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ATOMIC-SCALE STRUCTURE OF COPPER/COBALT MULTILAYERS AND COBALT/ALUMINA/COBALT MAGNETIC TUNNEL JUNCTIONS

A Dissertation
Presented to the Faculty of the Graduate School of Cornell University in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

by
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August 2001
Biographical sketch

Monica Plisch attended the University of Illinois at Urbana from 1990 to 1994. She graduated with Highest Honors, receiving a Bachelor of Science in Engineering Physics and an International Minor in Japanese Studies. She came to Cornell University in August of 1994 supported by a fellowship from the National Science Foundation. The Master of Science in Physics was awarded January 1999 and the Doctor of Philosophy in Physics was awarded August 2001.
In memory of my father,

Donovan C. Plisch

August 9, 1939 - November 27, 1996
Acknowledgements

First I would like to thank my special committee members, especially Bob Buhrman for serving as my thesis advisor. I appreciate the freedom he gave me in choosing a project and pursuing my own directions while providing me with helpful suggestions and gentle critiques from time to time. I am grateful to John Silcox for providing many insights to microscopy side of my work. I also would like to thank Dan Ralph and Neil Ashcroft for serving on my special committee, Dan as chairman.

Dave Muller was instrumental in the completion of my dissertation. While at Cornell as a graduate student with the Silcox group and later as Visiting Scientist, he trained me in operating the STEM, provided me with data processing routines, explained EELS theory to me and gave me numerous valuable insights to my data. This dissertation stands on the shoulders of Dave’s many important contributions to the field of atomic-scale EELS, and would not be possible without his work.

I would like to thank the many Buhrman group members who worked alongside me, providing technical and moral support. Richard Louie, Shashi Upadhyay, and Jordan Katine worked with me in building and the sputter deposition chamber. Janis Chang added oxidation capabilities to the chamber
and assisted me in growing magnetic tunnel junction samples. Preeti Chalsani provided evaporated cobalt/aluminum bilayer samples. Bill Rippard assisted me in spin-etching silicon wafers. Finally, I'd like to thank Jason Sydow for riding my first motorcycle in near-freezing temperatures back to Ithaca.

I would also like to acknowledge support from members of the Silcox and Ralph groups. Nan Jiang and Andre Mkhoyan assisted with TEM imaging, Richard Vanfleet provided a leg up with STEM simulations, and Tyler Eustis provided me with a sapphire sample. Mandar Deshmukh assisted with evaporation of the amorphous alumina sample.

I wish to thank Earl Kirkland and Mick Thomas for their tireless work in maintaining and upgrading the STEM, making it into a world class instrument. Mick's training and countless pointers in sample preparation were invaluable as was his patience and ever-cheerful attitude. Earl provided frequent technical assistance in many areas for which I am grateful.

The National Science Foundation provided me with fellowship support for my first three years of graduate school. This allowed me to avoid the additional pressures of teaching in my first year and to experience it in a more pleasurable and relaxed way during my latter years.

Last, but definitely not least, I would like to thank the countless friends who helped me celebrate my achievements and grieve my losses. Each of them also helped me to develop other sides of myself, without which I would never have run a marathon, performed Argentine tango, competed in a pool tournament, and organized a transgender studies conference. These and many other activities helped keep me sane during my seven years in graduate school.
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Chapter 1

Introduction

1.1 Spin-polarized transport

A new field called “spin-polarized transport” has grown dramatically over the last three decades. Its origin lies in the quantum mechanical fact that electrons have spin as well as charge. The spin-polarization $P$ of an electron population is defined as

$$P = \frac{N_u - N_d}{N_u + N_d}$$

where $N_u$ is the number of up-spin electrons and $N_d$ is the number of down-spin electrons. There are several ways of realizing an electron population with nonzero spin-polarization. An important example is a ferromagnet, which has a naturally occurring imbalance between up- and down-spin electrons (which is the origin of its magnetic moment). Metallic ferromagnets such as cobalt, iron and nickel have mobile electrons, and current in such materials is spin-polarized.
Spin-polarized current can be injected from a ferromagnet into other metals. Spin relaxation lengths tend to be relatively long, and an electron can typically undergo many scattering events without losing its orientation. This is because spin-flip interactions are relatively rare events, occurring only through exchange coupling with other electrons in the vicinity of a magnetic atom or via spin-orbit coupling to impurity atoms or defects. Such a long spin relaxation length is critical for making devices that utilize spin-polarized transport.

