structures, such as GMR or TMR, as memory elements. MRAMs can also be used as reprogrammable logic devices that integrate both the storage and processing of information, making it the *universal memory* element and unlocking more innovative applications. The progress in this application has been limited by a number of issues including fundamental limits, such as superparamagnetism in the memory elements, and practical limits, such as leakage current and interfaces in the memory elements.

As shown in Fig. 1-3, they have a cross-point architecture, where a magnetoresistive element is located at the crossing point between two metal lines. The information is stored by the relative orientation of the two magnetic layers. The challenge is achieving high

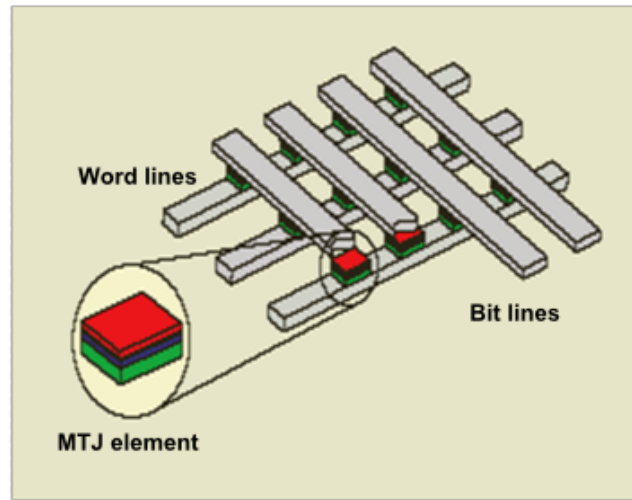


Figure 1-3: A magnetic random access memory (MRAM) with cross point architecture composed of magnetic tunnel junction (MTJs). The ‘Word’ and ‘Bit’ lines are current carrying conductors used to write/read information into/from each element [14].

tunneling magnetoresistance (TMR) values with small RA-product¹ and fast switching of the layer(s) reproducible. Several ways for achieving the addressing (read/write) process have been proposed. The one that looks most promising is spin-torque, which does not use the fields generated by the word or bit lines. In this regard tunnel junctions present an advantage where the current density required to change the magnetization direction of the memory element is not as high, and leakage-current from adjacent MR elements is minimal compared to systems with GMR memory elements. Ney et al. also proposed that the capability to switch the bottom layer this would make each element a reprogrammable logic element [15].

Another vital achievement is the synthetic antiferromagnet (SAF), composed of two ferromagnetic layers separated by a thin Ru layer. The coupling between the ferromagnetic layers can be adjusted by changing the thickness of the Ru spacer layer, whereby

¹RA-product is a merit function that determines the quality of a tunneling junction. It is the product of the area and the resistance across the junction.

the two ferromagnetic layers exhibit either parallel or antiparallel coupling. The whole trilayer structure acts as single ferromagnetic or antiferromagnetic layer. This approach is the method of choice for setting the magnetization direction of the reference layer (see Fig. 1-3). Recently, FreeScaleTM using MTJs with magnetic-flux-matched SAF as a free-layer, successfully manufactured a 4 Mbit magnetic random access memory (MRAM) chip [13].

Another application of tunnel junctions in spin transport is the injection and detection of spin polarized current. An all-electrical spin-filter transistor (SFT), a transistor that uses a spin-filter with ferromagnetic barrier as spin-injector and spin-detector of spin-polarized current, was proposed by Sugahara and Tanaka [16]. Recently, Schmehl et al. demonstrated spin injection to semiconductors using doped EuO (with higher T_C) [17].

Before proceeding further into detailed description of the types of tunnel junctions, let's explore the magnetoresistance (MR) in multilayer structures and why it lends itself to two common applications: magnetic field sensor and binary memory element.

Magnetoresistance in Multilayer Structures

Magnetoresistance² (MR) is the change in the electrical resistance of a structure due to applied external magnetic field. A rather simplistic example that illustrates the origin of this effect is shown in Fig. 1-4. The illustration shows the significant change in magnetoconductance $(R)^{-1}$ that can be observed at room temperature with appropriate control of the magnetic ordering of a ferromagnetic material [18]. At high temperatures, the spins are randomly oriented in the paramagnetic phase as shown on the top-right corner of the illustration. When cooled below the magnetic ordering temperature of the ferromagnet (T_C), Ni becomes ferromagnetic and its resistance drops as shown by data points (solid line). Suppose the disordered paramagnetic phase were to be extended into the low temperature

²Magnetoresistance was first observed in metals by William Thompson, later Lord Kelvin, in 1856.

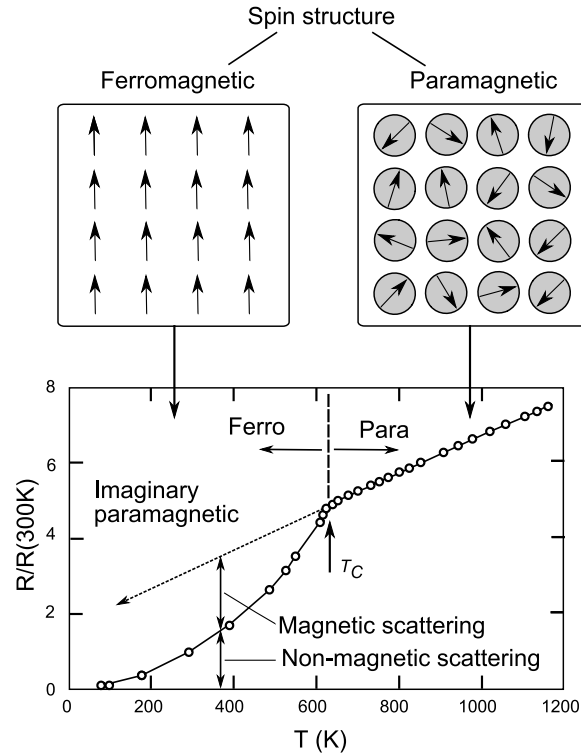


Figure 1-4: Resistivity versus temperature of pure Ni metal. T_C indicates the Curie temperature. The dashed line is a linear extrapolation of the resistivity curve in from paramagnetic into ferromagnetic region for comparison. Figure from [18].

region beyond $T < T_C$. For this case, let's consider a linear extrapolation of resistance (as shown by the dashed line). Two contributions to the resistance can be identified; from magnetic scattering about 50% and the remaining 50% is from nonmagnetic scattering. The resistance of the material can be switched between 'low' and 'high' resistance by controlling the contribution of the magnetic scattering due to the magnetic order and disorder in the material respectively. These well defined binary states are ideal for building a memory element. On the other hand, the effect of magnetic ordering of the structure by external magnetic field can be measured by monitoring the the change in resistance.

More elaborate multilayer magnetic hetrostructures are used for sensing very small changes in magnetic fields such as those generated by a memory element of magnetic storage media. As illustrated by this simple thought experiment, the ability to control and

manipulate magnetic ordering in magnetic structure is central to a great many technological applications.

Depending on the origin and nature of the change in resistance, there are different types of magnetoresistance. They include anomalous magnetoresistance, anisotropic magnetoresistance, intergranular magnetoresistance, giant magnetoresistance (GMR), tunneling magnetoresistance (TMR), and colossal magnetoresistance. The change in resistance can be viewed as controllable magnetic order (disorder) introduced by an external applied magnetic field.

Even though AMR has been around for a long time and TMR is the one that makes intuitive sense to understand, it was GMR that revolutionized the hard disk drive storage industry and made the unprecedented impact of magnetic devices and applications in information storage possible. It sparked the ongoing keen interest in magnetic systems and is driving basic and applied research.

With 29% MR value in GMR structures, compared to less than 10% MR in MTJs 1990s, GMR became the structure of choice and was implemented for magnetic read-heads in hard disk drives. This initial remarkable application of GMR structures greatly increased the interest to improve the structures and find other applications like memory elements in magnetic random access memory (MRAM) [5, 14]. Instead of a single trilayer structure (shown in Fig. 1-1), use of super-lattices brought a concerted effort to MR processes and led to remarkable and widespread technological applications. GMR also became the testing ground for further innovative solutions to many problems associated with fabrication, tribology, materials studies, development and led to further refinement of fabrication and characterization methods and techniques. As a result of this concerted and intense effort, the number of magnetoresistance based sensor applications flourished.

The difficulties associated with manufacturing high quality interfaces and electrodes with the desired magnetic, chemical, structural and other bulk properties limited the appli-

cation of magnetic tunnel junction read heads in hard disk drives for a number of years. However, the time it took for the spin-dependent tunneling based devices to come to the market is much shorter (about 8 years) compared to other technologies such as exchange bias, which took over 40 years. In the meantime, there was sufficient interest in tunneling systems and the attention was mainly directed towards examining spin properties of ferromagnetic materials and was employed to characterize quality of interfaces [2, 3].

The major difference between EuO based spin-filter tunnel junctions and MgO based magnetic tunneling junctions is, however, the limiting factor in the spin-filter is the exchange split energy of the conduction band of the ferromagnetic material used. In MTJ systems, the TMR values is controlled by the choice of the electrodes and insulating barrier used, as will be discussed later.

Interfaces: Chemical and Magnetic

The multi-functionality, speed, reprogrammable logic and enhanced storage capacity, nonvolatile memory, and numerous magneto-optic and electro-optic applications have contributed immensely to the growing interest in spintronic devices [19]. One of the major challenges, however, is the limited understanding of the role of interfaces and how interfaces affect the operation and performance of spintronic devices.

The challenging aspect of interfaces is that they are buried between the layers. This makes detecting the signal from the interfaces very difficult. Conventional surface techniques do not work as the weak effect of the interface is overshadowed by the bulk properties.

The narrow region where two thin films come into contact is what we are referring to as the *interface*. There could be intermixing, alloying, oxidation, migration, segregation of one species, or a component of the layers at this unavoidable contact region, giving rise to

unexpected structural, chemical, and magnetic properties. These changes at the interface may give rise to defects, roughness, uncompensated spins, and others. At the heart of all these studies is an attempt to understand the ‘how and what and why’ of the dynamics at the interfaces. The improvements that have been reported and lead to the remarkable changes are mainly due to the advances in fabrication and control of the properties of interfaces.

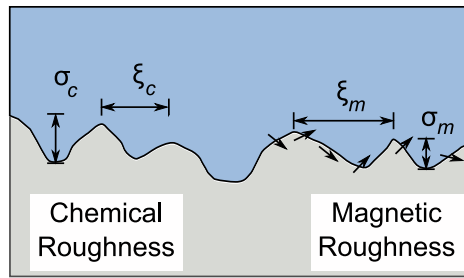


Figure 1-5: The morphology of the interface between two layers are parameterized by the perpendicular roughness (σ) and the in-plane correlation length (ξ). In magnetic multilayers, the magnetic interface may be different from the chemical interface.

The morphology of the surface or interface can generally be described by height-height correlation function. According to the Born Approximation (BA) based the model developed by Sinha et al. [20] and Lee et al. [21], the three important parameters that describe the interface are: (1) perpendicular roughness (σ); (2) the correlation length (in-plane roughness, ξ); and (3) the Hurst parameter H . The diagram in Fig. 1-5 illustrates in-plane and out-of-plane parameters. A magnetic material may have chemical and magnetic interfaces that could be different parameters, as show in Fig. 1-5. The out-of-plane roughness parameter σ is the root mean of the amplitude of the hills, whereas the correlation length a measure of the lateral length scale of the roughness. The Hurst parameter determines how smooth or jagged an interface is. Jagged surfaces have smaller H values, while smooth interfaces have higher H values (close to 1). These interface roughness parameters can affect macroscopic behaviour of multilayer systems. For intance, Freeland

et al. showed that the coercive field (H_C) can be directly related to the in-plane chemical correlation length(ξ) [22].

Quantifying the thickness of this interface region is very difficult. Several approaches can be used to estimate it [23]. In this study, we used a simple model (described in Chapter 4 on page 49) that uses the capability of the technique and additional information obtained from a different measurement to estimate this region.

The 3 – 12 Å thick interfaces can significantly change the spin coherence and momentum and thus the tunneling properties of electrons as they cross to the next layer. Compared to other regions, the interface is a substantially thin section of the entire structure, about 3 to 10 atoms thick. In the nanoscale range, the interface will be even thinner and have very profound effects. In most cases, the magnetic interface (which will be discussed below), defined by the spins at the interface, is not as well delineated (slightly thicker) and is smoother than the chemical interface [24–26].

Changes that occur at the interface due to oxidation or intermixing are not desirable because they can severely affect the performance of the devices. Many of these undesirable effects can be eliminated by working in a cleaner environment (high vacuum), ridding the system of contaminants, or solving many materials issues including finding the correct lattice matches, annealing, growing the systems at elevated or chilled temperatures. For instance, the coherent (interface state matched) tunneling from the ferromagnetic electrode through the oriented barrier was made possible only after the interfaces between the barrier and electrodes were substantially improved, making MgO based magnetic tunnel junction systems yield extremely high TMR values that broke the 100% polarization limit. as predicted by Butler et al. [27].

The complexity and challenges these interfaces present, both at the theoretical and experimental level, are intriguing. They have a huge impact on the operation of and performance of a given device and yet they are often not examined or set aside for later examina-

tion. The fascinating aspect of this project was how exploring this thin region of the whole structure, which has been viewed as insignificant and not worth the effort, ended up being extremely important to the research on thin and ultra-thin films.

First, the ability to precisely control the thickness, composition, and placement of these layers in the fabrication process; secondly, the ability to characterize, image and evaluate the interaction and dynamics at the interface with unprecedented resolution without destroying the interfaces; and thirdly the ability to model the dynamics and interaction from different angles using sophisticated modeling packages have made many things that were impossible or unthinkable not too long ago. Yet, many questions still remain. This is the main impetus to conduct fundamental studies to provide insight into what is happening at these interfaces and to be able to engineer the structures to yield the desired properties. For example, the work done by De Teresa et al. [28] showed that, indeed, the interfaces are more important in determining the tunneling properties of a junction than the bulk. This revelation opens a new way to achieve the desired objective: a system with higher TMR value.

Interface Magnetism

Often, in multilayers composed of thin magnetic films often new and unique magnetic properties emerge at the interface. The study of these exotic properties or phenomena is called *interface magnetism* [29]. For instance, putting a ferromagnetic (FM) layer next to an antiferromagnetic (AF) layer and subjecting the bilayer to a thermomagnetic process³ can result in pinned magnetization of the ferromagnetic layer. This process, known as *exchange bias*,⁴ is extensively used to engineer the magnetic hysteretic property of devices such as magnetic field sensors and spin-valves. On the other hand, if a thin insulator such as Al_2O_3

³Cooling the structure in applied field below the ordering temperature of the AF layer.

⁴For details on exchange bias, see Appendix B.

[30,31], TiO_2 [32], or MgO [13] is sandwiched between two ferromagnetic electrodes (see Fig. 1-1), current can tunnel through the insulating barrier. The tunneling current can be controlled by using ferromagnetic electrodes, and the conductance is determined by the relative orientation of the two electrodes' magnetization.

In a trilayer with a nonmagnetic metal such as Cu inserted between two ferromagnetic electrodes such as Fe, Co, and $\text{Ni}_{80}\text{Fe}_{20}$ (Permalloy), the resistance depends on the relative magnetization direction of the two electrodes.⁵ This is another example of an interface phenomenon that results in different magnetoresistance values depending on the orientation of the magnetization of the ferromagnetic electrodes. When it was discovered in the late 1980s, it was the highest observed change in magnetoresistance and was called *giant magnetoresistance* (GMR) [33, 34]. These interface phenomena are the basis of the many magnetic field sensors, magnetic read heads, and memory [5, 14].

In the design of devices composed of multilayers, the quality of the interfaces may severely limit the operation and performance of a device. Often, chemical and magnetic roughness or an interface with properties different from the bulk are pointed to as the main source of discrepancy between theoretically expected and experimentally measured values [35]. But not all changes at the interface are detrimental; in fact some are beneficial. For instance, Fullerton et al. [36] and Parkin [37] reported that the interface can be engineered to achieve even higher GMR values in devices by modifying just the interface, either by peppering the interface with Co or making it slightly rougher. Another interesting case is the choice of electrode and barrier in magnetic tunneling junctions (MTJs). Tunneling junctions made of single crystal Fe (100) electrodes with a single crystal MgO (100) barrier are relatively easy to model [27, 35, 38]. For experimental and practical applications, however, scalable fabrication techniques such as deposition by sputtering, which

⁵This is due to spin-dependent scattering of conduction electrons which was proposed and successfully explained by A. Fert, 2007 Physics Nobel Laureate [33].

result in amorphous electrodes, are preferred to MBE (molecular beam epitaxy). MBE is the method of choice for preparing single crystal layers epitaxially. Even though amorphous electrodes are easier to manufacture, coherent tunneling in amorphous systems is not well understood and is very complex to model. The explanation given is that during annealing, the electrodes recrystallize, yielding grain-by-grain matching between the two electrodes.

Early on, the importance of these interfaces was recognized, and many of the remarkable advances in fabrication, characterization, and imaging techniques have resulted in a better understanding of how the physics of interfaces gives rise to these phenomena. This leads to the interesting discussion of how to address the issues associated with interfacial roughness. Characterizing interfaces of magnetic heterostructures is a major challenge. The magnetic properties of the interfaces could be very different from the parent layers that form the interface. Conventional magnetometry techniques, such as vibrating sample magnetometry (VSM) and magneto-optic Kerr effect (MOKE), measure the properties of the entire structure and thus cannot be used to study the small effect of interfaces.

Novel approaches have been effectively utilized to study interfaces. For instance, one approach used atomic force microscopy (AFM) to study the different interfaces of an MTJ structure by imaging the top surface of each layer and characterizing its roughness *in vacuo* before depositing the next film [39]. However, it is the interaction and growth dynamics between the different layers at the interfaces that are responsible for the interfacial phenomena. Thus, results from this scheme may not appropriately represent the magnetism at the interface. In this study, we used interface sensitive x-ray tools with magnetic contrast to examine the magnetic response of the interfaces in magnetic tunnel junctions.

Spin-dependent Tunneling (SDT)

Spin-dependent tunneling is a quantum mechanical process that results in spin polarized current due to preferential tunneling of the majority spin electrons through a tunneling junction. A typical tunneling junction is composed of an insulating barrier sandwiched between two electrodes (see Fig. 1-1).

There are two basic spin-dependent tunneling systems. In the more traditional tunneling junction, a nonmagnetic insulator is sandwiched between two ferromagnetic electrodes (FM/I/FM structure) with tunnel barriers such as Al_2O_3 , TiO_2 , and MgO . In this system, often referred as a *magnetic tunnel junction* (MTJ), the ferromagnetic electrodes used and the electrodes' relative orientation of magnetization were presumed to be the determinant parameters. Numerous theoretical and experimental studies have, however, showed the important role of electrode–insulator interfaces as well as the properties of the entire junction, including the atomic, electronic and magnetic properties of the barrier [27, 28, 40–42].⁶

In the second system, a ferromagnetic insulator is used as a tunneling barrier between two nonmagnetic electrodes, i.e. a metal/FM/metal junction. Since the conduction band of the ferromagnetic barrier is exchange split, the tunneling barrier heights for the spin-up and spin-down electrons are different. When an unpolarized current is injected into the junction, the tunneling current will mainly composed of spin-up electrons resulting in spin-polarized current. This is the basis of the spin-filter tunnel junction. The common types of ferromagnetic barriers include chalcogenides of europium such as EuO , EuS , EuSe [43], and others such as CoFe_2O_3 [44].

⁶This model for spin-dependent tunneling was proposed and shown for the first time by Michel Jullière in 1975 [3]

Dissertation Overview

Understanding the complexity of the interactions that take place at the interfaces in magnetic devices made from multilayer structures still remains a major challenge in improving existing devices and implementing new ones. The vector nature of the magnetic interfaces and the cross-correlation with the chemical interface heighten the challenge. The main goal of this project was to carefully look at interfaces directly by using soft x-ray techniques to examine how the interfaces affect the magnetic properties of spin-filter tunnel junctions.

Chapter 2 introduces tunneling junctions and the process of spin filtering in magnetic tunnel junctions and spin-filter junctions. Description of the x-ray experimental techniques used is given in Chapter 3 and the measurement procedures and data analysis involved are outlined. Chapter 3 is devoted mainly to the scattering technique, x-ray resonant magnetic scattering (XRMS), which was used to directly study the buried interfaces and buried layers with elemental specificity and magnetic contrast.

In Chapter 4, building on the material introduced in Chapter 2 on tunnel junctions, we discuss spin filtering with ferromagnetic EuO, and XAS and XMCD characterization of EuO films grown on different electrodes. We also present direct interface characterization that was done to examine the effect of capping layers and buffer layer thickness and composition on the bottom (electrode-EuO) and top (EuO-electrode) interfaces. In Chapter 5 we summarize our results and discuss the implications of this work.

How interfacial roughness is viewed affects the solutions sought. Often, interfaces are considered as the source of many problems in multilayer structures. Major technological improvements were indeed achieved due to advances in controlling the quality and composition of interfaces and, sometimes, the intentional introduction of defects. Striving to achieve ideal, atomically flat, smooth and perfect interfaces may not be an answer to all

issues often attributed to interface effects. In this dissertation, we adopted the paradigm all interfacial effects, such as roughness, are not inherently bad. We focus on studying the buried layers a spin-filter tunnel junction and examined how the thickness of the barrier and the choice of electrodes affect the interfaces.

CHAPTER 2

TUNNELING JUNCTIONS AND SPIN-DEPENDENT TUNNELING

In this chapter the basic principles of spin-dependent tunneling in tunnel junctions composed of an oxide barrier sandwiched between two electrodes will be described. Depending on the composition of the tunneling junction, spin filtering is accomplished either by the ferromagnetic electrode or the ferromagnetic oxide barrier. First, important concepts that govern tunneling processes will be briefly reviewed, followed by details of the two tunneling systems.

Introduction

Spin-dependent tunneling (SDT), the preferential tunneling of electrons with a given spin state, is one of the most remarkable phenomena that opened understanding of fundamental properties of magnetic systems. This discovery led to wide-ranging important technological applications. Like many phenomena in magnetism, spin-dependent tunneling took over 35 years before devices to make it into consumer products. Compared to other phenomena, however, it is one of the most successful and rapidly implemented technologies that resulted in significant and sustained increase in the density and storage capacity of hard disk drives. This was achieved by replacing the GMR read-head.

The quantum mechanical process of Electron tunneling through an insulating barrier is a quantum mechanical process. It was first discovered by Friedrich Hund¹ in 1927. Several decades later, in the 1960s Giaever [45,46] accurately measured the density of states and the superconducting gap. In 1967, Esaki et al. [47] observed the dependence of the tunneling

¹Hund is more notably remembered by rules that describe the ground state filling known as Hund's rules.

current of a tunneling junction on external applied magnetic field and proposed a solid-state spin filter.

Then in early 1970s, in their pioneering work, Meservey and Tedrow [2] developed the technique of spin-polarized electron tunneling to study the spin-dependent features of the density of states of transition metals using Al as the superconducting electrode and Al_2O_3 as the tunneling barrier [48]. Spin polarization values obtained for transition metals Fe, Ni and Co several decades ago using spin-polarized tunneling (SPT) spectroscopy [48] are remarkably accurate and have been confirmed by other methods [49]. SPT spectroscopy is still used to determine polarization of oxides such as EuO and others [44, 50, 51].

Simmons [52] developed the theoretical model of the phenomena for different types of tunneling barriers and showed that the tunneling current depends exponentially on the barrier thickness. In most systems of technological importance, however, the Brinkman-Dynes-Rowell (BDR) model [53] and Landauer formalism [54] are more widely used [42]. Most recently, the details of the spin-dependent tunneling in tunneling junctions with MgO barrier was proposed by Butler et al. [27] and Mathon and Umerski [40]. Detailed and extensive review of this topic can be found in references [5, 48, 51].

Numerous devices that take advantage of this process were proposed [5, 48]. In 1995, the discovery of room temperature tunneling magnetoresistance in magnetic tunneling junctions (MTJ) devices independently by Miyazaki and Tezuka [30] and Moodera et al. [31] using Al_2O_3 barriers renewed the interest in spin-dependent tunneling.

Magnetic Tunneling Junction

Tunneling magnetoresistance (TMR) is defined as the ratio of the difference in resistance between anti-parallel (AP) and parallel (P) alignment configuration, as shown in Fig. 2-1, of the magnetization of the electrodes divided by the parallel alignment resistance.

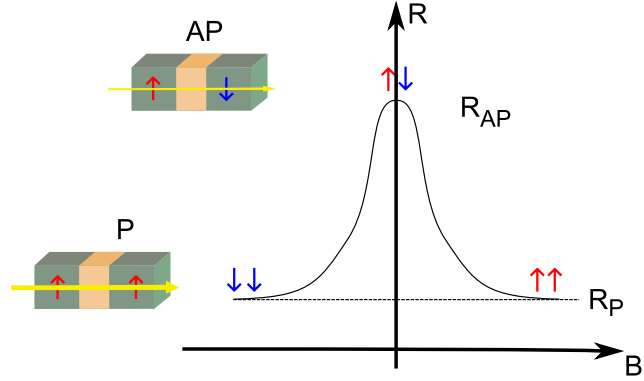


Figure 2-1: Magnetoresistance in a magnetic tunnel junction. The resistance across the trilayer structure depends on the relative orientation of magnetization of the two ferromagnetic layers. The up(down) arrows indicate magnetization of ferromagnetic layers and the thickness of the yellow lines show the intensity of the tunneling current. Figure from [42].

Spin-dependent tunneling across a magnetic tunneling junction depends on the ferromagnetic electrodes used, the barrier and the electrode-barrier interfaces. The tunneling probability of an electron with spin-up or spin-down states depends on the availability of majority or minority spin states that it can scatter into. The availability of states is determined by the relative magnetization orientation of the two ferromagnetic electrodes.

Fabrication of thin alumina (AlO_x) barriers sandwiched between two ferromagnetic (FM) electrodes was first pioneered by Jullière in 1975 who observed a change in the resistance of the tunneling junction as the relative magnetization of the two FM electrodes is switched from parallel to anti-parallel configuration. The TMR is given by Jullière's equation

$$TMR = \frac{2P_1P_2}{1 - P_1P_2} \quad (2.1)$$

where P_1 and P_2 are the polarizations of electrodes 1 and 2 at the Fermi level. Low temperature TMR values of different systems were not encouraging until Moodera et al.'s work [51] that first demonstrated room temperature TMR using an alumina tunneling barrier.

As Eq. 2.1 indicates, higher TMR values can be achieved by using highly spin po-

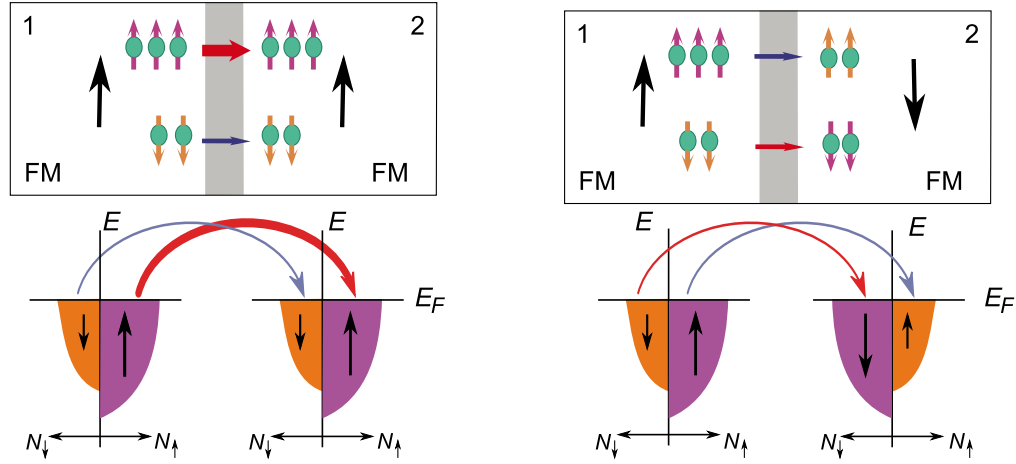


Figure 2-2: Spin-dependent tunneling in ferromagnet/insulator/ferromagnet (FM/I/FM) tri-layer structure. The fraction of majority (minority) spins tunneling from FM₁ to FM₂ through the insulating barrier depends on the relative magnetization orientation of the two electrodes which determine the availability of states to scatter into. Figure adapted from [13].

larized electrodes. The polarization of the most common ferromagnetic electrodes were determined, by the Meservey-Tedrow spin-polarized tunneling spectroscopy. The highest achievable TMR values using Fe ($P_{Fe} = 0.44$) and Co ($P_{Co} = 0.34$) electrodes are 48 % and 26 % respectively [2, 42, 48, 49]. An often suggested approach has been to use materials with $P = 1$, called *half metals*. Making such materials has been challenging because interfaces reduce the effective polarization of the junction (both bulk and interface).

The main challenge was fabricating of pinhole-free barriers, smooth interfaces, and high TMR values at room temperature. Not all problems were, however, associated with interfaces quality. For example, the TMR value depends on achieving and controlling the relative magnetization orientations of the two ferromagnetic electrodes. Miyazaki and Tezuka [30] reported that the magnetoconductance is given as $G = G_o (1 - \cos \theta)$ showing the cosine dependence of the conductance on the angle θ between the two electrodes.

The reason for this same problem that plagued GMR systems, was shown by Idzerda

et al. [7] using soft x-ray techniques which provide magnetic contrast. They showed that the switching of the two ferromagnetic layers is not as well-defined or abrupt, as initially expected. Instead, when switching the soft (free) layer drags the second layer resulting in an ill-defined anti-aligned configuration that gives MR values much lower than expected.

Several approaches were taken to tackle this issue of achieving reproducible, controlled anti-aligned configuration. The approach Miyazaki and Tezuka [30] adapted was to have Fe electrodes grown at different temperatures so that films will have different coercive fields. The layer grown at elevated temperature will have a lower coercive field (H_C) compared to the layer deposited at room temperature. The other approach was to use different electrodes, such as Fe and Co or various combination of Fe and Co. This issue took a long time to resolve until the spin-valve structure with exchange bias was developed and the materials aspect of this issue was properly addressed.

Exchange bias provided a lasting solution to this problem. Exchange bias is used to set the magnetization of one of the two ferromagnetic layers, called the *reference* layer of the trilayer structure. This layer is antiferromagnetically coupled across a spacer layer to the *pinning* layer of the spin-valves. Figure 2-3 shows such a structure with the pinning layer where the magnetization of the CoFe layer is pinned by the antiferromagnetic PtMn layer. The magnetization of the ‘Reference’ CoFeB layer (see Fig. 2-3) is set by this pinning layer that couples to the CoFe across the Ru spacer. This approach was first demonstrated by Dienty et al. [18, 55].

The ferromagnet’s magnetization is anchored by the antiferromagnetic (AF) layer in a direction set during the in-applied-field annealing process. This results in a much higher coercive field and may shift the center of the hysteresis loop to one side. The ability to adjust the coercive fields of different layers in a given structure has had a pronounced impact on technical application, especially in tailoring the magnetic response of structures for different applications. It has allowed the switching fields of the free-layer to be of the

order of a few Oersted's even at room temperature without affecting the pinned layer. Magnetic field sensors and other magnetoelectronic devices, such as read-heads, use stacks of magnetic thin films that provide mechanical and thermal stability and the desired magnetic response (see Fig. 2-3).

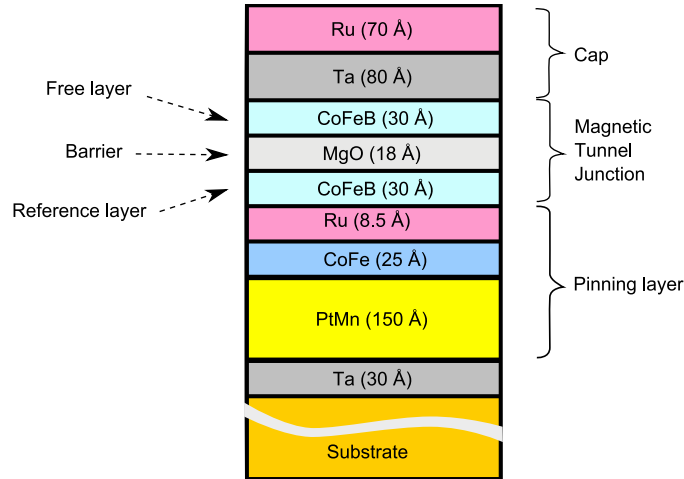


Figure 2-3: Structure of a magnetic tunneling junction with MgO barrier, CoFeB free layer, PtMn/CoFe pinning trilayer and CoFeB reference layer.

The two most common applications of MTJs are memory elements in MRAMs and read-heads in hard disk drives as discussed in Chapter 1. In MTJs, it is the relative magnetization of the two electrodes that provides the spin selection and the spin filtering is accomplished by the ferromagnetic electrodes. In the next section, we discuss the second method of spin filtering using a ferromagnetic barrier.

Spin Filtering with Ferromagnetic Insulator

The exchange split conduction band of the ferromagnetic insulator creates different barrier heights for the spin-up and spin-down states. At temperatures above the Curie temperature (T_C) of the ferromagnet, both spin-up and spin-down tunneling electrons experience the same barrier height, shown by the dashed line in Fig. 2-4. Below T_C , however, the

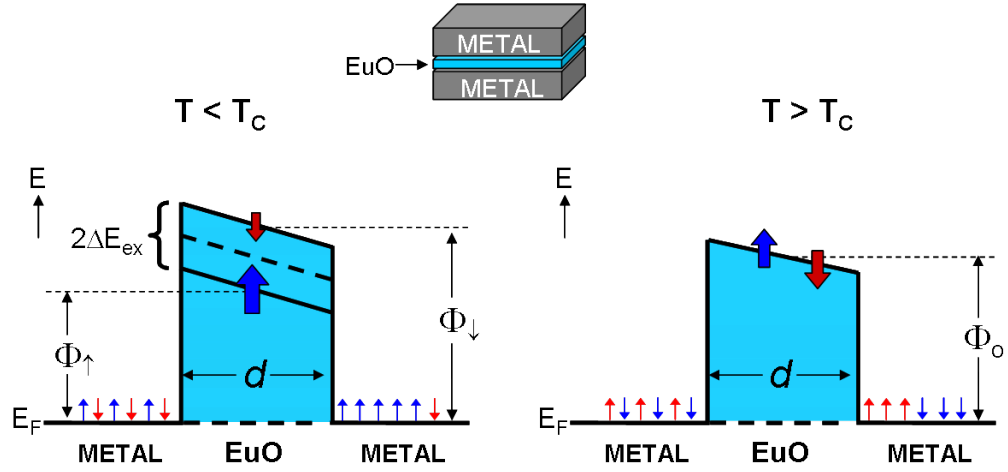


Figure 2-4: Spin filtering effect with EuO tunneling barrier. Top: The junction comprises of a ferromagnetic tunnel barrier sandwiched between two metallic electrodes. Right: Above the Curie temperature ($T_C = 69$ K), both spin-up and spin-down electrons experience the same barrier height Φ_0 . Left: Below T_C , the conduction band is exchange split ($2\Delta E_{ex} = 0.54$ eV), which results in different barrier heights $\Phi_{\uparrow(\downarrow)}$ for the spin up(down) electrons. Magnitude of the tunneling current is shown by the thickness of the solid up(down) arrows. Figure adapted from [44].

tunneling barrier heights $\phi_{\uparrow}$ and $\phi_{\downarrow}$ for the spin-up and spin-down electrons respectively are different (see Fig. 2-4). In the unpolarized current injected from the electrode on the left, the number of spin-up and spin-down electrons is the same. After tunneling through the barrier, however, there are fewer spin-down electrons than spin-up because the tunneling probability depends on the barrier height. The tunneling current is spin-polarized and the tunneling junction acts as a spin-filter. In this case, spin-flip is not considered and no spin-orbit interaction or interactions with phonons or magnons are taken into account [51].

In the next chapter, we discuss the interface sensitive soft x-ray based techniques utilized to study spin-filter tunnel junction with an EuO barrier .

CHAPTER 3

X-RAY CHARACTERIZATION OF
BURIED INTERFACES AND BURIED LAYERS

Soft x-ray based techniques provide element selectivity and interface sensitivity with magnetic contrast. We used these synchrotron based techniques to examine and characterize the chemical and magnetic properties of buried layers and buried interfaces. Information obtained using these techniques on tunneling junctions, introduced in the previous chapter. Here, experimental details and analysis of the spectra obtained using different techniques, focusing on resonant scattering technique, will be discussed.

Synchrotron Characterization Techniques

Major advances in surface science have moved the frontiers of technology making fabrication of spin-based electronic (spintronic) devices with greater control possible. In turn, this has pushed the demand for new characterization techniques that provide better resolution with minimal damage to the sample and capabilities to isolate the contribution from the interface from that of the bulk. Synchrotron-based soft x-ray¹ tools have provided substantial breakthroughs in material science and magnetism in recent history. These soft x-ray based techniques have been instrumental in addressing important questions in magnetism and providing elegant answers. Question such as layer switching in multilayer structures were resolved conclusively, and unambiguously, without destroying the samples [11]. Lessons learned and advancements achieved in instrumentation and theoretical work on hard x-rays and neutron scattering were important for the remarkably quick ad-

¹Soft x-ray range 150 – 1500 eV and hard x-ray range 1.5 – 150 keV.

vances in soft x-ray techniques. What makes it relevant and extremely useful is the energy range it covers.

Synchrotron techniques are powerful probes that are interface sensitive with elemental specificity and magnetic contrast. This energy range that spans between 150 – 1500 eV, commonly referred to as the *soft x-ray* range, encompasses transitions from core levels of the interesting transition metals ($2p \rightarrow 3d$) and rare earth ($3d \rightarrow 4f$) elements covering several technologically important and novel compounds (oxides) and magnetic materials.

The experiments reported in this work were done at beamline U4B at the National Synchrotron Light Source (NSLS) located at Brookhaven National Laboratory, New York and beamline 4.0.2 located at the Advanced Light Source (ALS) at Berkeley, California. The beamline U4B is located at a bend magnet while beamline 4.0.2 at ALS is an undulator beamline. The low temperature magnetic characterization measurements on EuO were done at ALS which has high magnetic field (± 7000 Oe).

Interface Sensitivity with Magnetic Contrast

The main challenge in studying interfaces of systems composed of magnetic and non-magnetic multilayer is the need to have the whole structure as the sample. By examining the surface of each layer, as it is being stacked on, one can obtain important information about the structure of the multilayer. To investigate the spin transport property of the entire structure and examine the role of interfaces, the multilayer must be studied as a whole, not a single layer by layer. This requirement severely limits the utility and number of techniques available in the study of buried layers and buried interfaces. With the ever-increasing demand for smaller and smaller device sizes, the need to have better understanding of the processes at such extremely small length scales is more important than ever.

The second component of a synchrotron are the stations where the radiation is collected

and the experiments are performed. These beamlines, usually comprise x-ray optics and the experimental chambers. The optics are used to collimate and refocus the incoming beam and choose the desired photon energy. From the high flux x-rays provided by the storage ring, the energy is selected using a grating monochromator. This ability to tune the energy of the incident photon over a wide energy range is what gives these synchrotron based soft x-ray techniques their element selectivity. The resolution of energy selected is further improved by using slits that correct small linear dispersion. Appropriately placed entrance and exit slits that correct for small linear dispersion of the beam improve the spectral resolution of the incoming beam. At beamline U4B, depending on the energy range where the measurement is conducted and entrance/exit slits setting, energy resolution down to 0.3 eV can be achieved

Helicity of the incoming light is also selected by adjusting the position of the mirrors that collect the radiation in a bend-magnet end-station. This is a very important component for magnetic characterization. Light collected above (below) the synchrotron plane is right (left) circularly polarized. Linearly polarized light is collected at the synchrotron plane.

Depending on what is being measured (photons or electrons) and how the measurement is performed (absorption, reflection or transmission), there are different complementary measurement techniques. The techniques are total electron yield (TEY) where the sample current is measured, or partial electron yield (PEY), fluorescence yield (FY) or partial fluorescence yield (PFY), transmission or reflected photons. Detailed description of these techniques is given in Ref. [56].

Experimental Chamber

The electron yield signal is composed of photoelectrons, Auger electrons and secondary electrons generated from the inelastic cascade process for the high energy primary electrons. The high-energy Auger electrons created in the core-hole decay are predominantly

responsible for the secondary electron signal which dominates the total electron yield [57]. Changes in the incoming flux, due to changes in the storage ring or a glitch, are monitored by measuring incident flux I_0 using a highly transmitting Au grid located as close the chamber as possible. Dividing the measured intensity by I_0 corrects for variations in the incident flux.

Details of the EuO sample structures and preparation is given in the next chapter. The requirements for x-ray characterization were sample size (actual dimension of the wafer), thickness of the relevant layers so that the interfaces of interest could be probed with a decent signal and capping material and thickness to provide good protection for the structure without interfering with the measurement.

The samples used in the x-ray characterization were specifically prepared for the strict conditions that take into account the issues associated with the type of the measurement. These include the thickness of the capping, which had to be 40 – 80 Å, preferably made of Al that is sufficient to protect the underlayer from oxidation and damage during shipping and keep the sample in best condition possible without interfering with the measurements.

In the following section, we describe the techniques used to examine the different layers and interfaces of tunneling junctions. The techniques are x-ray absorption spectroscopy (XAS) in absorption mode and reflectivity measurements, x-ray resonant scattering (XRS), along with their magnetic counterparts x-ray magnetic circular dichroism (XMCD), and x-ray resonant magnetic scattering (XRMS) respectively. Details of XMCD can be found in review articles [6, 56].

Reflectivity: XRS and XRMS

X-ray resonant scattering (XRS) is a surface and interface sensitive non-destructive and element specific probe. Taking the difference between the scattered intensity of left-

and right-circularly polarized light provides magnetic contrast or x-ray resonant magnetic scattering (XRMS). XRMS shares the sensitivity of XMCD and has the added advantage of determining the spatial modulation of the magnetization.

Here the focus is on scattering measurements that are element selective, due to resonant enhancement of the reflected intensity at the absorption edge of the element involved. They can probe deeper in the material and do not suffer from saturation and self-absorption effects as XAS. Resonant enhancement of the reflected intensity at the absorption edge of the elements present gives this technique its unique ability to study systems with elemental resolution. Magnetic contrast is achieved by using circularly polarized light. Based on the relative orientation of the incident light's polarization and the magnetization of the sample, the weak magnetic scattering can be comparable to the chemical scattering if the energy is properly tuned to the transitions allowed by the dipole selection rules [26, 58].

Scattering Setup

The scattering measurements can be done using linear or circularly polarized light with an energy resolution of 0.3 – 0.5 eV [10, 58]. A goniometer with sample stage and detector arm that can be moved independently to perform different types of scattering measurements. The x-ray scattering experiments presented here were done in a scattering configuration shown in the inset of Fig. 3-2 where the scattering plane is always in the x-z plane and both the sample and detector are rotated about the y axis. The sample angle (ω) and detector angle (2θ), are measured with respect to the direction of the incident light, as shown in Fig. 3-2. The magnetic field is applied parallel to the sample surface in the scattering plane by an *in situ* electromagnet, with a maximum steady field of ± 300 Oe and pulsed fields of ± 1 kOe at the gap [58].

To improve the quality of the signal from the photodiodes and eliminate noise, we use an in-line amplifier mounted as close to the photodiodes as possible in the detector

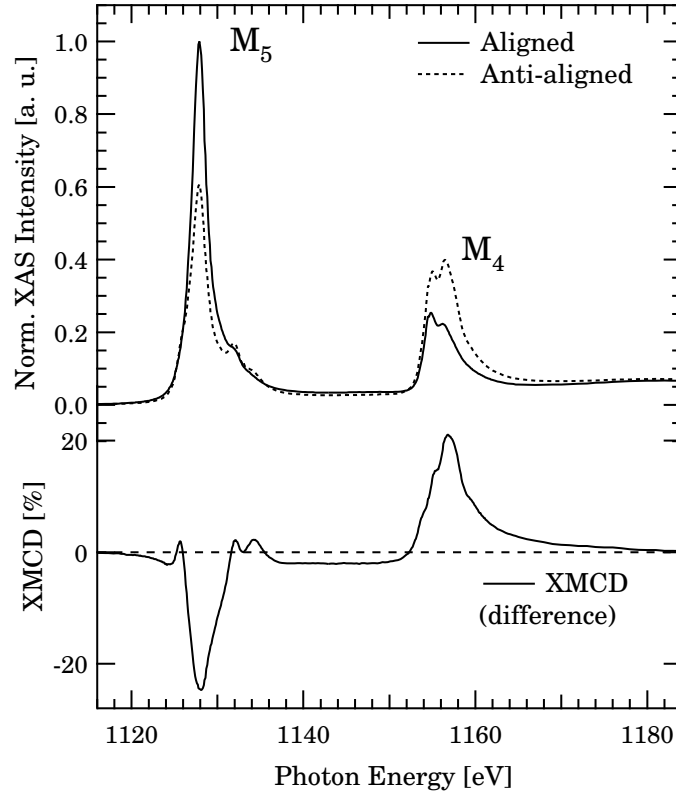


Figure 3-1: X-ray absorption spectra for a 20 Å EuO sample grown Si in the anti-aligned (solid) and aligned (dashed) configurations. The peaks depicted as M_5 and M_4 represent transition to Eu's localized $4f$ states from $3d_{5/2}$ and $3d_{3/2}$ respectively. Magnetic contrast is achieved by taking the difference between the aligned and anti-aligned spectra (top), which gives the XMCD signal. At 14 K, the measured XMCD signal of this sample is 25%.

arm. The amplifier, with its wide dynamic range, boosts the signal and provides better quality measured signal. In some measurements, the magnitude of the reflected intensity may change by as much as six orders of magnitude. Thus, care must be taken so as not to saturate the detector when it is moving through the most intense peak of the rocking sample scan, the specular peak (see Fig. 3-5).

The sample platen that mounts onto the sample stage can hold sample size 8×20 mm. The lowest temperature that can be achieved at the sample stage of the scattering chamber with liquid nitrogen is 150 K. Thus, the focus of our studies on EuO samples, with T_C of

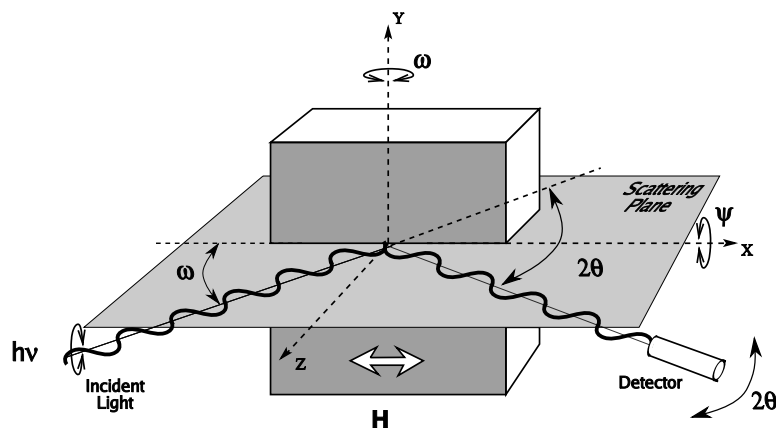


Figure 3-2: Beamline U4B's scattering chamber configuration. The sample stage has five degrees of freedom (x , y , z , sample angle (ω), roll (ψ)). The energy and polarization of the incident light can be tuned to the desired absorption edge at a selected polarization (linear, left- or right circular). The detector can be rotated (2θ) independently and the applied field in the x -direction can be varied.

69 K for bulk and even lower for thinner films, was on chemical interfaces characterization.

Depending on the dimensions of the sample and requirements of the measurement and signal-to-noise ratio, the vertical and horizontal size of the incident beam are adjusted by a set of slits located just before the beam enters the scattering chamber. Mounted on the detector arm are multiple photodiodes with varying slits sizes for different types of measurements. When measuring the diffuse background in rocking scans, the intensity is so small that a detector with wider slits (0.342 deg.) is used at the expense of angular resolution, whereas in specular scans, intensity may be sacrificed for angular resolution by using a detector with narrow slits (0.054 deg wide).

Proper alignment depends on getting the axis of rotation of the sample to match the rotation axis of the detector. With the five (5) degrees of freedom in the sample manipulation stage (x , y , z , ω , and ψ (roll)), one has to take into account and correct for backlash which introduces error in the sample angle, detector angle and the roll position (ψ) as well as the weight of the sample stage arm as it is extended which can introduce error in the height (z - position). Contribution from stray reflected light is a common source of noise and arti-

facts. To reduce their effect, all windows must be closed, scattering chamber isolated from the down-stream chambers of the beamline, ion gauges turned off and ion pump partially closed. Measurements are usually done at pressure in low sevens (10^{-7} Torr).

To reduce the turnaround between different samples and cut down on time needed to perform the alignment, two or more samples or a wedge sample can be loaded. Despite the obvious advantages this approach introduces some challenges such as working with a thinner beam (about 2–3 mm). As the sample stage is extended or retracted by about 2 inches into or from the chamber to choose the appropriate sample, the stage flexes about 5 mm which introduces a significant change in z-position. This can, however, be fixed by quick realignment procedure to correct height.

Finally, we measure hysteresis loops (with element specificity) by sweeping the magnetic field while keeping all other parameters constant [24,58]. This is similar to the longitudinal magneto-optical Kerr effect (L-MOKE) but uses circularly polarized light that can be used for element specific magnetic hysteresis (ESMH) loop measurements. When scattering measurements are performed, the specular reflected x-rays sample the entire film's thickness, yielding information about the entire film.

Types of Scattering Measurements

The scattering setup, with 9 different parameters that can be independently varied, is a data-rich experimental setup with large phase space. The first place to start when working with a new system is to identify the elements present and do a quick energy scan at the absorption edges of elements available in the system. In this section we now describe the different measurements where one or a combination of the parameters are varied. Next, the different types of measurements will be introduced according to the sequence of how a typical set of measurements would be performed on a new system or a new set of samples.

At the angles identified from the specular scans, energy scans are performed to determine the energy values of interest for further interface studies or magnetic characterization. The objective is to systematically probe the phase space defined by energy and polarization of the incident photon, sample and detector angles in the case of magnetic characterization.

For energy scans, the photon energy is varied while keeping all other variables constant. The resonantly enhanced scattering at the absorption edges of elements in the film can be measured. In the case of specular scans, the energy of the incident photons is tuned to the absorption edge of the element being studied. Then, both the sample and detector angles are scanned such that the specular condition ($\theta = 2\theta$) is maintained throughout the scan. This allows us to examine specific layers or interfaces in the multilayer structure with element specificity. We can obtain magnetic contrast, given by the XRMS signal, in the above-mentioned measurements by using circularly polarized light.

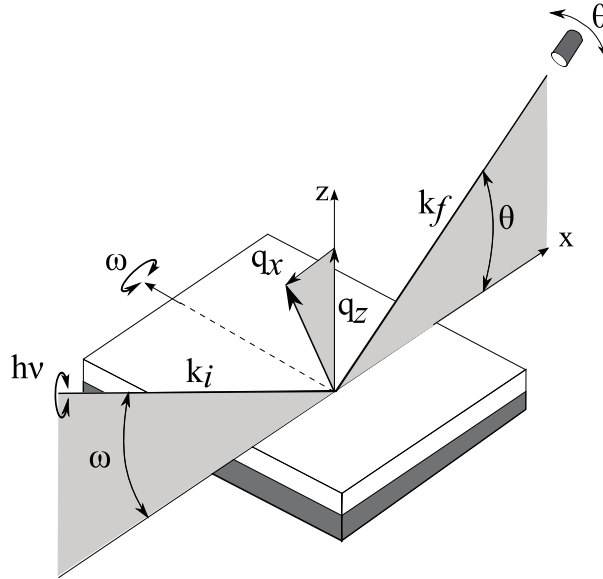


Figure 3-3: Momentum transfer vector $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ and its in-plane (q_x) and out-of-plane (q_z) components.