1.1.1 Historical sketch

The most definitive and elegant experiment to detect spin-polarized transport was in 1970. This experiment measured the spin-polarization of current originating in various ferromagnetic materials using ferromagnet/insulator/superconductor structures [Meservey70]. Electrons tunneled out of the ferromagnet through the nonmagnetic barrier into a superconductor, which acted as a spin detector. An applied field $H$ split the sharply peaked density of states of the superconductor into up-spin and down-spin components separated by an energy of $\pm \mu H$, where $\mu$ is the electron spin magnetic moment. Thus at certain bias voltages, tunneling by up-spin or down-spin electrons was heavily favored. Careful analysis of the current as a function of bias voltage and applied field revealed the spin-polarization of the current transmitted through the barrier.

Since the 1970 experiment, several devices that utilize spin-polarized current have been discovered. In 1975, the first successful magnetic tunnel junction was fabricated [Juliere75]. In these ferromagnet/insulator/ferromagnet structures one ferromagnet acts as a “polarizer” of spin current
and the other as an "analyzer." Thus conduction of current depends on the
relative alignment of the magnetization of each magnetic layers, and such
structures can exhibit a fractional change in resistance of up to 40% [Lu98].
Spin valves can be conceptualized in a similar way. They are a derivative of
magnetic multilayers, which were discovered in 1988 [Baibich88]. Spin valves
are ferromagnet/normal metal/ferromagnet structures and typically exhibit
magnetoresistance values on the order of 10% [Parkin93].

The field of spin-polarized transport has provided new challenges and
opportunities to improve the microscopic theory of magnetism.
Understanding of fundamental concepts such as spin-dependent scattering,
spin relaxation, spin-dependent band structure and spin-spin interactions has
increased dramatically with this surge of interest in magnetism. Experimental
means of fabricating and probing magnetic structures have likewise seen
dramatic improvements. However, many phenomena exhibited by devices
that utilize spin-polarized transport are still unexplained, and much work
remains before a coherent microscopic theory of magnetism emerges.

1.1.2 Technological applications

Spin valves and magnetic tunnel junctions are both two-state devices,
with parallel and anti-parallel alignment of the magnetic layers defining the
two states. The magnetoresistance values of these devices are an order of
magnitude larger than those of materials exhibiting anisotropic
magnetoresistance (AMR). This has technological importance, since AMR
materials previously had the highest known magnetoresistance values in
practical materials. Spin valves and magnetic tunnel junctions are easily
incorporated into integrated circuits since the thin film growth techniques used to fabricate such devices are standard microfabrication processes.

Spin valves and magnetic tunnel junctions already being used in several technological applications, and are being developed for use in others [Daughton99]. Spin-valve read heads have enabled very high packing densities for hard disk drives, up to 24 Gbits per square inch. Magnetic tunnel junction sensors have the potential to sense fields as small as 1 pT. Both spin-valve and magnetic tunnel junction structures are being developed for use in non-volatile random access memory, which could rival the performance of semiconductor memory and have the non-volatility of a hard disk drive.

1.2 Magnetic multilayers and spin valves

Magnetic multilayers consist of several bilayer periods, each containing a ferromagnetic and a nonmagnetic metallic layer. Individual layer thicknesses range approximately from 10 to 30 Å thick. The conduction of electrons through a magnetic multilayer depends on the relative alignment of the magnetizations of the ferromagnetic layers. Typically, there is a high-resistance state at zero applied field when adjacent ferromagnetic layers align anti-parallel. There is a low-resistance state at high field when the ferromagnetic layers are forced into parallel alignment. Since the change in resistance can be a large fraction of the multilayer resistance, this phenomenon has been called “giant magnetoresistance.”

Giant magnetoresistance (GMR) is defined as

\[ GMR = \frac{R_{AP} - R_p}{R_p}, \]
where $R_{ap}$ is the resistance with anti-parallel alignment of the ferromagnetic layers and $R_p$ is the resistance with parallel alignment. Figure 1.1 shows a magnetoresistance measurement for a multilayer structure composed of 23 bilayer periods, each containing a 11.5 Å cobalt layer and a 19 Å copper layer. GMR values can exceed 60% at room temperature [Parkin91] and 200% at 4.2 K [Schad94].