At a relatively high angle, we perform an energy scan around the range of the elements that are being studied. At high angles, the scattering XRS spectra look much like XAS

scans, if the system is not set up for energy scan in the TEY mode. The main purpose of this procedure is two-fold. On the one hand it is to locate where the energy values of interest lie and make sure everything in the setup is running in the expected way by verifying the XAS scan with similar scans done in the absorption chamber. On the other hand, this scan is used to correct any energy shift that may occur due to drift in the monochromator.

The second step is to identify the sample angles of interest by performing a complete specular scan. In this scan, the sample angle (ω) and detector angle (2θ) are moved such that the specular condition is maintained while the scattered intensity is collected. These measurements are done at the energy values selected from the XAS (in TEY mode). At higher sample angle, there is a precipitous decrease in the intensity (see Fig. 3-4). Thus, the detectors must have a wide dynamic range to go over 4 up to 6 orders of magnitude change in intensity. This wide response is importance in the off-specular (rocking sample) scan.

We obtain quantitative roughness information, including out-of-plane (σ) roughness and in-plane correlation length (ξ) by performing rocking sample experiments [24]. In this scan, the detector angle (2θ) is kept fixed while the sample is rocked by scanning the sample angle (ω) from zero degrees to 2θ to cover the full horizon. Figure 3-5 depicts a typical diffuse scattering background due to interface roughness, that channels reflected flux away from the specular peak, results in a wide, low intensity reflection which is convoluted with the sharp specular peak around $\omega = \theta$ ($q_x = 0$). The ratio of the diffuse integrated area to the total integrated area is a measure of the out-of-plane roughness [24]. The width of the diffuse part is related to the in-plane correlation length.

At the selected energy and specular angles, determined from the earlier measurements, we perform sample rocking scans to characterize the interfaces and compute the interfacial roughness parameters. If the reflected intensity is too low or if the background is noisy, the rock sample scan can be done at reduced angular and energy resolution by opening

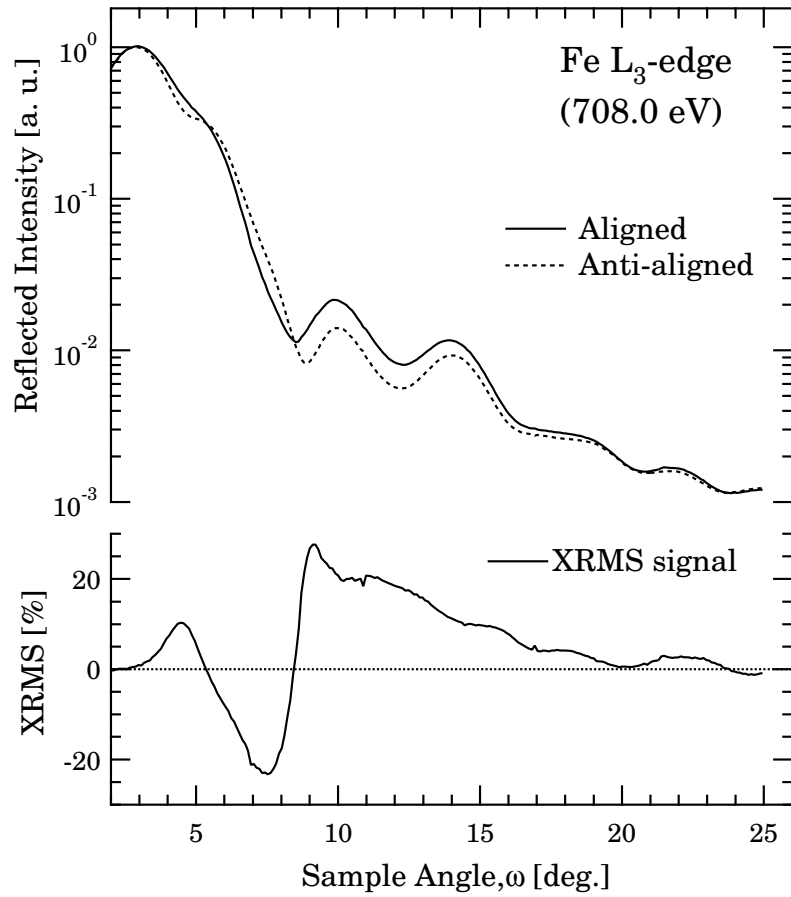


Figure 3-4: Specular ($\theta - 2\theta$) scans at the Fe L_3 edge (708.0 eV) in the aligned (solid line) and anti-aligned (dashed line) configuration. The difference (XRMS signal), which provides the magnetic information, is shown on the bottom panel.

the slits. For a smooth surface or interface, the sample rocking spectra look like a delta function centered at $\omega = \theta$ with a very flat background. Presence of a diffuse background (as shown in Fig. 3-5), is an indication of rougher interface (or surface) that channels flux away from the specular peak and into the background [22]. If there are multiple interfaces, each interface can be examined by tuning to the absorption edge of elements present in the sample and performing rocking sample scans at selected angles.

By using circular polarized x-rays, the scattering intensity has strong magnetic contrast. Measuring spectra for photon helicity and magnetic moment parallel (I^+) and anti-

parallel (I^-), the average spectra $[(I^+ + I^-)/2]$, the XRS spectra] and the asymmetry spectra $[(I^+ - I^-)]$, the x-ray resonant magnetic scattering, or XRMS, spectra] can be obtained.

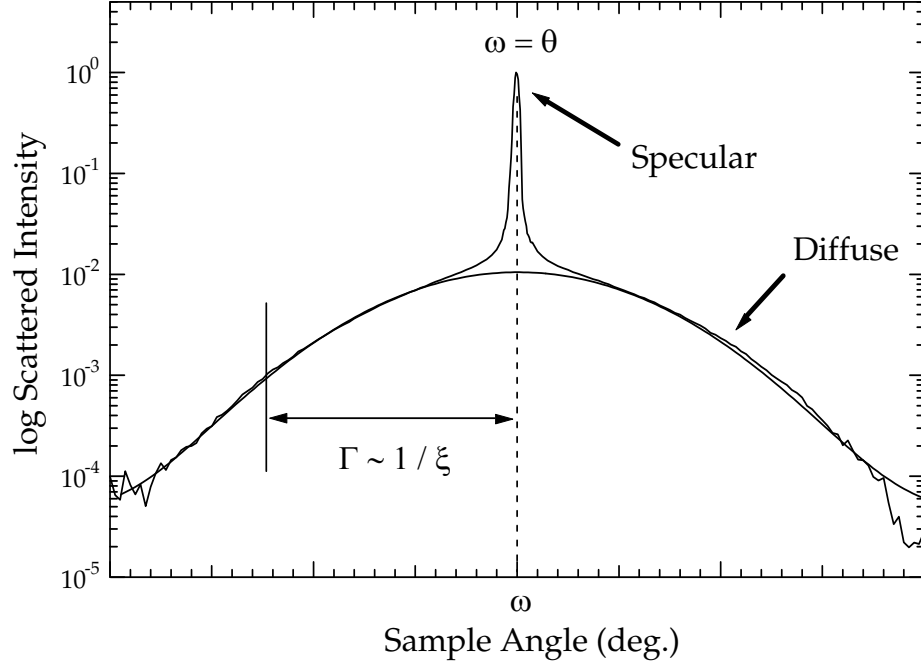


Figure 3-5: Typical rocking sample (diffuse) scan that has a specular peak at the center $\omega = \theta$ and diffuse background. The area under the specular peak is a measure of the perpendicular roughness and the correlation length is inversely proportional to the width of the diffuse background [22].

If we record the scattering intensity as a function of applied magnetic field, while holding the sample angle fixed at the specular scattering condition ($q_x = 0$ or $\omega = \theta$), or slightly offset from specular, we can acquire the specular and diffuse hysteresis loops, respectively [11]. The specular scattering hysteresis loops are indicative of the net moment of the film, whereas the off-specular scattering intensity is indicative of variations in the magnetic roughness at the interface or in-plane magnetic ordering [10, 12].

Summary

In this chapter, we discussed the different characterization techniques used in this project. These include synchrotron-based soft x-ray techniques used to examine the buried interfaces and buried layers. Information obtained using these techniques was used in association with data obtained from other techniques, such as SQUID magnetometry and spin transportation measurements. In the next chapter, we present our results from the x-ray measurements performed on spin-filter junctions with EuO barrier.

CHAPTER 4

SPIN-FILTER TUNNELING JUNCTION USING A FERROMAGNETIC EuO BARRIER

In this chapter, we present chemical and magnetic characterization of EuO films as a function of film thickness and choice of electrodes. Using element-specific and interface sensitive soft x-ray based techniques, we examined the buried bottom (electrode-EuO) and top (EuO-electrode) interfaces. Following a brief review of the previous work on EuO, details of the fabrication and characterization of EuO samples will be described. We conclude with results from the first successful fabrication of high quality ultrathin films with chemical and magnetic properties comparable to bulk.

Introduction

Europium monoxide's remarkable electrical, magnetic, and optical properties make it a candidate for applications in spin-based all-electrical devices and a prototype for studying the physics of spin filtering. This prospect of easy incorporation with existing semiconductor based technology has made EuO a very attractive system to study [17, 44, 59]. The challenge has been to fabricate stoichiometric ultrathin (~ 20 Å) films. More recently, Santos showed near 100% spin-polarized current using a EuO barrier [44]. Schmehl et al. also reported spin polarization of more than 90% in doped epitaxial EuO films measured by point contact Andreev reflectivity (PCAR) and injected polarized current into Si and GaAs [17]. Unlike a typical magnetic tunnel junction (MTJ), in a spin-filter a ferromagnetic semiconductor barrier, such as EuO, is sandwiched between two nonmagnetic electrodes. The spin-up and spin-down electrons of the unpolarized current experience different

tunneling barrier heights due to the exchange split conduction band of the ferromagnetic barrier resulting in spin-polarized tunneling current (see Fig. 2-4).

To identify the factors that affect chemical and magnetic properties of thin EuO films, we systematically studied a series of EuO samples using the soft x-ray techniques described in the previous chapter. Questions addressed in this work include: does the choice of buffer layer and its thickness affect the quality of the bottom and top EuO interfaces? Most importantly, how does the thickness of the oxide layer,¹ affect the magnetic property of the EuO barrier and the barrier's filtering efficiency? This study was done in conjunction with other techniques that were used to examine the transport and magnetic properties of the system. This chapter will address important questions, including identifying the most important factors that affect the magnetic and chemical properties of the EuO tunneling barrier. It will cover the work done to examine the effect of choice of buffer layer, electrodes used and thickness of the deposited oxide barrier.

This project was conducted over a number of years, and results reported here were used as feedback to improve the fabrication process and the quality of the structures. Here, we present the first successful fabrication of ultrathin ($< 20 \text{ \AA}$) EuO films with properties consistent with the bulk. First, we examined the quality of the buried oxide layer using element specific soft x-ray techniques sensitive to the oxides present. Then we characterized the buried bottom (electrode-EuO) and top (EuO-electrode) interfaces with angle-dependent XAS and scattering (XRS) measurements. Finally, we compared the magnetic properties from SQUID magnetometry measurements with XMCD measurements.

EuO: a Novel Oxide

In the late 1970's, studies on EuO were deemed a closed subject because the work done on this Heisenberg ferromagnet was so extensive and comprehensive [60]. Its rocksalt

¹EuO film thicknesses were measured by the thickness monitor during the film growth. There is about 15% uncertainty in these thickness values [44].

structure (FCC) with lattice spacing of 5.144 Å and Curie temperature (T_C) of 69 K, and its metal-to-insulator transition (MIT) in Eu-rich EuO were thoroughly investigated. From optical, neutron and other studies, the structural, electronic, and magnetic properties of this highly unstable oxide of europium were well established. For technological applications, the optical band gap $E_{g,opt} = 1.2$ eV, which matches that of silicon (1.1 eV), a very exciting system is its exchange split conduction band ferromagnetic semiconductor [44]. When used as a barrier, it can spin filter the tunneling electrons and generate spin-polarized tunneling current. The exchange splitting of 0.54 eV [50] is significant and makes EuO a model system for exploring spin filtering across a tunneling barrier. This splitting value is high compared to the 0.36 eV of EuS, another spin filter barrier [44]. For a detailed review on spin-filters, see Ref. [51].

Sample Fabrication and Characterization

The EuO samples used in this project were grown by reactive thermal evaporation of pure europium in the presence of oxygen on HF etched Si(100) wafer. The Eu_2O_3 reference sample was deposited from a pure Eu_2O_3 powder source. Magnetometry and transport characterization were also done at the facility in MIT using SQUID to determine the quality of the samples. For further details on fabrication of the structures and magnetic and transport measurements, refer to Dr. Santos's thesis [44]. In the initial phase of the project, the samples studied had the basic structure: Si wafer/EuO/electrode/Al, as shown in Fig. 4-1a, where the nonmagnetic electrode was either Al, Ag or Y. The samples were capped with a 40 to 80 Å Al layer, a thickness sufficient to protect the EuO layer without affecting the x-ray measurements.

To reduce sample variability due to growth conditions, most of the samples reported here were grown under the same conditions in the same batch. Since the focus of this

study was to investigate the electrode-EuO (top) and EuO-electrode (bottom) interfaces, a shadow mask setup was used to cover sections of the same EuO film with different electrode materials. To guarantee that the samples with different EuO thicknesses have identical EuO-electrode interfaces, they were grown in a shutter-opening mode. The shutter is opened in incremental steps of 3 mm yielding a *stair-step* structure as depicted in Fig. 4-1.

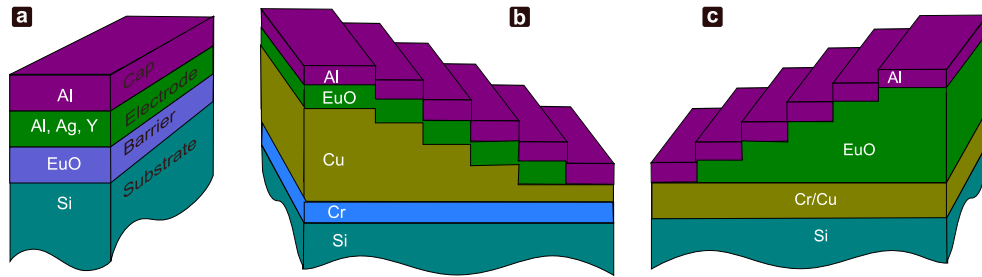


Figure 4-1: Basic structure of the EuO samples used in the study. Left: A single piece sample used to study the top (EuO-electrode) interfaces and the effect of top electrode material. Middle: Wedge sample grown in shutter-opening sequence where the sample is initially covered except the first step. By opening the shutter (moving it from left-to-right), the steps of the wedge sample is grown. This approach ensures that the interface with the next layer is identical for all steps. Right: In shutter-closing mode, the sample is completely exposed. Then the shutter is gradually closed, forming the wedge structure. In this mode, the interface with the preceding layer is identical for all steps.

As stated earlier, fabricating the oxide layer with the correct stoichiometric ratio requires strict adherence to growth conditions including careful preparation of the substrate, cleaning the chamber of any contaminants, and constant monitoring of Eu evaporation rate and oxygen flow rate into the chamber [50]. Using overlayer elements that readily oxidize such as yttrium, increases the complexity of the growth process. Thickness of the deposited films is monitored by a water-cooled quartz-crystal microbalance (QCM).

Wedge (Stair-step) Samples

The use of wedge samples is an attractive approach that provides several advantages. Wedge structures are often used to study the effect of thickness or composition of a given layer by placing a marker layer underneath. First it reduces sample-to-sample variation significantly. Second, it provides a template where only one parameter can be varied and its effect carefully examined. Finally, by choosing the appropriate shutter-opening or shutter-closing sequence, a wedge sample for examining the top or bottom interface can be grown. In the case of shutter-opening mode, the interface with the next layer is identical for all steps of the wedge 4-1 (b). On the other hand, in shutter-closing growth mode, the interface with the previous layer is the same for all steps, as shown in 4-1 (c). Our wedge samples are composed of a series of 3 mm-wide steps. The width of each step is determined by the step-size of the shutter mechanism in the growth chamber. This step-size was the same as the x-ray beam spot size in the scattering measurements that provides sufficiently reflected intensity for most of our measurements at such high energy (Eu $M_{4,5}$).

To eliminate uncertainty when comparing results from different measurement techniques, when possible, twin sample-sets were grown. One half is used for magnetometry measurements and the other half is used for x-ray characterization. In the next section, we discuss details of the measurements and the analysis procedures used to characterize the top and bottom interfaces.

Tunnel Barrier Quality and Oxides Present

Following the fabrication of the structures, careful characterization is done by our colleagues Dr. Tiffany Santos and Dr. Jagadeesh Moodera at the MIT Center for Materials Sciences and Engineering (CMSE). The measurements include spin-polarized tunneling spectroscopy [50] to determine the degree of polarization of the tunnel junction, and su-

perconducting quantum interference device (SQUID) magnetometry to determine low temperature hysteresis loops and the temperature dependence of the magnetization (M versus T curves). X-ray characterization was conducted at the MSU Nanostructures Growth and X-ray Characterization Facility, located at the National Synchrotron Light Source (NSLS) beamline U4B and at the Advanced Light Source (ALS) beamline 4.0.2. As discussed in Chapter 3, the absorption measurements (XAS and XMCD) were done in the total electron yield mode in the absorption chamber. The scattering (XRS) measurements were done in the reflectivity chamber, and the signal is collected with a photodiode. These measurements were done using linearly and circularly polarized x-rays with energy resolution up to 0.3 eV.

Oxides of Europium

Figure 4-2 shows the XAS spectra of the two dominant oxides of europium. Identifying the two oxides is made easier by the distinct signature peaks. Near the M_5 edge, there are five peaks that indicate the oxidation state of the europium. We used these M-edge peaks B and D (associated with EuO) and peaks A, C and E, (associated with Eu_2O_3), to identify and quantify the relative abundance of the two species. Details of the deconvolution process are given in Appendix C.

Choice of Electrode

To understand how the choice of the top electrode affects the properties of the EuO layer and oxide-electrode interface, we profiled the types of oxides present in a series of EuO films with the basic structure shown in Fig. 4-1 (a) with different overlayers. Figure 4-3 shows XAS spectra from 40 Å EuO samples with 20 Å Al, Ag and Y electrodes with the corresponding fraction of Eu_2O_3 indicated for each electrode. The samples were grown in the same session using a shutter and a mask setup to deposit different top electrodes.

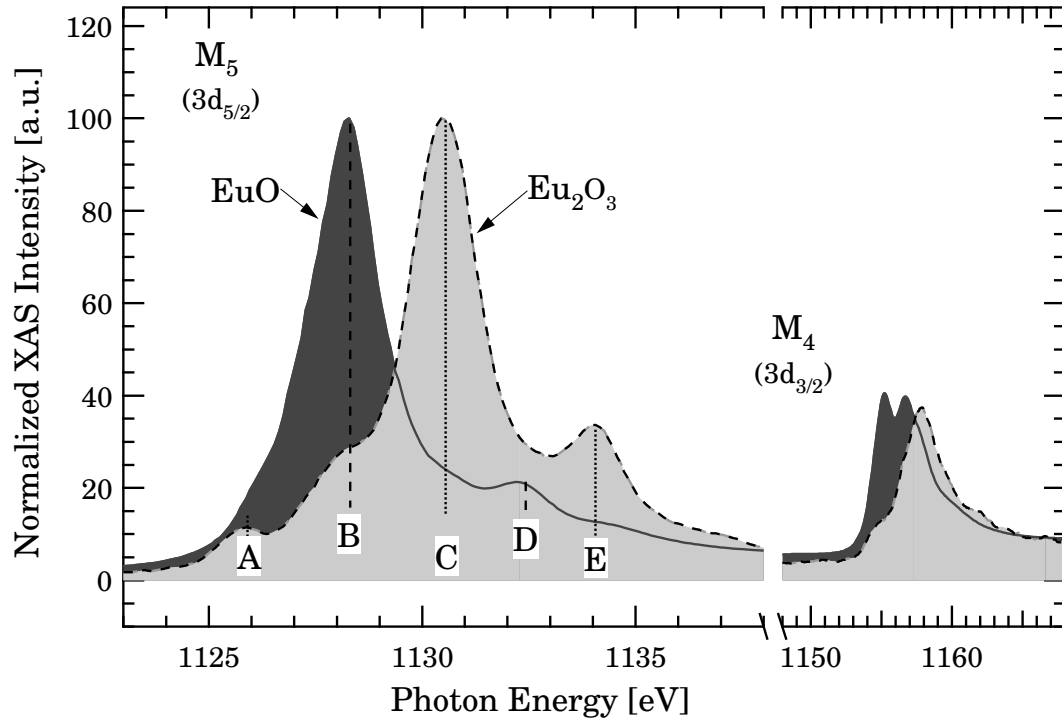


Figure 4-2: XAS spectra at the Eu $M_{4,5}$ -edge of the two common oxides of europium. At the M_5 , the peaks labeled as B and D (dashed line) and those labeled A, C, and E (dotted line) are the signature peaks of EuO and Eu_2O_3 respectively.

The fractions of EuO and Eu_2O_3 were computed by decomposing the XAS spectra of the samples with different electrodes against our reference spectra (see Appendix B).

Of the electrodes examined, yttrium was found to decrease the formation of the non-magnetic oxide, Eu_2O_3 (less than 10%) and preserve the quality of the EuO film, whereas in the samples with the Al and Ag overlayers, the fractions of Eu_2O_3 were 28% and 41% respectively. These values were corrected for saturation effect using the method suggested by Chakarin et al. [61], Nakajima et al. [57], and Idzerda et al. [56], resulting in a residual from the analysis of less than 5%.

Santos and Moodera showed spin filtering effect the tunneling current with ferromagnetic EuO as the tunnel barrier, using a superconducting Al electrode as the spin detec-

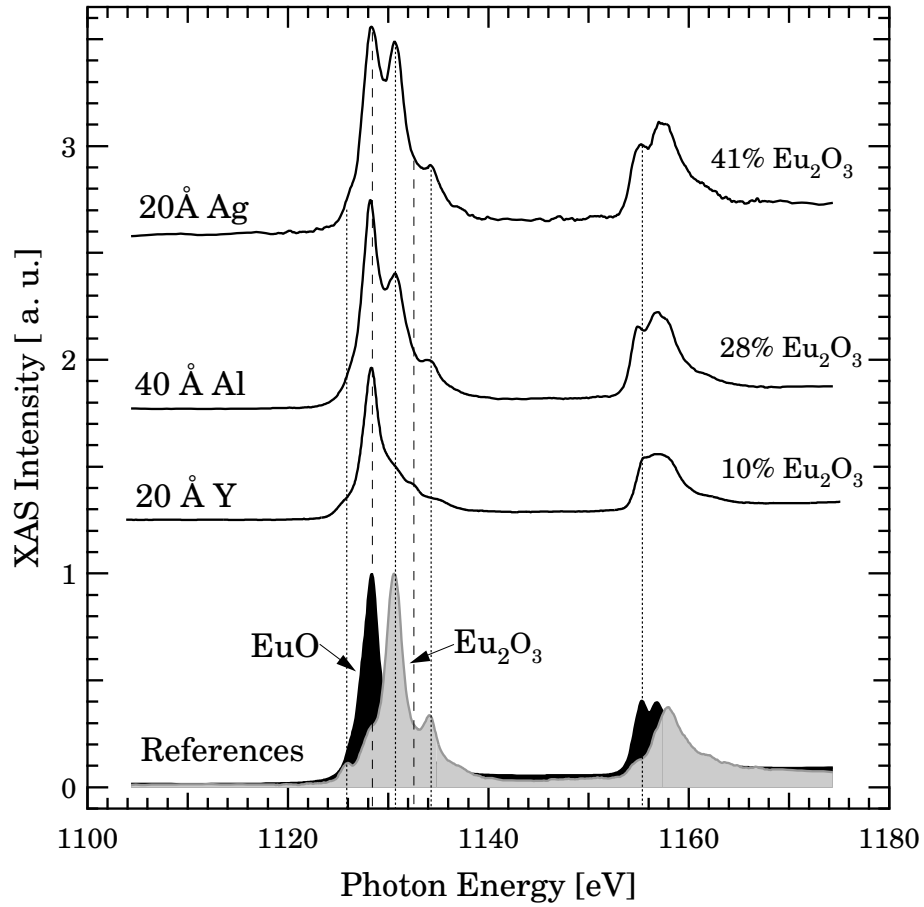


Figure 4-3: XAS spectra of EuO films with different electrodes, Y, Al, and Ag. Reference spectra of EuO and Eu_2O_3 used in the analysis are shown at the bottom of the panel. Percentages of the minority oxide present are listed on the right side of the spectra.

tor [50]. They reported that the tunnel junction with a yttrium electrode had the largest polarization of the tunneling current of 29% compared to 9% for the tunnel junction with Ag electrode. They proposed that the yttrium overlayer prevented further oxidation of the underlying EuO film by forming Y_2O_3 layer, which has lower heat of formation ($\Delta H_f = -1760$ kJ/mole) than Eu_2O_3 ($\Delta H_f = -1730$ kJ/mole) [50, 62].

Scattering measurements done on samples with different electrodes and different EuO thicknesses than those used in the analysis presented in the previous sections. Interface

studies using XAS revealed that samples with a large fraction of Eu_2O_3 have interfaces with high roughness. Table 4.1 summarizes the roughness parameters described in Fig. 1-5: out of plane roughness (σ) and in-plane correlation length (Γ) for samples with different electrodes. The in-plane roughness varies greatly with the fraction of Eu_2O_3 .

Electrode	Eu_2O_3	in-plane (Γ)	RMS (σ)
Ag	35 %	326 Å	7.0 Å
Al	20 %	845 Å	4.1 Å
Y	5 %	986 Å	3.9 Å

Table 4.1: Fraction of Eu_2O_3 and roughness parameters for EuO films with different electrodes.

To examine the EuO-electrode interfaces, we performed rocking sample scans on the EuO films with different electrodes. Listed in Table 4.1 are roughness parameters extracted from these measurements. For comparison, the fraction of Eu_2O_3 determined from XAS analysis for each sample with a different electrode are also shown in the table. Compared to Y and Al, the sample with the Ag electrode has the highest perpendicular roughness of 7 Å and the shortest correlation length. The perpendicular roughness values are much closer in Y and Al electrodes. The data suggests the elevated fraction of Eu_2O_3 in Ag electrode corresponds to rougher EuO/Ag interface. There is a definite correspondence between interface roughness and the Eu_2O_3 abundance. From this set of data, however, it was not possible to conclude whether Eu_2O_3 caused rougher interfaces or vice versa.

Angle-dependent XAS and Eu_2O_3

Figure 4-4 shows XAS scan done at different angles on an 80 Å thick EuO film capped with Al. This approach provides a depth profile of the oxide layer measured here [57]. At low sample angles (ω), the presence of a dominant Eu_2O_3 signature peak, indicates the presence of significant Eu_2O_3 . With an increasing sample angle, a strong EuO's signature peak emerges in the spectra. The fraction of the two oxides as a function of sample angle

is shown in Fig. 4-4 (right). The beam penetrates only the top section of the sample in the low angle (small ω) measurements, and penetrates deeper at higher ω . Thus, the significant presence of Eu_2O_3 at low angles which then diminishes at higher sample angles shows, shows that the Eu_2O_3 is indeed *localized* at the top EuO-electrode interface. This thin layer of Eu_2O_3 is responsible for the degradation of spin-filter efficiency of the tunnel junction [50].

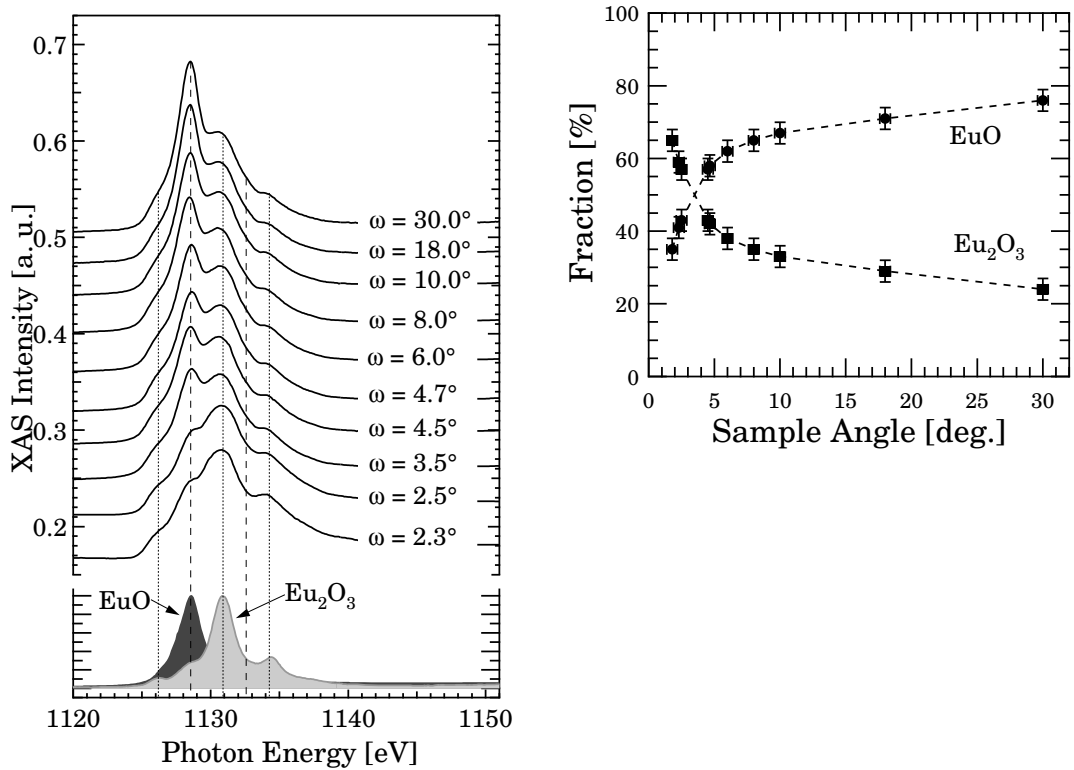


Figure 4-4: Left: XAS spectra done at different sample angles (ω). At low angles, the Eu_2O_3 peak is dominant. At higher angles ω , the EuO peak dominates in the XAS spectra. The diminishing fraction of Eu_2O_3 , with increasing probing depth, indicates that Eu_2O_3 is localized at the interface. Right: Fraction of the two oxides as a function of sample angle. The dashed lines are guides to the eye.

The purpose of this angle-dependent XAS measurement is to locate the Eu_2O_3 . The most likely location is at the interface between EuO and the top electrode. Careful examination of the angle-dependent XAS shows that at lower angles, the spectra are dominated

by Eu_2O_3 (as indicated by the signature Eu_2O_3 peak). At these low angles, the top section contributes more to the measured intensity. As a result, we are sensitive to the top part of the layer. With increasing sample angle, the EuO signature peak emerges, which indicate the lower section of the film is mainly composed of the desired oxide.

The fraction of the two oxides at different sample angles is summarized in Fig. 4-4 (right). Circles show the fraction of Eu_2O_3 . This result provides insight into the structure of the oxides and answers two question. First, it shows that indeed the undesired oxide Eu_2O_3 is located at the EuO-electrode interface. Secondly, Eu_2O_3 is not intermixed with the good oxide throughout the layer. Eu_2O_3 most likely forms at the interface during the growth process. This explains why there is significant degradation in the spin-filtering efficiency in the junction with the highest fraction of Eu_2O_3 . This result clearly showed the location of the Eu_2O_3 . Reducing the formation of this oxide would significantly improve the efficiency of the junction. As will be shown shortly, reducing this Eu_2O_3 at the interface resulted in higher quality, smoother, uniform EuO films.

Oxide Layer Thickness

Next, we looked at the effect of the EuO film's thickness on the quality of the tunneling barrier. Thinner films are preferred in tunneling junctions. From the angle-dependent XAS measurements, we have identified the presence of a thin Eu_2O_3 layer at the interface. The question is then, how can we determine the thickness of this undesired oxide? Most importantly, how can we reduce or eliminate this undesirable oxide? To examine the effect of the deposited europium oxide thickness, we performed XAS measurements on EuO films, grown in the same batch, with thicknesses varying from 40 to 80 Å, each capped with a 40 Å Al layer using the mask and shutter setup described above. From the XAS spectra shown in Fig. 4-5 (left), it is evident that all samples are predominantly EuO (indicated by the large EuO signature peak B). As the deposited EuO thickness is increased, we see a

relative decrease in the features associated with the Eu_2O_3 (peak C). The relative fraction of the two oxides extracted for different thicknesses is shown in Fig. 4-5 (right-bottom). In these samples this small decrease in the fraction of Eu_2O_3 with increasing deposited film thickness does not mean the amount of Eu_2O_3 is changing.

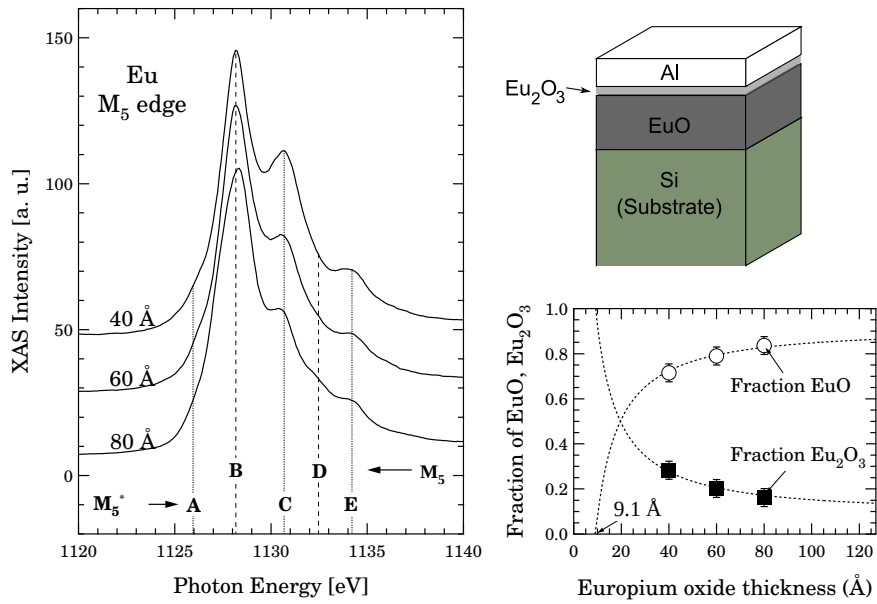


Figure 4-5: Left: XAS spectra for different EuO thicknesses capped with 40 Å of aluminum. Right-top: Structure of the layers used in the model to extract thickness of the Eu_2O_3 at the EuO-electrode interface from the fit. This arrangement is based on results shown in Fig. 4-3 that confirmed the location of Eu_2O_3 . Bottom-right: Thickness dependence of the percentage of each oxide and fit (dashed lines). The thickness of Eu_2O_3 is the value where EuO goes to zero, which in this case is 9.1 Å.

As indicated by the angle dependent measurement in Fig. 4-4, this slight decrease can be explained by examining the measurement process. For XAS measurements in total electron yield (TEY) mode, the major contribution to the measured sample current comes from the secondary electrons generated in the absorption process [57]. As these electrons make

their way out of the sample, they are attenuated in exponential fashion. Due to the limited escape depth of the electrons, the contribution from that constant thickness overlayer is seen to diminish in relative intensity compared to the underlayer signal as the underlayer thickness increases. The capping layer and everything above the section of the sample of interest attenuates the signal from that region. Thus, the contribution needs to be weighted, as shown by [56, 57, 61, 63].

Using a simple model, given in Ref. [61], where the Eu_2O_3 is held constant,² which compares the weighted contribution from such an overlayer at the interface, we estimated the thickness of Eu_2O_3 at the EuO-electrode interface (see Fig 4-4). For an escape depth of 80 Å (Ref. [63]) the fit gives a $9.1 (\pm 1.4)$ Å thick Eu_2O_3 layer at the interface, as shown in Fig. 4-5 (right-top). Subsequent EuO films, even thinner ones, have a higher fraction of EuO. This encouraging result is mainly due to the improvements in the fabrication procedures and choice of appropriate buffer layer that promotes the growth of higher quality EuO films.

Direct Investigation of Buried Interfaces

In the previous sections, the focus was on examining the quality of the EuO barrier and the effect of the choice of electrodes. Now we turn our attention to the interfaces between EuO and electrodes and answer the question: Is the top interface the same as the bottom interface? Here we present results from direct examination of the bottom interface of the tunnel junctions grown on Cr/Cu buffer layer. The relevant interfaces were studied first with XAS and then XRS. We also present angle-dependent XAS measurements done to examine the top (EuO-electrode) interface of films with buffer. These results are compared to the films grown, earlier in the project, without the buffer layer.

²This scheme is similar to the approach used by Ohldag et al. [23] to estimate the thickness of CoO-NiO at the Co/NiO interface.

As discussed in the previous sections, the main focus of the XAS and XMCD studies was the chemical and magnetic properties of the buried EuO layer and the buried EuO-electrode (top) interface. Here, the emphasis is on comparing the bottom (electrode-EuO) and top (EuO-electrode) interfaces separately. Moreover, the overall structure of the junction was modified by adding a Cr/Cu buffer layer. The chromium seed layer was essential for the proper growth of the Cu layer, which in turn affected the quality of the EuO layer. Copper was chosen because its lattice match with EuO and Cu is less likely to form CuO in the presence of EuO. Heat of formation of CuO is $\Delta H_f = -150$ kJ/mole, which is much higher than that of EuO. Fig. 4-6 shows Cu $L_{2,3}$ edge scans on samples with different EuO film thicknesses and reference XAS spectra metallic Cu and CuO [64]. The Cu-edge spectra indicate that the Cu layer is metallic with no CuO.

This structure in Fig. 4-1 (b) that has EuO films of different thicknesses grown on a Cr (20 Å)/ Cu(90 Å) buffer layer and capped with Y (20 Å)/Al (80 Å) or Al(80 Å) presents several advantages. First, by tuning to the europium absorption edge and performing XAS analysis, we can determine the oxidation state of the europium oxide film and quantify the abundance of the two oxides. Secondly, the thickness and composition of the buffer layer can be easily varied. This provides a convenient method to examine the bottom electrode's impact on the interfaces, the EuO layer, and the spin transport properties of the entire structure. Most importantly, the relevant buried interfaces, namely Cr/Cu, Cu/EuO and EuO/Y can be examined separately by choosing the appropriate scattering conditions using the element-selective and interface sensitive techniques described in Chapter 3. In this case, having layers composed of elements with absorption edges far apart, as listed in Table 4.2, made the separation and study of these interfaces straightforward.

To examine the buried interfaces, we performed rocking sample (diffuse) scans at photo energy and sample angle selected from specular scans and energy scans (not show). Figure 4-7 shows rocking sample (diffuse) scans normalized to the maxima of the diffuse back-

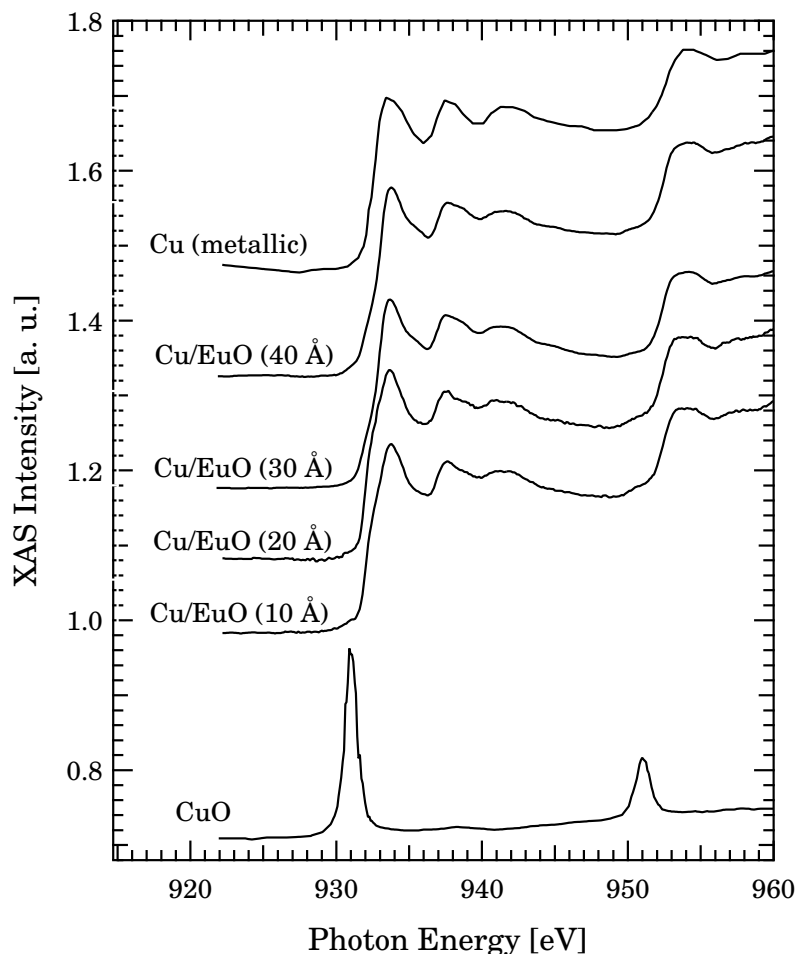


Figure 4-6: XAS spectra at the Cu $L_{2,3}$ edge indicate the Cu/EuO (bottom) interface does not contain CuO. Comparing the XAS spectra done for EuO thicknesses 10 – 40 Å grown on Cr/Cu buffer layer against the spectra of pure Cu metal (top) and oxidized CuO (bottom) confirms the bottom Cu electrode is metallic with no oxidation at the interface. Cu and CuO reference spectra from [64].

ground. These diffuse scans were done at 1128.2 eV (Eu M_5), 933.8 eV (Cu L_3) and 574.0 eV (Cr L_3) to examine the EuO/Al, Cu/EuO, and Cr/Cu interfaces respectively. The photon energy were determined by the element available in the layer below the interface we are examining. To examine the EuO/Y interface, we would tune the photon energy to the Eu M_5 edge. Table 4.2 summarizes the energy were the scans were done, the interface examine at selected energy, and the absorption edge of the element in the layer.

Photo energy (eV)	Absorption edge	Interface	RMS (σ)
574.0	Cr L ₃	Cr/Cu	4.6 (.4) Å
933.8	Cu L ₃	Cu/EuO (bottom)	3.7 (.4) Å
1125.0	pre-Eu M ₅	Cu/EuO (bottom)	3.6 (.4) Å
1128.2	Eu M ₅	EuO/Y (top)	2.8 (.4) Å

Table 4.2: Roughness values at the top and bottom interfaces of Cr/Cu/EuO/Y/Al structure extracted from sample rocking scans done at $\omega = 6$ degrees.

The perpendicular roughness values extracted from the rocking scans show that the top interface is smoother than the bottom interface or the Cr/Cu interface. This can be attributed to the polycrystalline EuO that evens out the roughness introduced during the growth of the multilayer structure. The top interface of the EuO films grown on Cr/Cu buffer is even smoother than those shown in Table 4.1.

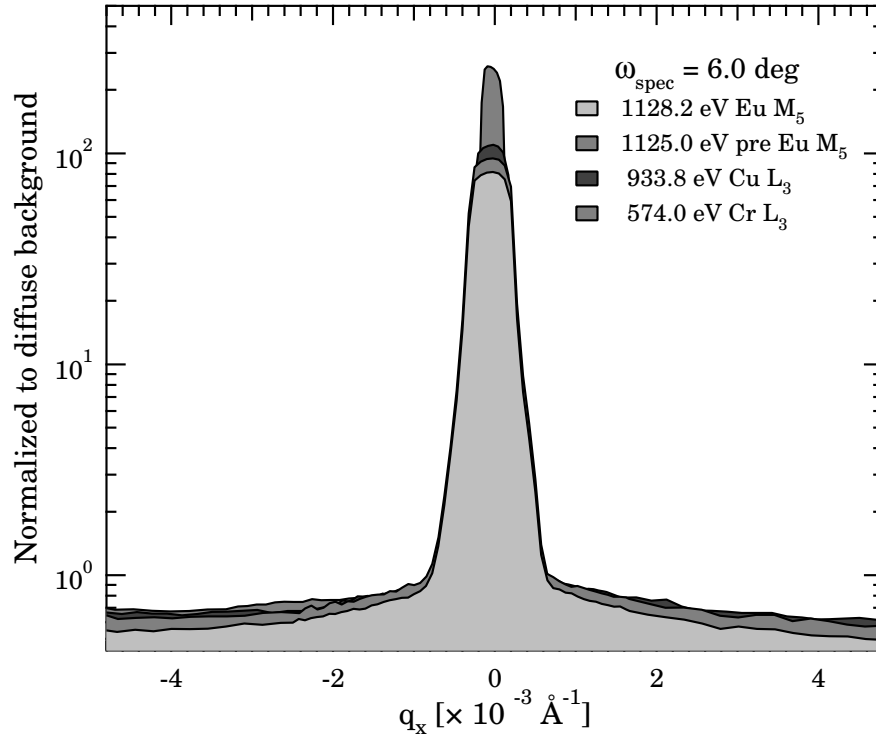


Figure 4-7: Rocking scans performed at $\omega = 6$ degrees and different energy values to probe the Cr/Cu, Cu/EuO and EuO/Y interfaces. The scans were normalized to the maximum of the diffuse background.

For comparison purposes, we did one more diffuse at a selected energy we are calling pre-Eu M_5 edge to probe the bottom Cu/EuO interface. This value was chosen such that the incident photons can penetrate past the EuO layer and be reflected from the bottom interface. The condition that meets these requirements was chosen as follows. The sample angle and photon energy just before the Eu M_5 edge such that the absorption intensity is about 10% of maximum XAS intensity, while the scattered intensity is more than 80% of the maximum of the XRS intensity. The pre-Eu M_5 (1125.0 eV at 6 degrees) was then selected following a series of XAS and XRS scans done at the Eu M_5 edge at several sample angle ω .

The diffuse scan done at the pre-Eu M_5 edge is shown in Fig. 4-7. The perpendicular (rms) roughness at this value is equal to rms value extracted from the Cu L_3 edge scan. Thus, the approach we used does measure the roughness of the bottom interface. Our direct investigation of the buried interfaces reveals that EuO layers grown on Cr/Cu buffer layer are more than 90% EuO, there is little or no Eu_2O_3 at the top EuO/Y interface even for the thinnest (10 Å) EuO films. Moreover, the top interface is smoother than the bottom electrode-EuO interface.

Magnetic Characterization of Ultrathin EuO Films

Equipped with a systematic approach to determine the quality of the EuO films using XAS chemical analysis, we conducted low temperature magnetic characterization of the EuO films. For this purpose we used x-ray magnetic circular dichroism (XMCD) at beamline 4.0.2 located at the Advanced Light Source (ALS). Figure 4-8 shows XMCD measurements on 20 Å EuO films with Y/Al and Al overlayer at the Eu $M_{4,5}$ -edges. Since Eu_2O_3 is nonmagnetic, the only contribution to the XMCD signal is from the ferromagnetic EuO film. The identical normalized XMCD spectra for both samples are identical.

The Eu_2O_3 present in the Al capped EuO film does not contribute to the measured XMCD signal. After correcting for angle of incidence and incomplete polarization [56], for this particular sample we found the XMCD value to be $31.0 (\pm 3.5)\%$ and $25(\pm 3.5)\%$ for the Y/Al and Al capped EuO films.. This is higher than XMCD values reported by others for ultrathin EuO films [65–67].

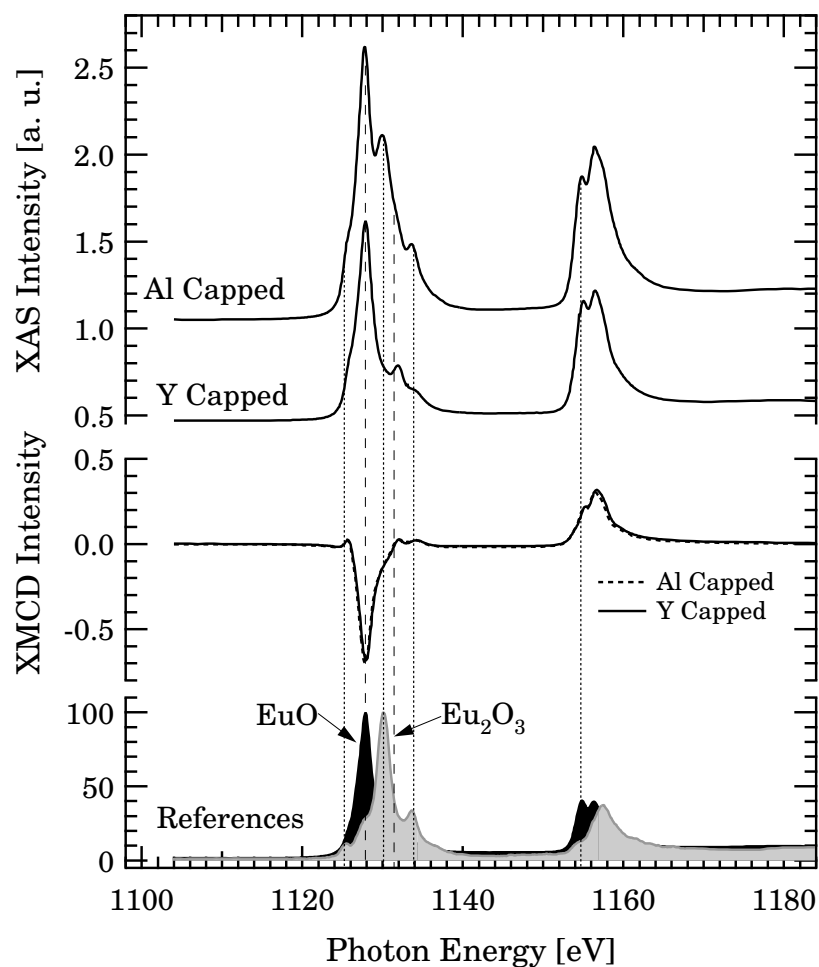


Figure 4-8: XMCD measurements on 20 Å EuO films capped with different electrodes. Top: XAS spectra of two samples capped with Al and Y electrodes show that the Al capped has a large fraction of Eu_2O_3 . The paramagnetic Eu_2O_3 does not contribute to the XMCD signal (Middle). The magnetic signal comes only from the ferromagnetic EuO as indicated by the identical normalized XMCD spectra of the the two samples. Bottom: Reference spectra of the two oxides.

Upon closer examination of the XAS spectra, we found that the fraction of Eu_2O_3 is rather small ($< 10\%$), which indicated the EuO samples are of high quality. Results from the analysis is shown in Fig.4-11. Angle-dependent XAS spectra for the thinnest step of 10 Å showed a very small amount of Eu_2O_3 at the EuO-electrode interface. For comparison, the angle-dependent fraction of EuO for 80 Å EuO (from Fig. 4-4) is also indicated in Fig. 4-9 (right). From these measurements we can rule out the presence of Eu_2O_3 at the top (EuO-electrode) interface.

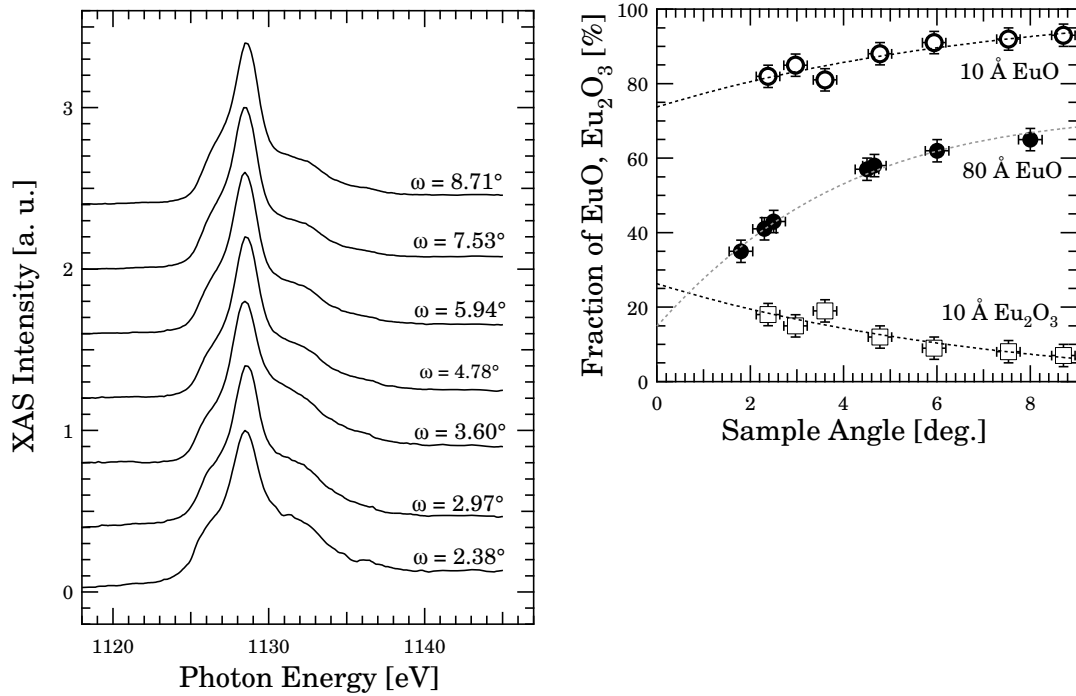


Figure 4-9: Left: Angle-dependent XAS spectra done on 10 Å EuO grown on Cr/Cu buffer with Y electrode. Right: Relative fraction of EuO and Eu_2O_3 as a function of sample angle extracted from the XAS spectra (shown on the left). For comparison, the fraction of EuO for the 80 Å (from Fig. 4-4) is also shown (solid circles).

To examine the cause of thickness dependence of the XMCD signal, we performed a series of measurements on EuO wedge samples where the only parameter varied was the EuO film thickness at 18 K. Figure 4-10 shows the XMCD signal for EuO film thicknesses

from 10–60 Å at the Eu M_5 -edge. The structure of the wedge sample, capped with Y/Al overlayer is depicted in the inset (lower-right). The XMCD values at M_5 -edge for different samples is shown in Fig. 4-11 with an average XMCD of 40.0 (± 3.5)%, the highest reported value for this range of thicknesses. XAS analysis done on wedge samples with Y and Al electrode (see Fig. 4-11(top)) shows the fraction of EuO is much higher than earlier results. In fact, it is over 90% EuO films and it is constant for all thicknesses.

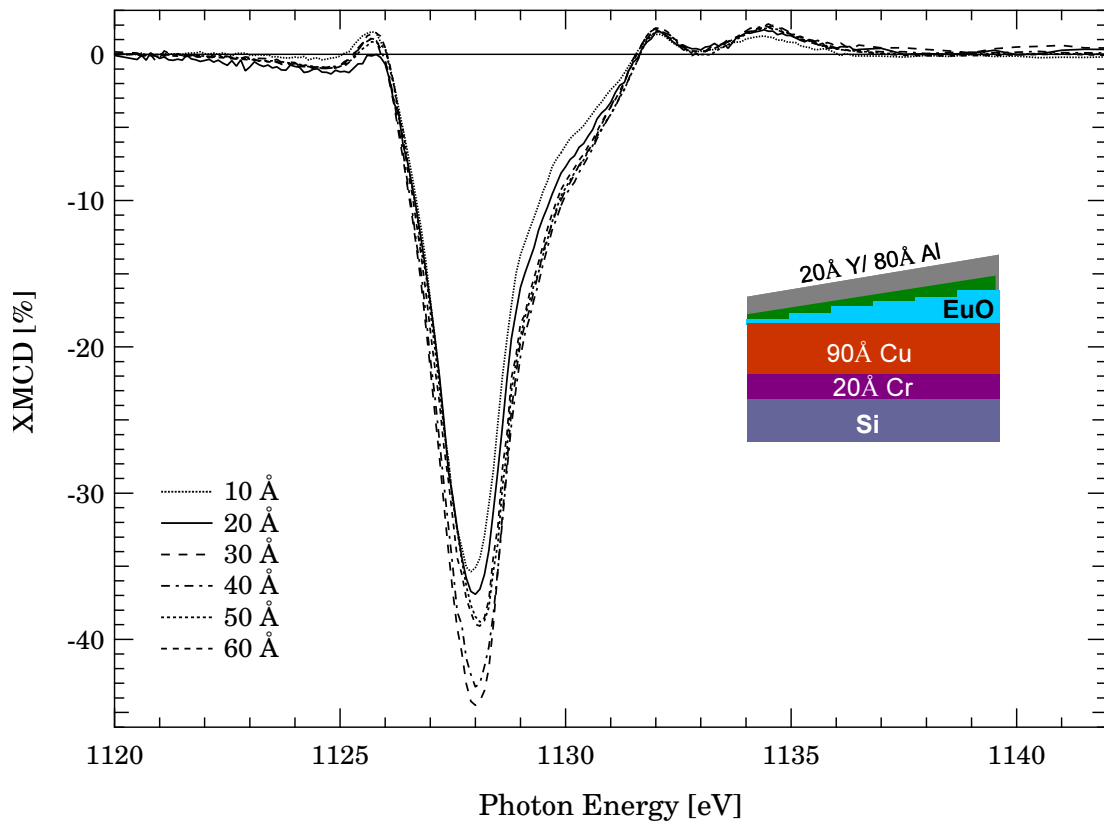


Figure 4-10: XMCD spectra at the europium M_5 -edge for the different steps (10 – 60 Å) of the EuO wedge. Right: Structure of EuO films grown on Cr/Cu buffer with Y electrode.

Possible reasons for the observed variation in measured XMCD can be due to thickness dependence of the saturation magnetization (M_S), Curie temperature (T_C), or a some combination of these factors. For instance, perhaps the EuO films have different magnetization values or the samples were not fully saturated during the MCD measurement. However, this

was also ruled out by magnetization versus temperature measurements (see Fig. 4-12) for EuO wedge samples grown on Cr/Cu buffer with a yttrium top electrode and capped with Al. Moreover, the XMCD measurements were done at saturation field values determined from SQUID magnetometry data. The magnetization versus temperature curves, as shown in Fig. 4-12 (A) with almost equal saturation magnetization (M_S), independent of the EuO film's thickness. The data shows the saturation moment is independent of thickness (see Fig. 4-12 (B)).

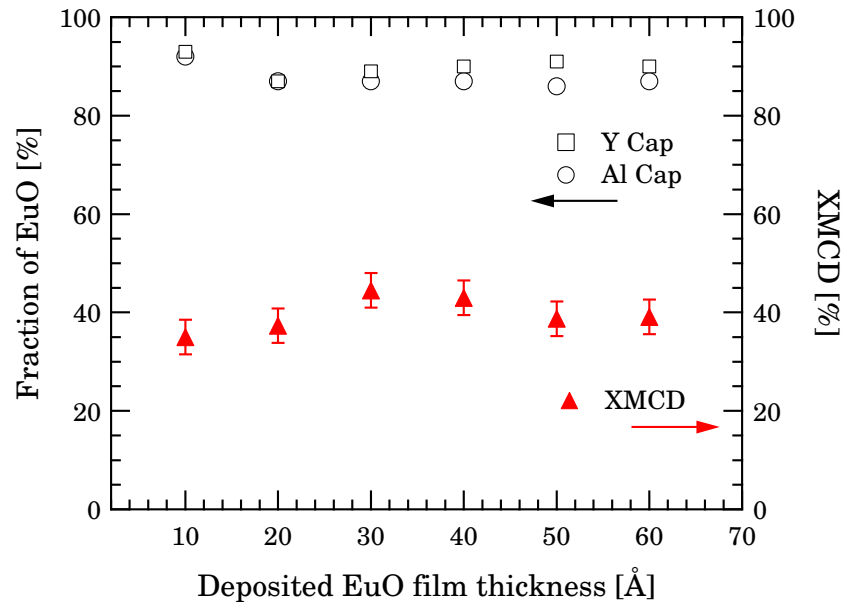


Figure 4-11: Fraction of EuO and XMCD signal for yttrium capped EuO wedge shown in Fig. 4-10. The measured XMCD, averaging at $40(\pm 3.5)\%$, is the highest value for ultrathin EuO films for these thicknesses. For comparison, the fraction of EuO for the Al capped EuO wedge is also shown (open circles).

The T_C values extracted from the temperature dependence of magnetization measurements for the wedge samples with Y (shown in Fig. 4-12 (A)) and Al (not shown) electrodes are plotted against the thickness of the EuO layer (Fig. 4-12 (C)). The Curie temperature is significantly reduced with decreasing EuO film thickness. This result is the first experimental confirmation [44] of the prediction by Schiller and Nolting [68]. Their calculated

thickness dependence of T_C for an ideal, self-supporting EuO film with no contact or substrate is shown by the solid line in Fig. 4-12 (C). The large offset between the calculated and measured values is because the theoretical model does not account for the effect of the substrate and other experimental constraints. As shown in Fig. 4-12 (D), a similar decrease is observed in the coercive field.

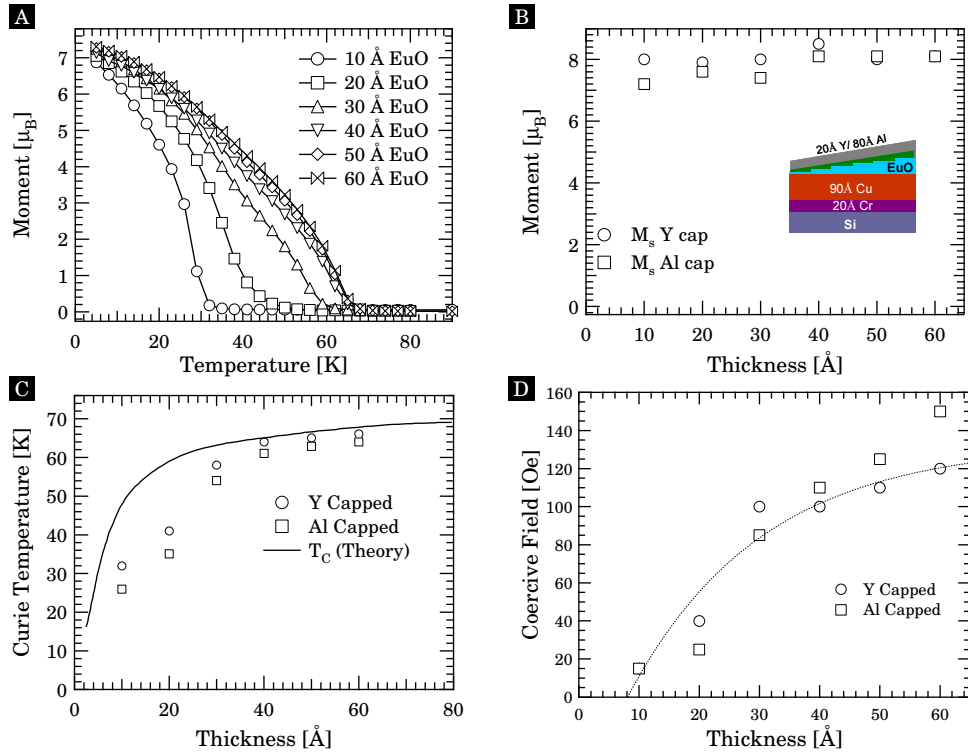


Figure 4-12: (A) Temperature dependence of magnetization for EuO wedge capped with Y. (B) The thickness independent saturation magnetization (M_s) attest to the quality of the EuO. films. Inset shows the structure of the wedge sample. (C) Dependence of T_C on EuO film thickness for wedge samples capped with Al and Y [44]. These experimental values follow the trend shown by the theoretical prediction (solid line) [68]. Comparison of T_C 's dependence on thickness of EuO film with theoretical values for two sets of wedge samples with Al and Y top electrodes. (D) Thickness dependence of the coercive field (dot-line is a guide to the eye). From [44,68].

Thin tunneling barriers have smaller junction resistance. Reducing the thickness of the EuO barrier, however, results in lower T_C and decreased $2\Delta E_{ex}$, the exchange splitting in the conduction. These are the two most important parameters on which the EuO barrier's filtering efficiency depends. The decrease in the exchange splitting is from 0.54 eV for bulk to 0.29 eV for a 25 Å EuO film [44]. This is a more fundamental and difficult issue. However, as Santos [44] showed, this reduced exchange splitting is sufficient to achieve spin-polarized current of 98%. One way to increase T_C is by doping the EuO film with Gd [17, 67]. Doping EuO, however, decreases the exchange splitting which is essential for spin filtering.

Summary

EuO based spin-filter tunnel junctions hold great promise for spin-injection and spintronic applications. We presented work done to understand how the choice of electrode and EuO film thickness affect the EuO-electrode interface. Our results show that yttrium not only prevents diffusion of oxygen by forming an oxygen barrier but it also preserves the quality and integrity of the EuO film by preventing the formation of a nonmagnetic, stable oxide, Eu_2O_3 . We also studied the factors that promote formation of the nonmagnetic stable oxide, Eu_2O_3 , and where it forms. Angle-dependent XAS measurements showed that if there is Eu_2O_3 , it is localized at the EuO-electrode interface. The thickness of the EuO layer, however, has little effect on the quality of the EuO-electrode interface.

Using XAS, XMCD and XRS, we examined the quality of the electrode-EuO and EuO-electrode interfaces, and studied the chemical and magnetic properties of the EuO films. We showed the choice of the bottom electrode is as important as the choice of the top electrode. Use of Cr/Cu buffer layer promotes the proper growth of EuO and thus the fabrication of EuO films with consistent magnetic properties.

Direct investigation of the bottom (electrode-EuO) and top (EuO-electrode) interfaces using soft x-ray scattering techniques showed that EuO samples with a Cr/Cu buffer layer are smoother compared to EuO films grown on a Si substrate or Al bottom electrode. The extracted roughness parameters of the different interfaces indicate that interface do not conform to the morphology of the layers below and the interfacial roughness is random. By using wedge (stair-step) EuO samples deposited on Cr/Cu, sample-to-sample variations were eliminated, yielding EuO samples with consistent bulk-like composition and magnetic properties even to the monolayer level.

XMCD studies, along with SQUID magnetometry results, showed that the thickness dependence of T_C is the major limiting factor in using ultrathin EuO films for spin-filtering devices. Even though high quality EuO layers with remarkably smooth interfaces were fabricated in this project, the application of EuO-based, all-electrical spin-filter devices needs more work. The system, however, provides a prototype to help understand the tunneling spin-filters and investigate other spin-filter systems.

CHAPTER 5

CONCLUSION AND OUTLOOK

In this chapter, we summarize the work done on EuO-based spin-filter tunneling junctions. We then highlight the implication of this work in the field of tunnel junction based spin filtering systems, focusing on the impact of interfaces on spin-dependent tunneling. We then discuss a direction for further work on interfaces and tunnel junctions.

One way to achieve spin-polarized current is by using spin filtering tunnel junctions. The operation and performance of such structures is strongly influenced by the quality of the interfaces through which the electrons have to tunnel. In EuO based spin-filter tunnel junction, the use of buffer Cr/Cu layer had led to enhancements of the desired properties. In this project, we studied the quality of the interfaces and examine the magnetic properties of the layers involved using soft x-ray techniques XMCD and XRS.

Using these techniques, we studied and quantified the fraction of EuO and Eu_2O_3 , and identified where the nonmagnetic oxide (Eu_2O_3) is located. By fitting these results with a simple model, we estimated the thickness of the Eu_2O_3 layer at the interface for samples grown early on in the project. We found the stable oxide, Eu_2O_3 , which degrades spin-filtering efficiency of the junction, is localized at the top (EuO-electrode) interface. Of the top electrode materials used, we found yttrium to be the best electrode that protects the EuO underlayer from further oxidation and formation of Eu_2O_3 . Feedback from the chemical analysis of the oxides and quality of the interfaces was used to further refine and improve the fabrication process. XAS measurements confirm that switching from single samples to wedge samples, minimized sample-to-sample variation significantly. Results from XMCD measurements done to study the magnetic properties of the ultrathin EuO

films are in excellent agreement with SQUID magnetometry data. Both measurements showed the remarkable improvement in the quality of the thin films deposited on Cr/Cu buffer layer. In the study, wedge samples with different compositions and thicknesses were used.

In tunnel junctions with a ferromagnetic EuO tunneling barrier, by varying thickness and composition of the buffer layer and the choice of the top electrode layer, we studied how these parameters modify the interfaces and properties of the oxide barrier. We quantified the relative fraction of the two oxides of europium and addressed questions raised early on in this work: (1) location and thickness of the undesired oxide and (2) quality of the electrode-EuO (bottom) interface. Using XMCD and XRS measurements, we characterized and quantified the amount of EuO (magnetic) and Eu_2O_3 (nonmagnetic), examined the relevant bottom (electrode-EuO) and top (EuO-electrode) interfaces, and studied the impact of these modified interfaces on the entire spin-filter tunnel junction.

We also examined the buried bottom (electrode-EuO) interfaces by depositing EuO on a Cr/Cu buffer layer and found that (a) there is no oxidation at the bottom interface and (b) the top (EuO-electrode) interface is smoother than the bottom interface. With the addition of more layers, the interfaces get smoother mainly because EuO is polycrystalline. The use of an appropriate buffer layer, in this case a 30 Å Cr/90 Å Cu, enhances the quality of the interface and maintains the chemical and magnetic properties of the EuO film.

From XMCD measurements, we found the average XMCD signal of 40.0 (± 3.5)%, the highest for such ultrathin EuO films. The XMCD response is consistent with the temperature dependence of magnetization measurements done by SQUID magnetometry. The T_C response observed here is the first experimental confirmation of Schiller and Nolting's theoretical prediction [68].

Compared to other candidates for magnetic tunneling barriers, EuO's high T_C (69 K) and its simple structure make it the system of choice to study and use as a prototype to

examine the spin filtering process. Room temperature spin-filter such as is CoFe_2O_4 with T_C . However, the filtering is tied to the complex band structure of the tunneling barrier material [17, 44]. Furthermore, EuO's T_C can be enhanced to around 150 K by doping it with other rare earth materials such as Gd [17, 67, 69]. Recently, EuO barriers have been used in conjunction with Al_2O_3 barriers in magnetic tunnel junctions yielding, enhanced tunneling magnetoresistance (TMR) of 280% at low temperature and, in some systems a negative TMR [44].

Spintronic devices that use spin-filter tunnel junctions for spin-injection and -detection in an all-electrical device, such as the spin-filter transistor suggested by Sugahara and Tanaka [16], are nearing reality. As recently Schmehl et al. [17] demonstrated, EuO was used to inject spin-polarized current into Si and GaAs. Moreover, there are open-ended questions as to the role of interfacial states in spin-filter tunnel junctions. Do these states promote or degrade the spin-filter efficiency of the ferromagnetic semiconductor barrier? Can coherent tunneling enhanced filtering be achieved by matching the interface states? It remains to be seen whether EuO can be used for coherent tunneling to achieve higher spin polarization by matching the interface states.

APPENDICES

APPENDIX A:
MAGNETIC CHARACTERIZATION OF CoFe/MgO AND
CoFeB/MgO INTERFACES

The use of CoFeB ferromagnetic electrodes in place of CoFe has been shown to significantly increase the tunneling magnetoresistance (TMR) of MgO based magnetic tunnel junctions (MTJs). By using soft x-ray scattering techniques, we show that the behavior of the magnetic moments located at the CoFe-MgO interface are drastically different from the rest of the CoFe film, whereas the magnetic response of the CoFeB-MgO interfacial moments is coherent with the film's bulk. Our results support the view that the high TMR values observed in MgO-based MTJs with CoFeB electrodes are due to the uniform magnetic response of the entire CoFeB electrode including the MgO interfacial moments.

Introduction

Considerable efforts have been devoted to improving the fabrication and performance of magnetic tunneling junctions (MTJs) because of their potential applications in next-generation devices such as read-heads for ultra-high density hard disk drives and magnetoresistive random access memories [31, 70]. The realization of extraordinarily high, room temperature tunneling magnetoresistance (TMR) in MTJs that use an MgO tunneling barrier [71–74], came well after Butler et al. predicted that coherent electron tunneling through MgO would lead to much higher TMR values [27]. Different materials have been used for ferromagnetic electrodes in these MTJs, with Co, Fe and Co-Fe alloys being the most popular. The CoFe electrode in an MTJ stack typically grows in the BCC polycrystalline structure [71, 73, 74]. However, when boron is added to CoFe, the resulting CoFeB becomes amorphous and the subsequent deposition of MgO results in a more crystalline insulating barrier, improving the coherent tunneling and significantly increasing the TMR value [73, 74].

To determine precisely how the improved crystalline quality enhances the spin-dependent tunneling across the electrode-MgO interface, we have used x-ray magnetic circular dichroism (XMCD) as well as diffuse and specular x-ray resonant magnetic scattering (XRMS) to

chemically and magnetically characterize each interface [58]. These nondestructive techniques provide element-specific, and interface sensitive information with magnetic contrast. X-ray resonance magnetic scattering is the angle dependent reflectance of circular polarized soft x-rays whose energy is tuned to the absorption edge of a magnetic element. It combines the chemical selectivity of x-ray resonant scattering with the magnetic contrast of magnetic circular dichroism, and has been successfully used to separately parameterize the magnetic and chemical roughness of interfaces [11, 22, 75], identify the order of layer switching [11], and separately monitor the hysteretic behavior of magnetic moments located at the interface or within the bulk [12].

Experimental

To address the effect of adding boron to CoFe electrodes and the interfacial behavior in MgO tunneling barriers, we used UHV magnetron sputtering system (Canon ANELVA C-7100) to prepare Ru(100Å)/electrode/MgO(18Å)/Ta(40Å) samples on Si substrates (with the native oxide still present), where the electrode is 30Å of either Co₇₀Fe₃₀ or Co₇₀Fe₂₀B₂₀. The structure of the samples studied is shown in Fig. A-1. The bottom Ru film initiates high quality electrode growth and the top Ta layer protects the MgO layer from oxidation and contamination. The MgO layers were grown using RF magnetron sputtering, while all other layers were grown using DC magnetron sputtering.

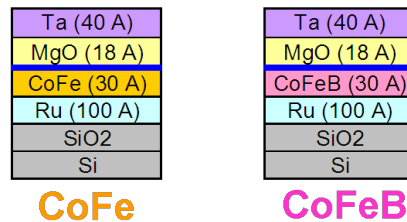


Figure A-1: Abridged MTJ structure used for CoFe/MgO and CoFeB/MgO interface characterization. The interfaces examined are shown by the solid (blue) line below the MgO layer.

The samples were cut in half and one half was annealed at 360 degree C for 2 hours in an 8 kOe magnetic field (similar annealing as of MTJ stacks). These annealing conditions were chosen because they yielded the highest TMR values in these MgO based MTJs [71, 73]. Typically, MTJs with CoFe electrodes exhibit room temperature TMR values below 100%, while those with CoFeB electrodes exhibit room temperature TMR values that exceed 200% [73].

The XMCD and XRMS measurements were carried out at beamline U4B at the National Synchrotron Light Source (NSLS) using 75% circularly polarized light with an energy resolution of 0.3 eV [76–80]. An *in situ* electromagnet, with a maximum continuous field of ± 300 Oe and pulsed fields of ± 1 kOe, provides a magnetic field parallel to the sample surface (along the beam direction) large enough to fully saturate the CoFe and CoFeB electrodes [11].

The x-ray scattering experiments were done in a scattering configuration shown in Fig. 3-3. The sample angle (ω) and detector angle (2θ) are defined with respect to the fixed incident beam direction and allow for the acquisition of the specular reflected intensity as a function of incident angle ($\omega - 2\theta$ scan) and the diffuse scattered intensity for a given detector angle (ω scan with fixed q_z). By aligning the sample and detector angle in a specular scattering geometry (so that $q_x = 0$ or $\omega = \theta$) and sweeping the photon energy, we can acquire the energy dependent scattering intensity which displays large scattering enhancements near the elemental absorption edges. This scattering intensity is dominated by scattering from a single element and is the x-ray resonant scattering (XRS) spectra.

By using circular polarized x-rays, the scattering intensity has strong magnetic contrast. Measuring spectra for photon helicity and magnetic moment parallel (I^+) and anti-parallel (I^-), the average spectra $[(I^+ + I^-)/2]$, the XRS spectra and the asymmetry spectra $[(I^+ - I^-)]$, the x-ray resonant magnetic scattering, or XRMS, spectra can be obtained. Finally, by fixing the photon energy, detector angle, sample angle, and photon helicity, the scattering

intensity can be measured as a function of the applied magnetic field in either a specular scattering condition ($q_x = 0$ or $\omega = \theta$), giving information about the bulk magnetic behavior, or in a diffuse scattering condition ($q_x \neq 0$ or $\omega = \theta + \theta_{\text{Offset}}$) giving information about the interfacial magnetic behavior [12]. If we record the scattering intensity as a function of applied magnetic field, while holding the sample angle fixed at the specular scattering condition ($q_x = 0$ or $\omega = \theta$), or slightly offset from specular ($q_x = 1 \times 10^{-4} \text{ }^{-1}$) as indicated by the arrows in Fig. A-2, we can acquire the specular and diffuse hysteresis loops, respectively [12]. The specular scattering hysteresis loops are indicative of the net moment (magnetic hysteresis loop) of the film whereas the off-specular scattering intensity is indicative of variations in the magnetic roughness of the interface.

Changes in the magnetic structure at the interface (and therefore diffuse scattered intensity) can arise either from interfacial magnetic domains responding to the applied field which reside only in the interface or penetrates the entire film. The former has a small net moment due to its small volume whereas the latter has a larger net moment and should therefore be represented in the bulk hysteresis loop.

Results and Discussion

The x-ray absorption spectroscopy (XAS) and XMCD of the as-grown and annealed CoFe and CoFeB samples were nearly identical (see Fig. A-2), confirming that the electrodes were fully metallic with no significant oxidation after annealing. Interestingly, although the XAS data were identical, the x-ray scattering data showed distinct differences, especially for the hysteretic behavior of the interfacial moments. To obtain the specular and off-specular hysteresis curves, we must first identify which photon energy and detector angle generates the largest scattering asymmetry and to identify the sample offset angle that gives a strong diffuse scattering. To do this, we measure the Co L_3 -edge diffuse x-ray resonant magnetic scattering (D-XRMS) curve, acquired at 778.8 eV (resonant with the Co

L_3 absorption edge) and at the detector position $2\theta = 14.96^\circ$ from grazing, by rocking the sample angle through the specular condition ($q_x = 0$ or $\omega = \theta$ at 7.48° , corresponding to a maximum in the specular $\theta - 2\theta$ asymmetry curve).

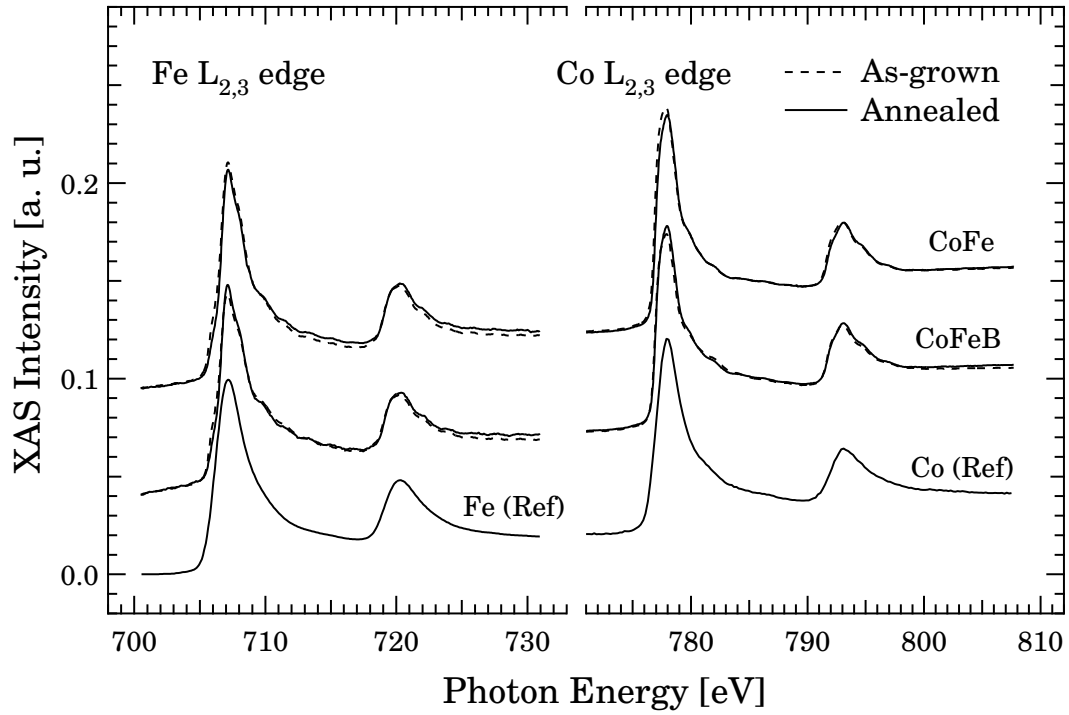


Figure A-2: XAS scans at the $L_{2,3}$ edges of Fe (left) and Co (right) show that both the CoFe and CoFeB electrodes are metallic. Addition of boron and annealing introduce no significant change. For comparison, XAS of metallic Fe and Co is shown (bottom) from Refs. [76, 81, 82].

Figure A-3 shows the log of the scattered x-ray intensity in the rocking scan geometry as a function of the momentum transfer in the sample plane, q_x , taken on a CoFeB sample before and after annealing (spectra are offset for clarity). The solid line shows the average scattering intensity (XRS spectra) and the dotted line represents the difference between scans taken with reverse sample magnetizations (XRMS spectra). In each case, the diffuse intensity is 3-4 orders of magnitude weaker than the specular scattered peak showing that these interfaces are of very high quality.

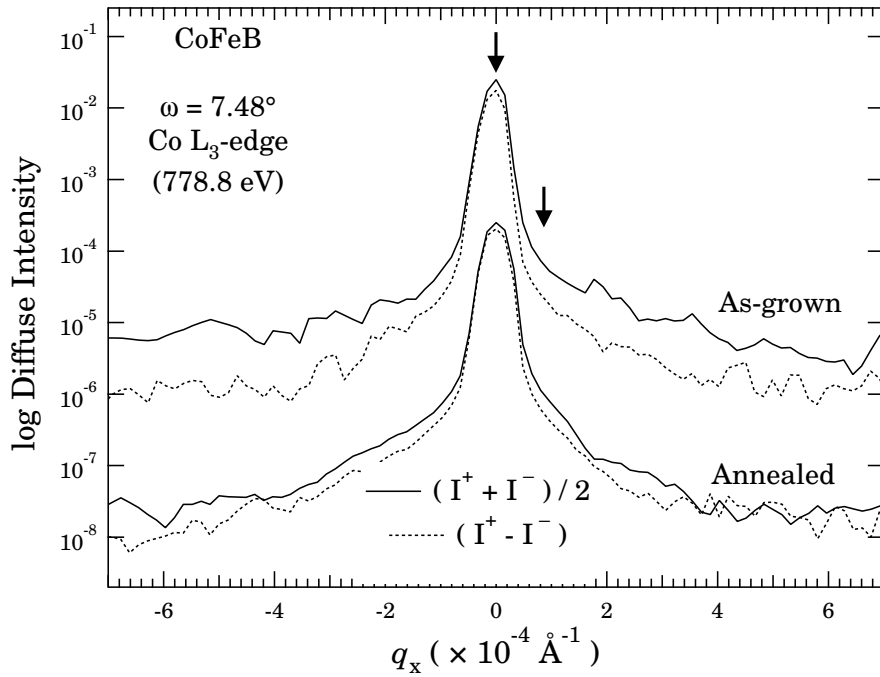


Figure A-3: Rocking scans as a function of in-plane momentum transfer, q_x , performed at the Co L_3 edge for the as-grown (upper) and annealed (lower) CoFeB electrode with the detector set at 7.48° (the spectra are offset for clarity).

First, we will compare the magnetic behavior of the two different composition electrodes to each other and examine the effect of annealing. The hysteresis loop of a film is normally measured by magnetometry. Because we will compare these bulk hysteresis loops to element resolved hysteresis loops and interfacial moment hysteresis loops (not obtainable by conventional magnetometry), we will measure the film hysteresis by x-ray scattering. In Fig. A-4 we compare the resonant scattering specular hysteresis loops at $\omega = \theta = 7.48^\circ$ (resonant with the Co L_3 -edge at 777.4 eV) for CoFeB (top) and CoFe (bottom) samples before and after annealing. It can be seen that the addition of boron in CoFe has profound effect on the electrode's magnetic behavior, yielding a much squarer and narrower hysteresis loop. These loops are identical to optical Kerr effect magnetometry loops. We performed multiple scans of the as-grown CoFeB hysteresis data to display

the presence of a small number of discrete, but irreproducible steps during the moment reversal, indicating that each field sweep creates the flipping a few very large magnetic domains (or cooperative flipping of many domains). After annealing, the hysteresis loops are completely reproducible, displaying a single, abrupt reversal in the hysteresis loop. On the other hand, the CoFe film shows a very different behavior. Prior to annealing, the films possess a slightly rounded hysteresis loop. After annealing, the hysteresis loops are significantly more rounded, consistent with grain formation and a distribution of coercive fields. For the annealed CoFe sample, we also show the hysteresis loop measured at 705.8 eV (resonant with Fe L_3 edge). This loop coincides with the Co edge loop, indicating that the element resolved hysteresis behavior is identical for the alloy film.¹

The improved switching behavior of the CoFe films with the incorporation of B and subsequent annealing explains the improvement in the TMR behavior but does not fully explain the magnitude of the increase in TMR values. Better insight can be obtained by comparing the hysteretic behavior of the magnetic moments at the electrode-MgO interface with B addition and annealing by examining the diffuse (nonzero q_x) hysteresis behavior of x-ray scattering at photon energies resonant with the Co L_3 -edge. In Fig. A-3 and A-6, we compare the hysteresis loops for as-grown and annealed CoFeB and CoFe samples measured at both specular ($q_x = 0$) and off-specular ($q_x \neq 0$) angles. Although the signal intensity is orders of magnitude smaller for the off-specular geometry, all hysteresis loops are normalized such that the intensity at saturation is equal to ± 1 . A striking difference is observed in the magnetic behavior of the interfaces. As can be seen in Fig. A-3, the specular and off-specular loops for the CoFeB sample are nearly identical, indicating that the interfacial moments flip in unison with bulk spins. Slightly elevated scattering intensities are observed during the initiation and completion of the film reversal process, which we

¹Elemental hysteresis loops were corrected for the different absorption strengths of the two magnetization directions (similar to the saturation effect corrections in XAS).

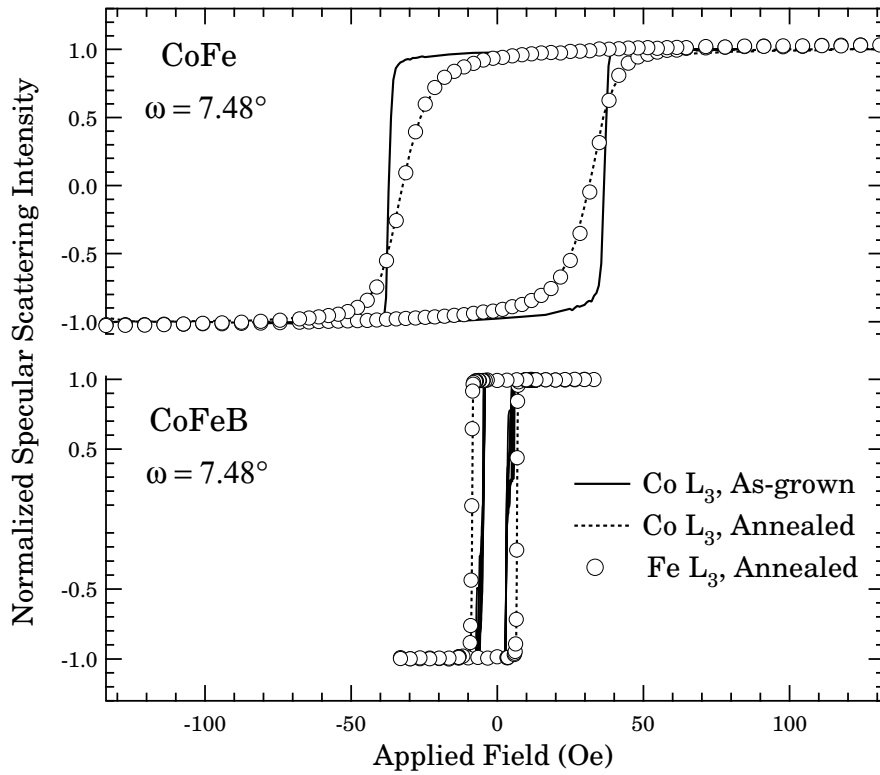


Figure A-4: Adding boron decreases the coercive field from about 36 Oe (top-dashed line) to 5 Oe (bottom-dashed line) and increases the squareness of the hysteresis curve. Annealing the CoFeB electrode, removed the jump (dashed lines) with a slight increase in H_C (solid line). Hysteresis loops done at the Fe L₃ edge (705.8 eV) are also shown (open circles). They are identical to loops done at the Co L₃ edge for the borided and unborided electrodes. These measurements were done at room temperature.

attribute to reversal of the moments associated with individual grains, something that does not affect the chemical roughness but does represent a new magnetic roughness contribution, increasing the magnetic component of the diffuse scattering.

On the other hand, for the CoFe sample (Fig. A-6), the off-specular hysteresis loop's shape is highly unusual. The nature of the measurement tells us that during magnetization reversal the interfacial spins in the CoFe film adopt a state of high in-plane magnetic disorder, momentarily giving rise to an increase in diffuse scattering intensity. This behavior is observed in both the as-grown and annealed CoFe films with the annealed films showing

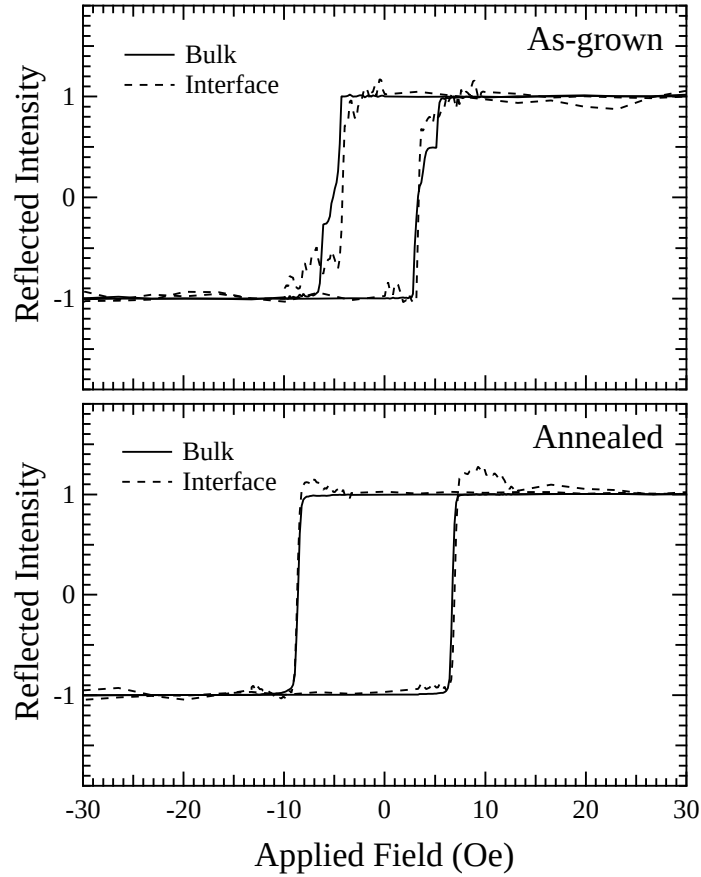


Figure A-5: Bulk (solid line) and interface (dashed lines) magnetic switching behavior of as-grown (top) and annealed (bottom) samples with CoFeB electrodes. Nearly identical bulk and interface hysteresis loops show the uniform magnetic response of samples with CoFeB electrodes.

nearly an order of magnitude increase in magnetic contribution to the off-specular scattering intensity. Clearly, the interfacial moments behave dramatically different than the bulk moments, and degrade coherent tunneling through the MgO barrier leading to lower TMR as first envisioned by Butler et al. [27, 40].

Summary

We find that the addition of boron to CoFe electrodes leads to the coherent magnetic response of interfacial and bulk magnetic moments. The CoFeB/MgO interfaces are found

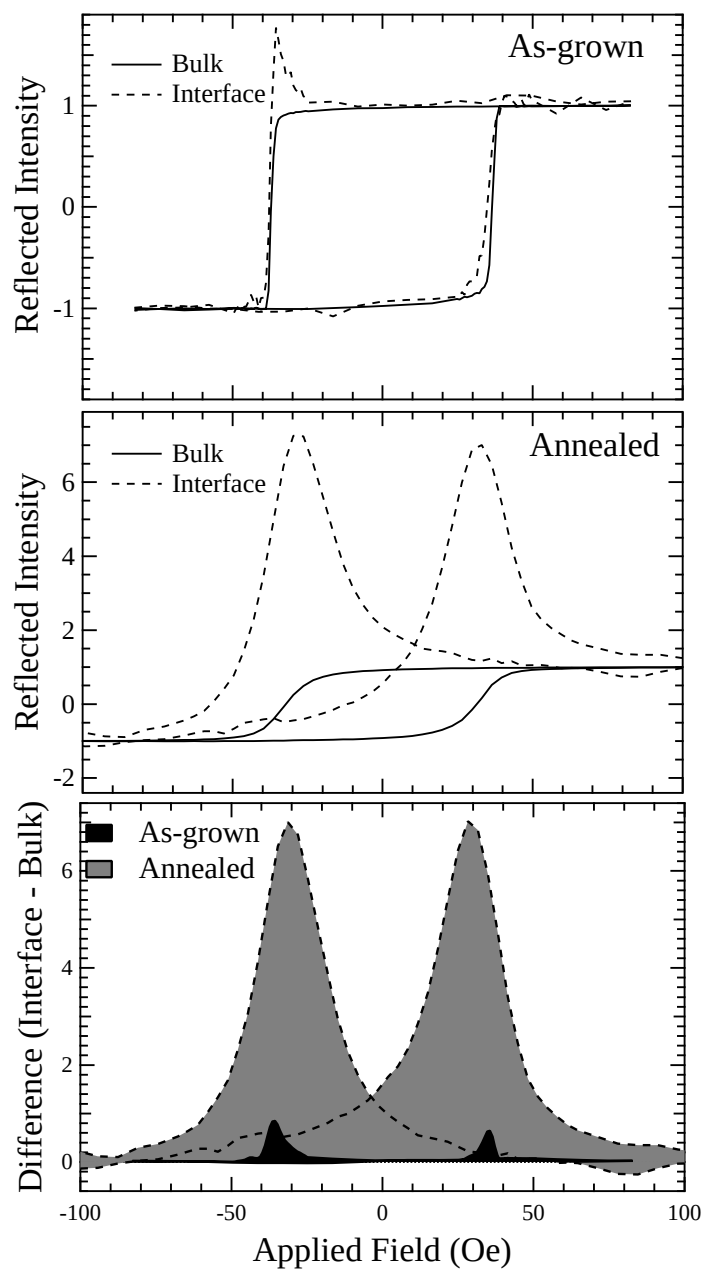


Figure A-6: Response of the bulk and interfacial moments shown by the specular (solid lines) and diffuse (dashed lines) hysteresis loops of the as grown (top) and annealed (middle) samples with CoFe electrodes. Bottom: The difference (Interface - Bulk) spectra for both samples.

to be smooth, promoting highly crystalline MgO growth and improved TMR in MgO based MTJ structures. The coercivity is found to be much lower than in non-boron containing electrodes and although annealing leads to a slight increase in coercivity (due to increased grain size), it also homogenizes the magnetic response and improves the squareness of CoFeB electrodes. Improving the interfacial moment behavior is key to further increase in the TMR values.

APPENDIX B:
MAGNETORESISTANCE BASED EXCHANGE BIAS SENSOR

External processes that alter the degree of exchange bias can be monitored by taking two magnetoresistance readings at selected field values. This method utilizes exchange bias to investigate interfaces and sensing applications. In this appendix, we discuss the the new sensing method and present modeling we did to identify the optimal material parameters and operation conditions.

Background

Discovered in cobalt particulates by Meiklejohn and Bean [4], exchange bias is an interface phenomenon observed in magnetic systems where an antiferromagnetic (AF) layer placed adjacent to a ferromagnetic (FM) layer introduces a coupling that results in a unidirectional shift of the hysteresis loop as the system is cooled below the Néel temperature (T_N) of the AF layer in the presence of a magnetic field [4, 83–85]. The exchange biasing process is illustrated in Fig. B-1. Although the AF layer is insensitive to an external field, cooling the system in an applied field indirectly affects the magnetic ordering of the AF through interfacial coupling with the ferromagnetic layer, promoting nucleation sites for the magnetic ordering of the antiferromagnetic layer. This usually results in a negative exchange bias (i.e., the hysteresis loop is shifted opposite to the applied field direction during cooling) as shown in Fig. B-1. Exchange biased systems show the following properties: (i) unidirectional shift in the hysteresis loops; (ii) blocking temperature, above which the exchange bias disappears; (iii) training effect (dependence of H_{EX} on the number of field reversals); and (iv) enhanced coercivity. This has made exchange bias a widely used technique in magnetic device engineering [71] and has prompted many studies [71, 83–90]. There is no definitive microscopic description of exchange bias, largely because it can be the result of so many interface phenomena, including domain wall formation at the AF/F interface; compensated and uncompensated spin in the AF layer; and net non-collinear magnetization of the AF interfacial layer [71, 83, 84, 86–89]. Results from these models

do not always quantitatively agree with experimental results, often because realistic atomic scale interfacial roughness must be included in the model.

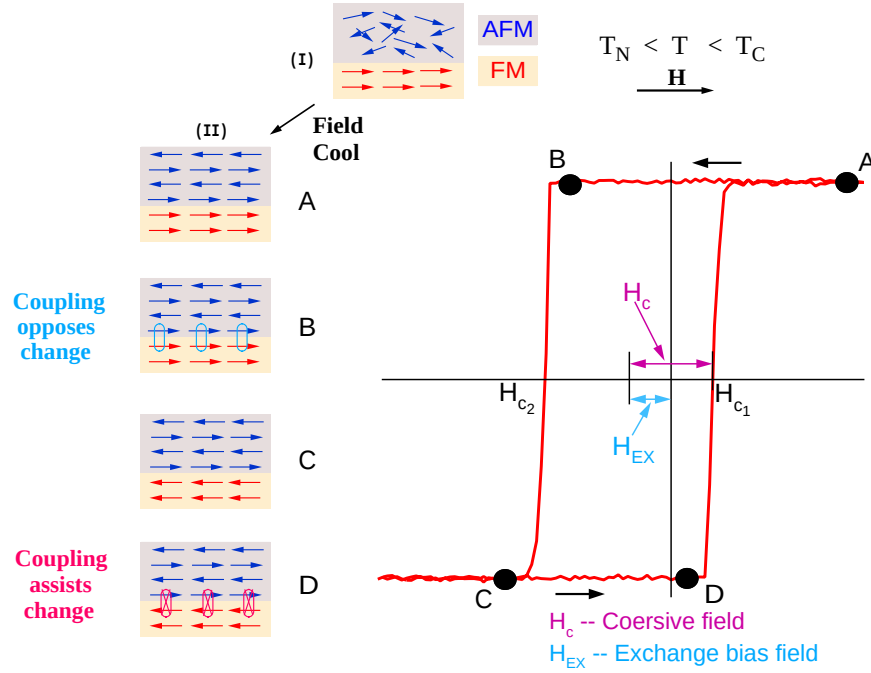


Figure B-1: Exchange bias process (described in text). Figure from [84].

Exchange bias is an essential aspect of many giant magnetoresistance (GMR) and tunneling magnetoresistance (TMR) device structures, including read heads, spin-valves, spin-dependent tunneling junctions, and sensors [71, 83, 84, 86]. For magnetic field based sensors, the sensor's responsiveness is engineered by biasing the hysteresis loop to an accessible region. This way, a slight variations in the applied magnetic field result in large conductivity changes. Since exchange bias is intimately connected to interfacial processes, it is greatly affected by factors such as interface quality, interfacial roughness, and intermixing. Normally, these factors are used to control the value of the exchange field, H_{EX} , but in this work the value of the exchange bias is used to monitor external processes that affect these factors. Applying methods that rely on an absolute measurement of the degree of exchange bias, entail the careful measurement of the hysteresis loop or the complete

magnetoresistance curve as the field is swept beyond both saturation fields, which requires a stable and controllable magnetic field. Instead, by indirectly monitoring only relative changes in H_{EX} , induced by external processes, we can simplify these requirements.

Measurement Principle

Typically, the magnetoresistance (MR) spectrum for a magnetic system is symmetric for the positive and negative going field sweeps, which cross each other at zero field. Because the MR is double valued, we can define a difference spectrum, ΔMR , of the MR for the positive and negative going sweeps. In exchange biased magnetic films, the exchange field introduces an offset in the intersection of the magnetoresistance spectra (point "A" of Fig. B-2) between the positive going sweep (field varied from $-H_{SAT}$ to H_{SAT}) and the negative going sweep (field direction reversed). In the difference spectrum (ΔMR), this is the zero crossing point (Fig. B-2 inset). An exchange biased system can have a non-zero ΔMR at zero field which depends on H_{EX} and the width of the MR curves. In fact, as demonstrated in Fig. B-2, the ΔMR value at zero applied field can be used as a measure of H_{EX} .

The objective is then to use this direct relation between H_{EX} and ΔMR to monitor processes that alter H_{EX} . The measurement procedure is as follows. Pulse the applied field to a value beyond the saturation field, H_{SAT} , forcing the MR value to follow the dashed lines (see Fig. B-2). When the applied field is removed, the MR relaxes, tracing the solid lines to points C or B from $\pm H_{SAT}$ respectively. ΔMR is then calculated by taking the difference in the measured MR resistance values: $\Delta MR = MR_B - MR_C$. This measurement process only requires the ability to pulse to high fields and make two subsequent conductivity measurements for the relative determination of H_{EX} . Any processes that alter H_{EX} would result in a variation in ΔMR . Unlike the measurement of H_{EX} from a magnetoresistance spectra, where locating the intersection point (A) is mandatory, determining ΔMR requires only two measurements of MR at zero field (points B and C), making this method a fast and easy

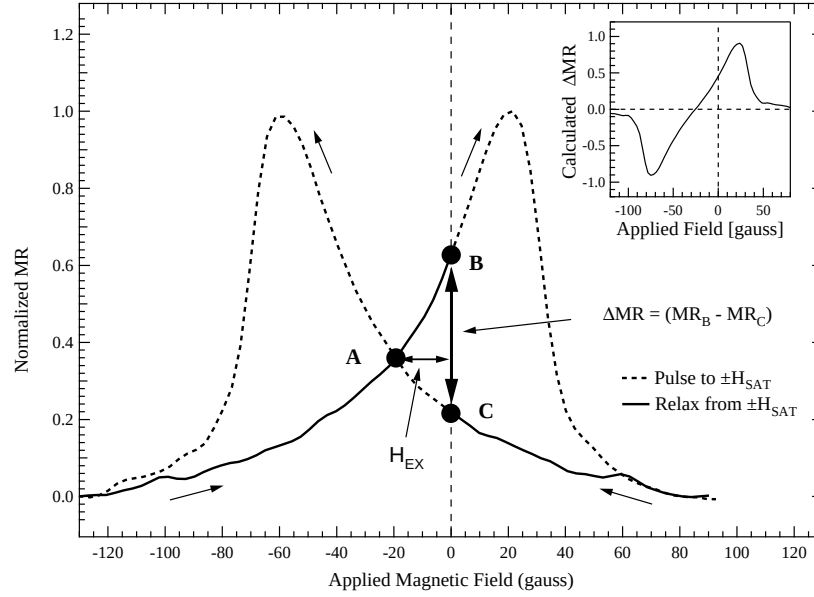


Figure B-2: An exchange biased magnetoresistance (MR) spectrum. When the system is pulsed to $\pm H_{\text{SAT}}$, its MR response follows the dashed lines and relaxes following the solid lines. The ΔMR at $H = 0$, which is a measure of H_{EX} , is the difference between the MR values at points B and C. Inset: Calculated ΔMR as a function of applied field. The section where ΔMR linear in H is the ideal operation region.

way to monitor factors that change H_{EX} . The success and sensitivity of this measurement depends on the detailed shape of the MR loops and the value of the exchange bias field. Only particular combinations of exchange bias, the field position of the maxima in the MR response, and the width of the MR loops will be useful. Since these characteristics are determined by the materials, interfacial structures, and growth methods used, it would be useful to define the interrelationships between these fields that would be of the greatest utility.

Experimental Setup

Exposing a freshly deposited layer of ferromagnetic material such as Co, Ni and Fe to oxygen promotes the formation of an antiferromagnetic oxide layer of $\sim 20 \text{ \AA}$. CoO's convenient Neél temperature of 290 K and blocking temperature, T_B , 260 K (temperature at

which exchange bias appears) [83] make it a prototypical system for building this type of sensor [71, 83, 87]. The CoO/Co bilayer also presents an added advantage in that Co forms a flat interface, has a large coercive field, and has an exchange bias of about 9.5 kOe at 10 K [90]. Once this magnetic ordering in the AF layer is established, it results in exchange bias of the ferromagnetic layer. As previously demonstrated [71], depositing a single or multiple Co/Cu layers before the AF/F layer improves the MR signal as in GMR sensor. The samples used were prepared by electron beam deposition in UHV in static applied field on a silicon substrate then exposed to atmosphere to partially oxidizes the top most Co film, forming an antiferromagnet/ferromagnet (CoO/Co) interface. The hysteresis and MR measurements were performed at the Magnetic Nanostructures Growth and Characterization Facility in Montana State University using a Quantum Design PPMS (Physical Properties Measurement System) and a custom-built magnetoresistance measuring station. Both systems use standard four-wire Van der Pauw resistance measurement, where the PPMS provides 8 T with a superconducting magnet over 2 – 330 K stable operation temperature range.

Modeling

From the example given in Fig B-2, there seems to be a large number of material parameters to be optimized: the exchange field, H_{EX} , the field of maximum MR, H_{MAX} , the saturation field, H_{SAT} , and the width of the MR peak. If we focus on the difference spectra, ΔMR , the parameters can be combined for a more universal description. To examine the effect of H_{EX} on the ΔMR spectra, the MR responses for the positive and negative field sweeps were modeled as two Gaussians centered at $\pm H_{MAX}$ as given by

$$MR = \exp \left(-4 \ln 2 \left(\frac{H_{APPLIED} \mp H_{MAX}}{H_{FWHM}} \right)^2 \right), \quad (B.1)$$

where H_{MAX} is the field giving the maximum magnetoresistance, H_{FWHM} is the width of the Gaussian MR response $\left(H_{\text{SIGMA}} = H_{\text{FWHM}} / \left(2\sqrt{2\ln 2}\right)\right)$, and H_{EX} is the exchange bias field. For a more universal description, H_{MAX} can be considered a scaling field. Similarly, H_{EX} represents an offset field, shifting the spectra to a new zero. Therefore, the important variable is not the applied field, but the scaled and offset field given by $H = (H_{\text{APPLIED}} - H_{\text{EX}}) / H_{\text{MAX}}$. The remaining parameter is H_{FWHM} , the width of the MR loop given in terms of the full-width-at-half-maximum.

Figure B-3 shows the modeled MR response, using this scaled and offset field, with different full-width-at-half-maximum (FWHM)² broadening (Fig B-3-top) as well as the calculated ΔMR for all fields, not just at zero field (Fig B-3-bottom). The field position of the two extremes of the ΔMR response determines the *operational range*, whereas the slope in this range determines the *sensitivity* to changes in H_{EX} . Interestingly, although the MR peak field is independent of the width of the MR spectrum, the peak in ΔMR is not. The operational range of this sensor depends on both. For a sharp MR response with a small relative H_{FWHM} (dashed lines in Fig. B-3-top and Fig. B-3-bottom, first solid lines), small variations in the exchange bias field result in large changes in ΔMR but over a narrow operational range. Similarly, a very broad MR response (a large relative H_{FWHM}) will result in a gradual change in ΔMR over a larger operational range.

Our described measurement procedure consists of determining ΔMR at zero applied field, ($H_{\text{APPLIED}} = 0$). In the absence of exchange bias ($H_{\text{EX}} = 0$), this corresponds to a scaled and offset field of $H = 0$ and $\Delta\text{MR} = 0$ in Fig. B-3. With exchange bias $H_{\text{EX}} \neq 0$, our measurement process still demands no applied field ($H_{\text{APPLIED}} = 0$) corresponding to a scaled and offset field of $H = H_{\text{EX}} / H_{\text{MAX}}$ and $\Delta\text{MR} \neq 0$. As H_{EX} changes, so does ΔMR .

²We have used the full-width-at-half-maximum because of its ease in determination.

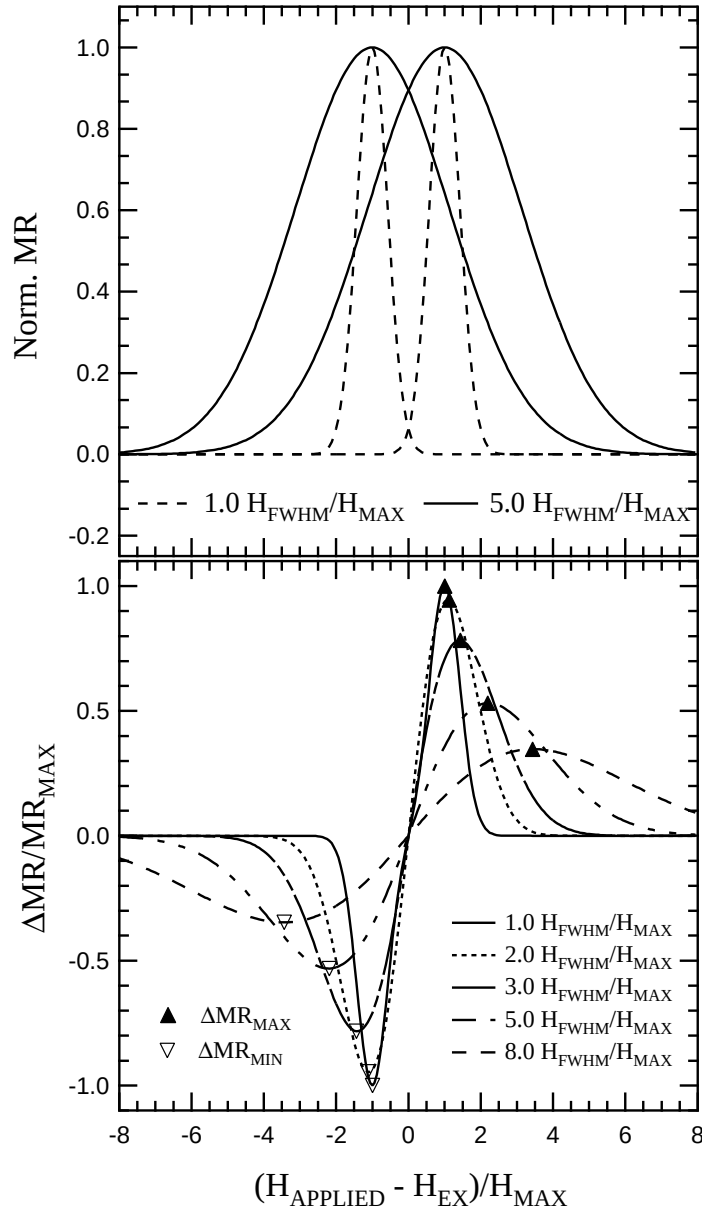


Figure B-3: Top: Gaussian modeling of the MR response for two values of the width. Bottom: calculated normalized ΔMR for different widths of the MR response. Optimal operation range defined by $\Delta\text{MR}_{\text{MAX}}$ (solid triangles) and $\Delta\text{MR}_{\text{MIN}}$ (open triangles).

Operation Field (H_{OP})

In essence, this H_{EX} shifts the crossing point of the spectra. The offset introduced by the

exchange bias could be viewed as an internal biasing field. This leads to the next question, why not introduce an external field, where the measurement is performed? Thus, instead of measuring the changes in MR at zero field, the ΔMR could be done at H_{OP} . In this method we propose that only two points will suffice to determine the relative change of H_{EX} .

By applying a static magnetic field, the operational point can be shifted from zero to H_{OP} (operational field) as shown in Fig. B-4. From a design and implementation point of view, conducting the ΔMR measurement at zero field (with $H_{OP} = 0$) is more convenient. However, operating at a field other than zero can dramatically increase the sensitivity of the measurement. This way the device can be tuned to operate at a desired value.

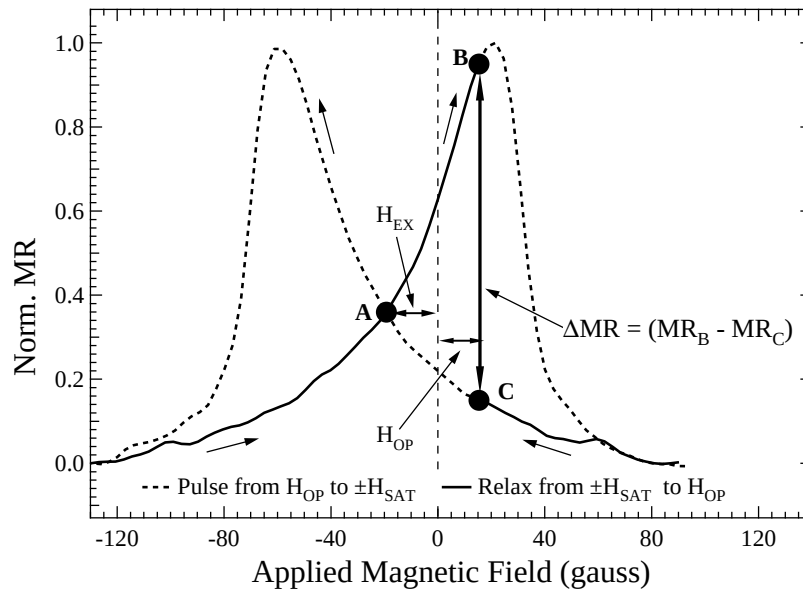


Figure B-4: Sensitivity can be improved by carrying out the measurement at $H_{OP} \neq 0$ instead of only at $H_{OP} = 0$, is shown in Fig. B-2.

In the description given in the previous section, H_{EX} was treated as an intrinsic, system dependent offset. Introducing H_{OP} does not affect the modeling, it only shifts H_{EX} to $H'_{EX} = H_{EX} + H_{OP}$. Figure B-4 shows the revised measurement sequence. The role of the static offset field is to change the field value where the two readings are done. There is a

trade-off between operational range and sensitivity (slope of the ΔMR curve) observed in Fig. B-3. In Fig. B-5 (Middle), we have plotted the variation of the normalized sensitivity and the operational range as a function of the width of the MR response at $H_{OP} = 0$.

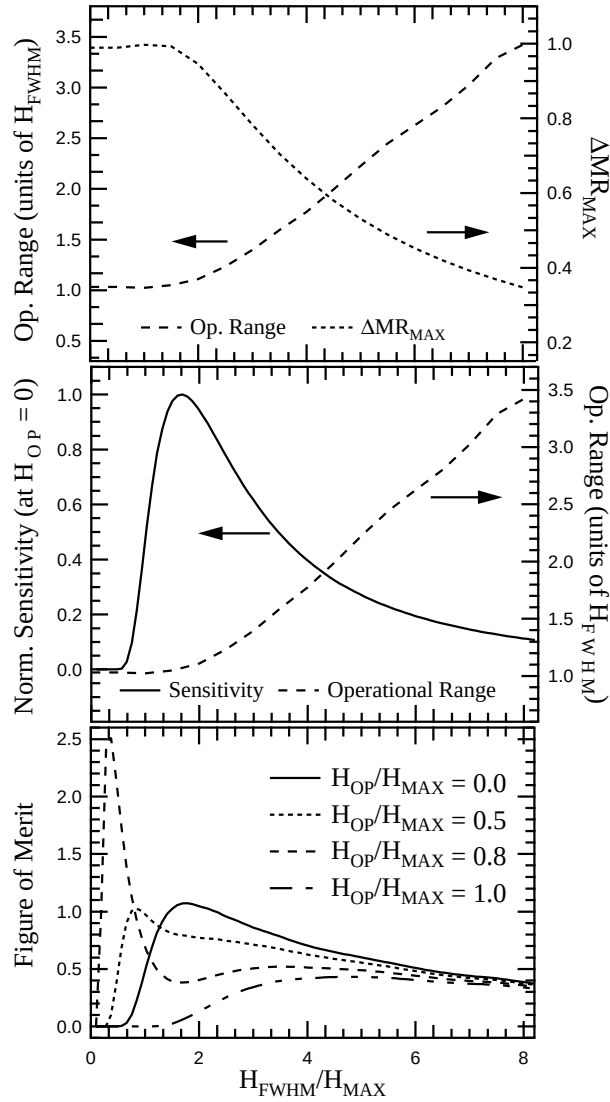


Figure B-5: Dependence of operation range, sensitivity and figure-of-merit (FoM) on full-width-at-half-maximum (FWHM) of the magnetoresistance (MR) curve.

The product of sensitivity and operational range gives a more generalized description, figure of merit (FoM), which illustrates the combined effect of these two important pa-

rameters. Figure B-5 (Bottom) shows the figure of merit for different H_{OP} values where the sensitivity was normalized to that of $H_{OP} = 0$. A closer look at the FoM for $H_{OP} = 0$ indicates that largest sensitivity with operational range equal to H_{MAX} can be achieved if the device is engineered to have H_{FWHM} almost twice H_{MAX} . MR width greater than twice H_{MAX} can increase the operational range but results in a significantly reduced sensitivity and ΔMR_{MAX} intensity (Fig. B-3 Top). The figure of merit plot for different H_{OP} values reveals a remarkable fact. The sensitivity of the system can be dramatically enhanced either by adjusting the H_{EX} of the device closer to H_{MAX} or operating at H_{OP} closer to H_{MAX} . As expected, this significant increase in sensitivity results in notably diminished operable range indicated by the FoM peak shifting towards zero in Fig. B-5 (Bottom). The modeling showed running a device with $H_{EX} < H_{MAX}$ and $H_{FWHM} = 2 \times H_{MAX}$ operated at zero field provides an optimal operation region without loss in sensitivity.

Summary

We have developed a convenient method for monitoring processes that modify interface magnetic structure through exchange bias by pulsing the applied field and evaluating the ΔMR at zero field ($H_{OP} = 0$) or at a static offset field ($H_{OP} \neq 0$). This approach of recording changes in ΔMR at H_{OP} instead of directly measuring H_{EX} provides a fast and convenient method to monitor conditions or processes that affect H_{EX} . The modeling identified optimal values for the relevant material parameters that candidates for this application need to have. Optimal performance can be achieved by engineering the device parameters so that the maximum in the magnetoresistance (H_{MAX} in our model) occurs near the exchange bias field, H_{EX} , and the width of the MR curve is twice the field value of this maximum MR. An alternative approach is to operate the device at H_{OP} slightly smaller than H_{MAX} . This can greatly reduce problems associated with engineering a device with the above stated characteristics allowing operation at a tunable field value.

APPENDIX C:

EXTRACTING FRACTION OF EuO AND Eu_2O_3 FROM XAS SPECTRA

Here we provide details of the steps involved in deconvoluting measured XAS spectra and comparing them to references of the available species. This approach provides a method to identify the available species and quantify their relative abundance. We give an example of the steps involved, which include validating the reference spectra, removing background from the measured XAS data and the actual deconvolution. The approach is presented in the framework of solving an over-determined linear equation and obtaining values that minimize the difference between the measured spectra and computed spectra.

Background and Reference XAS Spectra

The presence or absence of oxides in a given sample can be identified by looking for signature peaks in a given XAS spectrum. The relative abundance of each oxide or element available in the sample can be extracted by comparing the measured spectrum against references of the species present in the sample. This approach provides a method to determine the quality of deposited film and examine the relevant interfaces. This comparative analysis is also used in other measurements, such as XMCD, to determine the amount of magnetic oxides of iron [9].

The reliability of the values extracted using this procedure depends on the quality of the reference spectra. In this study, the two common oxides are EuO, a highly reactive ferromagnetic oxide, and the more stable oxide of europium Eu_2O_3 . To establish standards, we prepared series of reference samples that take into account measurement instrumentation and fabrication constraints. The Eu_2O_3 reference spectrum was taken from a 200 Å thick Eu_2O_3 sample prepared from Eu_2O_3 powder. For the EuO reference XAS spectrum, we used spectra obtained from a 20 Å EuO sample grown on Si with a 20 Å Y electrode capped with 40 Å Al. The XAS and XMCD spectra of this particular sample were consistent with that of EuO reported in literature.. The reference spectra obtained from our standards are shown in Fig. C-1 (shaded dark gray), along with the Eu^{2+} and Eu^{3+} XAS

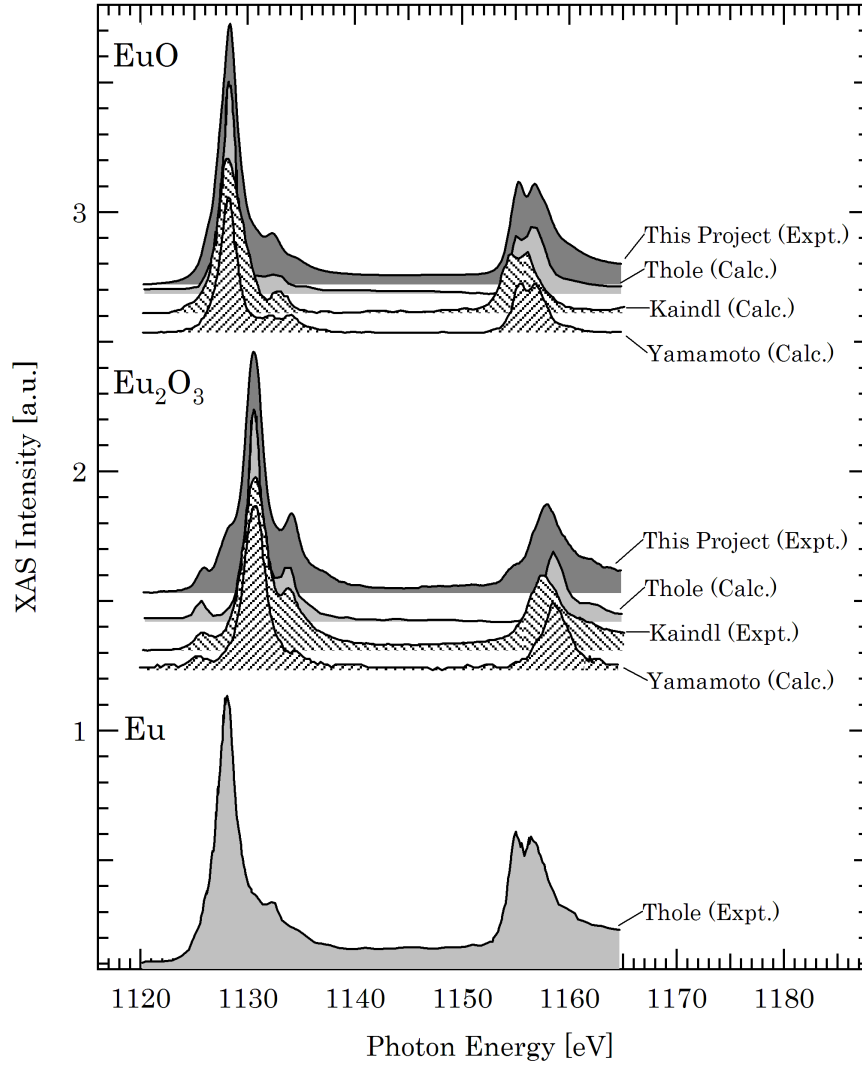


Figure C-1: Reference spectra for EuO (top) and Eu_2O_3 (middle) used in the analysis compared to XAS spectra reported in literature [63, 65, 91]. The spectrum for pure Eu (bottom) was obtained from ref. [63].

spectra at the europium $3d_{5/2}$ (M_5) and $3d_{3/2}$ (M_4) edges reported in literature (see in Fig. C-1 [63, 65, 66, 91]). The XAS spectra from our standard samples agree with the XAS spectra of the oxides under consideration. The small variation, even among the published spectra, can be attributed to either the experimental setup or the way the calculations were conducted. The analysis procedure, which will be discussed below, was applied to our

standard spectra using the spectra reported by Thole et al. [63] as the basis-set. We found that our reference EuO and Eu₂O₃ spectra have less than 5% of the other oxide and less than 10% pure Eu metal. The analysis reported in Chapter 4 was based on our reference spectra. All spectra were energy shifted so that the energy value for the M₅ peak is 1128.2 eV as reported by Thole et al. in Ref. [63].

XAS Spectra Decomposing Procedures

Figure C-2 shows the XAS spectrum at the europium M_{4,5} edges done on an 80 Å thick EuO sample capped with 40 Å Al. The steps involved in the decomposition process are: (1) removing background, (2) correcting energy shift, (3) matching pre- and post-edges to calculated values, and (4) decomposing the spectra and estimating the residual. The main sources of background in the XAS spectra are fluctuations in the incident beam and glitches during data acquisition. Normalizing the measured XAS spectra by the incident-photon-flux (I_0) corrects for factors that affect both the incident beam and the measured fluctuations in the storage ring, decay in the ring current, glitches during the measurement or other factors that may affect both the incoming beam and the measured scan. Often, there may be an additional experimental setup and system-specific background in the XAS spectra while different approaches can be used to remove this type of background, the method used in this work was to collect data over an extended range before the M₅ edge (about 20 eV) and after the M₄ edge (about 30 eV). These two regions, commonly referred to as the *head* and *tail* of the XAS spectra, provide a baseline to remove a small linear background from the spectra.

Once the background is removed, if necessary, the energy axis of the spectra is adjusted by introducing or removing an offset. These two types of energy corrections are relative and absolute. The per-scan correction, one source of which could be drift in the monochromator, is taken care of by collecting the spectra of a material with a known peak near the

energy range the measurement is done. This reference spectrum and the actual XAS scan are collected simultaneously on a different channels. Any relative shift between runs can then be corrected by comparing the spectra of the known material. On the other hand, the absolute energy correction is done by comparing the energy position of the relevant peaks to values reported in literature. As stated earlier, in this study we used the value given by Thole. Alternatively, values obtained from sources such as the X-ray data booklet [92] may also be used.

The normalized XAS spectra are then matched to off-resonance values obtained from Henke's table [92] to show the absolute absorption cross-section values. Then the XAS spectra are decomposed against the reference spectra using a linear least-squares (LLS) fitting procedure. In this scheme, the reference spectra are used as a basis-set, and the task is to find a solution to the over-determined set of linear equations that minimizes the difference between the measured and weighted sum [93]. The measured spectra can be described as

$$y(x) = \sum_{k=1}^N a_k X_k(x), \quad (\text{C.2})$$

where $X_k(x)$ are the basis functions and a_k are the weight functions. The merit function is then given as

$$\chi^2 = \sum_{i=1}^N \left[y_i - \sum_{k=1}^M a_k X(x_i) \right]^2. \quad (\text{C.3})$$

In matrix representation

$$\chi^2 = |\mathbf{y} - \mathbf{X} \bullet \mathbf{a}|^2, \quad (\text{C.4})$$

where $\mathbf{X}$ is an $N \times M$ matrix composed of the basis set, $\mathbf{a}$ is the weight (in this case the fraction of each oxide) and $\mathbf{y}$ is a one-dimensional vector (the measured XAS spectrum to be decomposed).

Figure C-2 shows the different spectra used in the analysis. We start with the measured

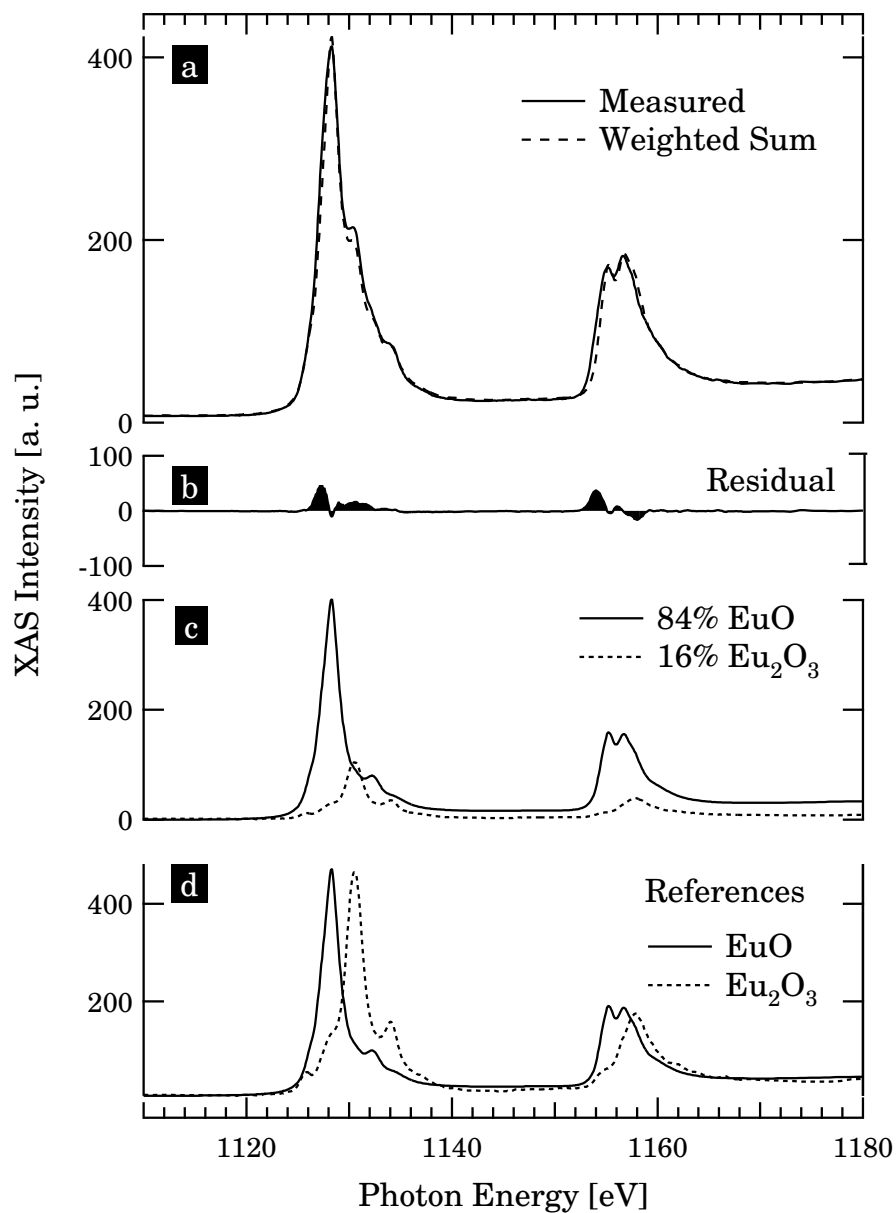


Figure C-2: Decomposition of XAS spectra at the europium $M_{4,5}$ edges. (a) The measured (solid line) and calculated (dashed line) spectra with the small residual (b). (c) The weighted component of the two oxides and (d) reference XAS spectra of EuO and Eu_2O_3 oxides.

spectra shown in panel (a) that has been prepared according to the process detailed above.

Then, using the functions MatrixLLS in WaveMetrics' IgorProTM or the left-matrix divide

(MLDIVIDE) in MathWorks' MatLabTM, the weights are given in variable **a**. IgorPro puts the computed values in an internal variable called M_B. In MatLab the '\' (backslash), a shorthand for left matrix divide, can also be used in the equation. The weight of each oxide that minimize Eq. C.3 are computed using the reference spectra shown in Fig. C-2 (d). This particular sample is composed of 84% EuO and 16% Eu₂O₃ as shown in panel (c). The weighted sum of the oxides is plotted in panel (a), and the difference (residual) is shown in panel (b).

REFERENCES

- [1] G. PRINZ and K. HATHAWAY. *Magnetoelectronics*. Physics Today **48**, 24 (1995).
- [2] R. MESERVEY and P. M. TEDROW. *Spin-polarized tunneling in ferromagnetic junctions*. Physics Reports **238**, 173 (1994).
- [3] M. JULLIÉRE. *Tunneling between ferromagnetic films*. Phys. Lett. **54A**, 225 (1975).
- [4] W. P. MEIKLEJOHN and C. P. BEAN. *New magnetic anisotropy*. Phys. Rev. **102**, 1413 (1956).
- [5] I. ZUTIC, J. FABIAN, and S. D. SARMA. *Spintronics: Fundamentals and applications*. Rev. Mod. Phys. **76**, 232 (2004).
- [6] J. B. KORTRIGHT, D. D. AWSCHALOM, J. STÖHR, S. D. BADER, Y. U. IDZERDA, S. S. P. PARKIN, I. K. SCHULLER, and H. C. SIEGMANN. *Research frontiers in magnetic materials at soft x-ray synchrotron radiation facilities*. J. Mag. Mag. Mater. **207**, 7 (1999).
- [7] Y. U. IDZERDA, V. CHAKARIAN, and J. W. FEELAND. *Quantifying magnetic domain correlations in multilayer films*. Phys. Rev. Lett. **82**, 1562 (1999).
- [8] Y. U. IDZERDA, C. T. CHEN, H.-J. LIN, H. TJENG, and G. MEIGS. *Application of magnetic circular dichroism to magnetic thin films*. Physica B **280**, 746 (1995).
- [9] A. LUSSIER, Y. U. IDZERDA, S. STADLER, S. B. OGALE, S. R. SHINDE, and V. VENKATESAN. *Characterization for strontium titanate/Fe₃O₄ and TiN/Fe₃O₄ interfaces*. J. Vac. Sci. Technol. B **20**, 1609 (2002).
- [10] C. H. MARROWS, P. STEADMAN, A. C. HAMPSON, L.-A. MICHEZ, B. J. HICKEY, N. D. TELLING, D. A. ARENA, J. DVORAK, and S. LANGRIDE. *Probing magnetic ordering in multilayers using soft x-ray resonant magnetic scattering*. Phys. Rev. B. **72**, 024 421 (2005).
- [11] J. W. FREELAND, V. CHAKARIAN, Y. U. IDZERDA, S. DOHERTY, J. G. ZHU, J.-H. PARK, and C.-C. KAO. *Identifying layer switching in magnetic multilayers with x-ray resonant magnetic scattering*. Appl. Phys. Lett. **71**, 276 (1997).
- [12] J. W. FREELAND, K. BUSSMANN, P. LUBITZ, Y. U. IDZERDA, and C. C. KAO. *Probing interfacial and bulk magnetic hysteresis in roughened CoFe thin films*. Appl. Phys. Lett. **73**, 2206 (1998).
- [13] J. G. ZHU and C. PARK. *Magnetic tunnel junctions*. Materials Today **9**, 36 (2006).
- [14] G. A. PRINZ. *Magnetoelectronics*. Science **282**, 1600 (1998).

- [15] A. NEY, C. PAMPUCH, R. KOCH, and K. H. PLOOG. *Programmable computing with a single magnetoresistive element*. Nature **425**, 485 (2003).
- [16] S. SUGAHARA and M. TANAKA. *A novel spin transistor based on spin-filtering in ferromagnetic barriers: a spin-filter transistor*. Physica E **21**, 996–1001 (2004).
- [17] A. SCHMEHL, V. VAITHYANATHAN, A. HERRNBERGER, S. THIEL, C. RICHTER, M. LIBERATI, T. HEEG, M. RÖCHERATH, L. F. KOURKOUTIS, S. MÜHLBAUER, P. BÖNI, D. A. MULLER, Y. BARASH, J. SCHUBERT, Y. IDZERDA, J. MANNHART, and D. G. SCHLOM. *Epitaxial integration of the highly spin-polarized ferromagnetic semiconductor EuO with Silicon and GaN*. Nature Materials **4**, 1 (2007).
- [18] T. SHINJO. *Spin Dependent Transport in Magnetic Nanostructures*, chapter Experiments of Giant Magnetoresistance, pages 1–46. Taylor & Francis MG Books Ltd, Bodmin (2002).
- [19] S. A. WOLF, D. D. AWSCHALOM, R. A. BUHRMAN, J. M. DUGHTON, S. VON MOLNÁR, M. L. ROUKES, A. Y. CHTCHELKANOVA, and D. M. TREGER. *A spin-based electronics of the future*. Science **294**, 1488 (2001).
- [20] S. K. SINHA, E. B. SIROTA, S. GAROFF, and H. B. STANLEY. *X-ray and neutron scattering from rough surfaces*. Phys. Rev. B **38**, 2297 (1988).
- [21] D. R. LEE, S. K. SINHA, D. HASKEL, Y. CHOI, J. C. LANG, S. A. STEPANOV, and G. SRAJER. *X-ray resonant magnetic scattering from structurally and magnetically rough interfaces in multilayered systems. II. Diffuse reflectivity*. Phys. Rev. B **68**, 224 410 (2003).
- [22] J. W. FREELAND, V. CHAKARIAN, K. BUSSMANN, Y. U. IDZERDA, H. WENDE, and C.-C. KAO. *Exploring magnetic roughness in CoFe thin films*. J. Appl. Phys. **83**, 6290 (1998).
- [23] H. ÖHLDAĞ, T. J. REGAN, J. STÖHR, A. SCHOLL, F. NOLTING, J. LÜNING, C. STAMM, S. ANDERS, and R. L. WHITE. *Spectroscopic identification and direct imaging of interfacial magnetic spins*. Phys. Rev. Lett. **87**, 247 201 (2001).
- [24] J. W. FREELAND, K. BUSSMANN, and Y. U. IDZERDA. *Connecting disorder and magnetic properties in CoFe thin films*. Appl. Phys. Lett. **76**, 2603 (2000).
- [25] J. W. FREELAND, K. BUSSMANN, Y. U. IDZERDA, and C.-C. KAO. *Understanding correlations between chemical and magnetic interfacial roughness*. Phys. Rev. B **60**, R9923–9926 (1999).
- [26] R. M. OSGOOD III, S. K. SINHA, J. W. FREELAND, Y. U. IDZERDA, and S. D. BADER. *X-ray scattering from magnetically and structurally rough surfaces*. J. Magn. Mater. **198**, 698–702 (1999).

- [27] W. H. BUTLER, X.-G. ZHANG, T. C. SCHULTHESS, and J. M. MACLAREN. *Spin-dependent tunneling conductance of Fe|MgO|Fe sandwiches*. Phys. Rev. B **63**, 054 416 (2001).
- [28] J. M. DE TERESA, A. BARTHÉLÉMY, A. FERT, J. P. CONTOUR, F. MONTAIGNE, and P. SENEOR. *Role of metal-oxide interface in determining the spin polarization of magnetic tunnel junctions*. Science **286**, 507 (1999).
- [29] J. GRABIS, A. BERGMANN, A. NEFEDOV, K. WESERHOLT, and H. ZABEL. *Element-specific characterization of the interface magnetism in $[\text{Co}_2\text{MnGe}/\text{Au}]_n$ multilayers by x-ray resonant magnetic scattering*. Phys. Rev. B **72**, 024 438 (2005).
- [30] T. MIYAZAKI and T. TEZUKA. *Giant magnetic tunneling effect in Fe/Al₂O₃/Fe junction*. J. Magn. Magn. Mater. **139**, L231 (1995).
- [31] J. S. MOODERA, L. R. KINDER, T. M. WONG, and R. MESERVEY. *Large Magnetoresistance at room temperature in ferromagnetic thin film tunnel junctions*. Phys. Rev. Lett. **74**, 3273 (1995).
- [32] K. KOBAYASHI and H. AKIMOTO. *TMR film and head technology*. Fujitsu Sci. Tech. J. **42**, 139 (2006).
- [33] M. N. BAIBICH, J. M. BROTO, A. FERT, F. N. V. DAU, F. PETROFF, P. EITENNE, G. CREUZET, A. FRIEDERICH, and J. CHAZELAS. *Giant magnetoresistance of (001)Fe/(001)Cr magnetic superlattices*. Phys. Rev. Lett. **61**, 2472 (1988).
- [34] G. BINASCH, P. GRÜNBERG, F. SAURENBACH, and W. ZINN. *Enhanced magnetoresistance in layered magnetic structures with antiferromagnetic interlayer exchange*. Phys. Rev. B **39**, 4828 (1989).
- [35] X.-G. ZHANG, W. H. BUTLER, and A. BANDYOPADHYAY. *Effects of the iron-oxide layer in Fe-FeO-MgO-Fe tunneling junctions*. Phys. Rev. B **68**, 092 492 (2003).
- [36] E. E. FULLERTON, D. M. KELLY, J. GUIMPEL, I. K. SCHULLER, and Y. BRUYNSERAEDE. *Roughness and giant magnetoresistance in Fe/Cr superlattice*. Phys. Rev. Lett. **68**, 859 (1992).
- [37] S. S. P. PARKIN. *Dramatic enhancement of interlayer exchange coupling and giant magnetoresistance in $\text{Ni}_{81}\text{Fe}_{19}/\text{Cu}$ multilayers by addition of thin Co interface layers*. Appl. Phys. Lett. **61**, 1358 (1992).
- [38] K. D. BELASCHENKO, J. VELEV, and E. Y. TSYMBAL. *Effect of interface states on spin-dependent tunneling in Fe/MgO/Fe tunnel junctions*. Phys. Rev. B **72**, 1040 404 (2005).

- [39] W. SHEN, D. MAZUMDAR, X. ZOU, X. LIU, B. D. SCHRAG, and G. XIAO. *Effect of film roughness in MgO-based magnetic tunnel junction*. Appl. Phys. Lett. **88**, 182 508 (2006).
- [40] J. MATHON and A. UMERSKY. *Theory of tunneling magnetoresistance of an epitaxial Fe/MgO/Fe(001) junction*. Phys. Rev. B **63**, 220 403R (2001).
- [41] E. Y. TSYMBAL and K. D. BELASHCHENKO. *Role of interface bonding in spin-dependent tunneling*. J. Appl. Phys **97**, 10C910 (2005).
- [42] C. HEILIGER, P. ZAHN, and I. MERTIG. *Microscopic origin of magnetoresistance*. Materials Today **9**, 46 (2006).
- [43] J. S. MOODERA, X. HAO, G. A. GIBSON, and R. MESERVEY. *Electron-spin polarization in tunnel junctions in zero applied field with ferromagnetic EuS barriers*. Phys. Rev. B **42**, 8235 (1988).
- [44] T. S. SANTOS. *Europium oxide as a perfect electron spin filter*. Ph.D. thesis, Massachusetts Institute of Technology, May (2007).
- [45] I. GIAEVER. *Energy gap in superconductors measured by electron tunneling*. Phys. Rev. Lett. **5**, 147 (1960).
- [46] I. GIAEVER. *Electron tunneling between two superconductors*. Phys. Rev. Lett. **5**, 464 (1960).
- [47] L. ESAKI, P. STILES, and S. VON MOLNA. *Magnetointernal field emission in junctions of magnetic insulators*. Phys. Rev. Lett. **19**, 852 (1967).
- [48] P. M. TEDROW and R. MESERVEY. *Spin polarization of electrons tunneling from Films of Fe, Co, Ni and Gd*. Phys. Rev. B **7**, 318–326 (1973).
- [49] R. J. SOULEN, J. M. BYERS, M. S. OSOFSKY, B. NADGORN, T. AMBROSE, S. F. CHENG, P. R. BROUSSARD, C. T. TANAKA, J. NOWAK, J. S. MOODERA, A. BARRY, and J. M. D. COEY. *Measuring the spin polarization of a metal with a superconducting point contact*. Science **282**, 85 (1998).
- [50] T. S. SANTOS and J. S. MOODERA. *Observation of spin filtering with a ferromagnetic EuO tunnel barrier*. Phys. Rev. B **69**, 241 203 R (2004).
- [51] J. S. MOODERA, T. S. SANTOS, and T. NAGAHAMA. *The phenomena of spin filter tunneling*. J. Phys. Condens. Matter **19**, 165 202 (2007).
- [52] J. G. SIMMONS. *Generalized formula for the electric tunnel effect between similar electrodes separated by a thin insulating film*. J. Appl. Phys. **34**, 1793 (1963).

- [53] W. F. BRINKMAN, R. C. DYNES, and J. M. ROWELL. *Tunneling conductance of asymmetrical barriers*. J. Appl. Phys. **41**, 1915–1921 (1970).
- [54] R. Z. LANDAUER. *Electrical transport in open and closed systems*. Physik B **68**, 217 (1987).
- [55] B. DIENY, V. S. SPERIOSU, S. S. P. PARKIN, B. A. GURNEY, D. R. WILHOIT, and D. MAURI. *Giant magnetoresistance in soft ferromagnetic multilayers*. Phys. Rev. B **43**, 1297 (1991).
- [56] Y. U. IDZERDA, C. T. CHEN, H.-J. LIN, G. MEIGS, G. H. HO., and C. C. KAO. *Soft x-ray magnetic circular dichroism and magnetic films*. Nucl. Instrum. Methods Phys. Rev. A **347**, 134 (1994).
- [57] R. NAKAJIMA, J. STÖHR, and Y. U. IDZERDA. *Electron-yield saturation effects in L-edge x-ray magnetic circular dichroism spectra of Fe, Co, and Ni*. Phys. Rev. B **59**, 6421 (1999).
- [58] Y. U. IDZERDA, V. CHAKARIAN, and J. W. FREELAND. *Soft x-ray magnetic circular dichroism at NSLS beamline U4B*. Synchrotron Radiation News **10**, 6 (1997).
- [59] J. LETTIERI, V. VAITHYANATHAN, S. K. EAH, J. STEPHENS., V. SIH, D. D. AWSCHALOM, J. LEVY, and D. G. SCHLOM. *Epitaxial growth and magnetic properties of EuO on (001) Si by molecular-beam epitaxy*. Appl. Phys. Lett. **83**, 975 (2003).
- [60] P. G. STEENEKEN, L. H. TJENG, I. ELFIMOV, G. A. SAWATZKY, G. GHIRINGHELLI, N. B. BROOKES, and D.-J. HUANG. *Exchange splitting and charge carrier spin polarization in EuO*. Phys. Rev. Lett. **88**, 047 201 R (2002).
- [61] V. CHAKARIAN, Y. U. IDZERDA, and C. T. CHEN. *Absolute helicity-dependent photoabsorption cross section of Fe thin films and quantitative evaluation of magnetic-moment determination*. Phys. Rev. B **57**, 5312 (1998).
- [62] G. V. SAMSONOV, editor. *The Oxide Handbook*. IFI/Plenum, New York, 2nd edition (1982).
- [63] B. T. THOLE, G. VAR DER LAAN, J. C. FUGGLE, G. A. SAWATZKY, R. C. KARNATAK, and J.-M. ESTEVA. *3d x-ray-absorption lines and the $3d^9 4f^{n+1}$ multiplets of the lanthanides*. Phys. Rev. B **32**, 5107 (1985).
- [64] M. SÁNCHEZ-AGUDO, F. YUBERO, G. G. FUENTES, A. GUTIÉRREZ, M. SACCHI, L. SORIANO, and J. M. SANZ. *Study of the growth of ultrathin films of NiO on Cu(111)*. Surface Interface Analysis **30**, 396 (2000).

- [65] K. YAMAMOTO, K. HORIBA, M. TAGUCHI, M. MATSUNAMI, N. KAMAKURA, A. CHAINANI, Y. TAKATA, K. MIMURA, M. SHIGA, H. WADA, Y. SENBA, H. OHASHI, and S. SHIN. *Temperature-dependent Eu 3d–4f x-ray absorption and resonant photoemission study of the valence transition in $\text{EuNi}_2(\text{Si}_{0.2}\text{Ge}_{0.2})_2$* . Phys. Rev. B **72**, 161 101 (2005).
- [66] J. HOLROYD, Y. U. IDZERDA, and S. STADLER. *Properties of thin film europium oxide by x-ray magnetic circular dichroism*. J. Appl. Phys **95**, 6571 (2004).
- [67] T. MATSUMOTO, K. YAMAGUCHI, M. YURI, K. KAWAGUCHI, N. KOSHIZAKI, and K. YAMADA. *Preparation of Gd-doped EuO_{1-x} thin films and the magnetic and magneto-transport properties*. J. Phys. Condens. Matter **16**, 6017 (2004).
- [68] R. SCHILLER and W. NOLTING. *Prediction of a surface state and a related surface insulator-metal transition for the (100) surface of stoichiometric EuO*. Phys. Rev. Lett. **86**, 3847–3850 (2001).
- [69] H. OTT, S. J. HEISE, R. S. Z. HU, C. F. CHANG, H. H. HSIEH, H.-J. LIN, C. T. CHEN, and L. H. TJENG. *Soft x-ray magnetic circular dichroism study on Gd-doped EuO thin films*. Phys. Rev. B **73**, 094 407 (2006).
- [70] W. J. GALLAGHER and S. S. P. PARKIN. *Development of the magnetic tunnel junction MRAM at IBM: From first junctions to a 16-Mb MRAM demonstrator chip*. IBM J. Res. Dev. **50**, 5 (2006).
- [71] S. S. P. PARKIN, C. KAISER, A. PANCHULA, P. M. RICE, B. HUGHES, M. SAMANTA, and S. HUN YANG. *Giant tunnelling magnetoresistance at room temperature with MgO (100) tunnel barrier*. Nature Materials **3**, 862 (2004).
- [72] S. YUASA, T. NAGAHAMA, A. FUKUSHIMA, Y. SUZUKI, and K. ANDO. *Giant room-temperature magnetoresistance in single-crystal Fe/MgO/Fe magnetic tunnel junctions*. Nature Materials **3**, 868 (2004).
- [73] D. D. DJAYAPRAWIRA, K. TSUNEKAWA, M. NAGAI, H. MAEHARA, S. YAMAGATA, N. WATANABE, S. YUASA, Y. SUZUKI, and K. ANDO. *230% room-temperature magnetoresistance in CoFeB/MgO/CoFeB magnetic tunnel junctions*. Appl. Phys. Lett. **86**, 092 502 (2005).
- [74] K. TSUNEKAWA, D. D. DJAYAPRAWIRA, M. NAGAI, H. MAEHARA, S. YAMAGATA, N. WATANABE, S. YUASA, Y. SUZUKI, and K. ANDO. *Giant tunneling magnetoresistance effect in low-resistance CoFeB/MgO(001)/CoFeB magnetic tunnel junctions for read-head applications*. Appl. Phys. Lett. **87**, 072 503 (2005).
- [75] J. F. MACKAY, C. TEICHERT, D. E. SAVAGE, and M. G. LAGALLY. *Element specific magnetization of buried interfaces probed by diffuse x-ray resonant magnetic scattering*. Phys. Rev. Lett. **77**, 3925 (1996).

- [76] C. T. CHEN, Y. U. IDZERDA, H.-J. LIN, G. MEIGS, A. CHAIKEN, G. A. PRINZ, and G. H. HO. *Element-specific magnetic hysteresis as a means for studying hetero-magnetic multilayers*. Phys. Rev. B **48**, 642 (1993).
- [77] Y. U. IDZERDA, L.-H. TJENG, H.-J. LIN, C. J. GUTIERREZ, G. MEIGS, and C. T. CHEN. *Magnetic structure of Fe/Cr/Fe trilayers*. Phys. Rev. B **48**, 4144–4147 (1993).
- [78] V. CHAKARIAN, Y. U. IDZERDA, C.-C. KAO, and C. T. CHEN. *Circular polarized xoft x-ray resonant magnetic scattering studies of FeCo/Mn/FeCo multilayers*. J. Magn. Magn. Mater **165**, 52 (1997).
- [79] J. M. TONNERRE, L. SEVE, D. RAOUX, G. SOULLIE, B. RODMACQ, and P. WOLFERS. *Soft X-ray resonant magnetic scattering from a magnetically coupled Ag/Ni multilayer*. Phys. Rev. Lett **75**, 740 (1995).
- [80] C.-C. KAO, C. T. CHEN, E. D. JOHNSON, D. P. SIDDONS, H. J. LIN, G. H. HO, G. MEIGS, J.-M. BROU, S. L. HULBERT, Y. U. IDZERDA, and C. VETTIER. *Dichroic interference effects in circularly polarized soft-x-ray resonant magnetic scattering*. Phys. Rev. B **50**, 9599 (1994).
- [81] M. SICOT, S. ANDRIEU, F. BERTRAN, and F. FORTUNA. *Electronic properties of Fe, Co, and Mn ultrathin films at the interface with MgO(001)*. Phys. Rev. B **72**, 144 414 (2005).
- [82] T. J. REGAN, H. OHLDAG, C. STAMM, F. NOLTING, J. LÜNING, J. STÖHR, and R. L. WHITE. *Chemical effects at metal/oxide interfaces studied by x-ray-absorption spectroscopy*. Phys. Rev. B **64**, 214 422 (2001).
- [83] J. NOGUÉS and I. K. SCHULLER. *Exchange bias*. J. Magn. Magn. Mater. **192**, 203 (1999).
- [84] A. E. BERKOWITZ and K. TAKANO. *Exchange anisotropy – a review*. J. Magn. Magn. Mater. **200**, 552–570 (1999).
- [85] S. MAAT, K. TAKANO, S. S. PARKIN, and E. E. FULLERTON. *Perpendicular exchange bias of Co/Pt ultrathin films*. Phys. Rev. Lett. **87**, 087 202 (2001).
- [86] M. KIWI. *Exchange bias theory*. J. Magn. Magn. Mater. **234**, 584 (2001).
- [87] D. SUESS, M. KIRSCHNER, T. SCHREFL, J. FIDLER, R. L. STAMPS, and J.-V. KIM. *Exchange bias of polycrystalline antiferromagnets with perfectly compensated interfaces*. Phys. Rev. B **67**, 054 419 (2003).
- [88] C. LEIGHTON, J. NOGUÉS, B. J. JÖNSSON-AKERMAN, and I. K. SHULLER. *Coercivity enhancement in exchange biased systems driven by interfacial magnetic frustration*. Phys. Rev. Lett. **84**, 3466 (2000).

- [89] N. C. KOON. *Calculations of exchange bias in thin films with ferromagnetic/antiferromagnetic interfaces*. Phys. Rev. Lett. **78**, 4865 (1997).
- [90] F. RADU, M. ETZKORN, R. SIEBRECHT, T. SCHMITTE, K. WESTERHOLT, and H. ZABEL. *Interfacial domain formation during magnetization reversal in exchange-biased CoO/Co bilayers*. Phys. Rev. B **67**, 134 409 (2003).
- [91] G. KAINDL, G. KALKOWSKI, W. D. BREWER, B. PERSCHIED, and F. HOLTZBERG. *M-edge x-ray absorption spectroscopy of 4f instabilities in rare-earth systems*. J. Appl. Phys **55**, 1910 (1984).
- [92] B. L. HENKE, E. M. GULLIKSON, and J. C. DAVIS. *X-ray interactions: Photoabsorption, scattering, transmission, and reflection at $E = 50$ – $30,000$ eV, $Z = 1$ – 92* . At. Data Nucl. Data Tables **54**, 181 (1993). And at http://henke.lbl.gov/optical_constants/.
- [93] W. H. PRESS, S. A. TEUKOLSKY, W. T. VETTERLING, and B. P. FLANNERY. *Numerical recipes in FORTRAN*, chapter 15, pages 665–670. Cambridge University Press, 2 edition (1992).