Anti-ferromagnetic alignment of adjacent ferromagnetic layers in magnetic multilayers at zero applied field is achieved by carefully choosing the thickness of the nonmagnetic layers. Interlayer exchange coupling mediated by conduction electrons oscillates between inducing ferromagnetic and anti-ferromagnetic alignment as a function of nonmagnetic layer thickness. The interlayer exchange coupling can be described by Ruderman-Kittel-Kasuya-Yosida (RKKY) theory. An overview of exchange theory is given in [Slonczewski95].

Spin-valves show that the phenomenon of giant magnetoresistance is separate from interlayer exchange coupling. Spin valves, which are ferromagnet/normal metal/ferromagnet structures, are the smallest subset of a magnetic multilayer to exhibit the GMR effect (on the order of 10%). Anti-parallel alignment of the two ferromagnetic layers is achieved not by RKKY coupling but by “pinning” one of the ferromagnetic layers using an adjacent antiferromagnetic layer (e.g. [Parkin93]). An applied field can change the orientation of the “free” magnetic layer to achieve parallel or anti-parallel alignment. Applications most often use spin valves since the
Figure 1.1: Magnetoresistance measurement of a copper/cobalt magnetic multilayer. The multilayer contained 23 bilayer periods, each containing a 11.5 Å cobalt layer and a 19 Å copper layer. The high resistance state is near zero field when layer magnetizations are aligned anti-parallel. Low resistance occurs at high field, which forces parallel alignment. The GMR is 28%.
switching fields are typically much lower than for RKKY-coupled multilayers.

1.2.1 Simple magnetoresistance model

A very simple model of giant magnetoresistance can be developed by considering a subsection of a magnetic multilayer containing only two ferromagnetic layers (see Figure 1.2). Due to spin-dependent scattering, the resistivity of up-spin electrons $\rho_\uparrow$ is different from that of down-spin electrons $\rho_\downarrow$ in a ferromagnetic material. Suppose that $\rho_\uparrow << \rho_\downarrow$ for the magnetic layers of the structure. Then for the case of parallel alignment of the layer magnetizations, the up-spin electrons are always weakly scattered whereas the spin-down electrons are strongly scattered. The “short circuit” for up-spin electrons means that the total resistivity is low. A resistor network representation of the parallel case leads to an equivalent resistance of

$$\rho_f = \frac{\rho_\uparrow \rho_\downarrow}{\rho_\uparrow + \rho_\downarrow} \approx \rho_\downarrow$$

for the multilayer subsection. For the case of anti-parallel alignment of the layer magnetizations, each spin direction is strongly scattered in one magnetic layer and weakly scattered in the other. There no longer exists a short circuit and the resistivity,

$$\rho_{AP} = \frac{\rho_\uparrow + \rho_\downarrow}{2},$$

is higher.

Several periods of the multilayer can be modeled by adding more resistors to each branch of the network. Such models show that GMR can
Figure 1.2: Diagrams for a simple theory of GMR. (above) A tri-layer subsection of a magnetic multilayer containing two ferromagnetic (FM) layers and one non-magnetic (NM) layer shows the two cases of parallel and anti-parallel alignment of the FM layers. Assuming down-spin electrons scatter more strongly than up-spin electrons, parallel alignment gives up-spins a "short circuit" resulting in an overall low resistance. The anti-parallel case gives higher resistance because each spin scatters strongly in alternating FM layers. (below) A resistor network model corresponding to the above tri-layer structures can be used to estimate GMR.
be increased by adding more periods to the multilayer structure. However, once the multilayer becomes thicker than the spin relaxation length, mixing between up-spin and down-spin channels occurs and GMR stops increasing. GMR also decreases with increasing temperature. This is due to the introduction of spin-fluctuations or magnons, which shorten the spin relaxation length.

Note that in this simple model, it is assumed that the average current flow is perpendicular to the plane of the layers (CPP). While this geometry has been achieved experimentally [Gijs94], it is more common for the current to flow in the plane of the layers (CIP). The model is still a reasonable qualitative description of CIP GMR since the mean free path is much greater than the thickness of an individual layer and an electron typically samples several layers between scattering events.

1.2.2 Origin of spin-dependent scattering

The origin of the spin-dependent scattering is a source of much theoretical controversy. One explanation is that roughness at ferromagnet/nonmagnet interfaces creates spin-dependent scattering potentials that lead to GMR (see e.g. [Zhang92]). An alternative explanation is that the spin-dependent band structure leads to spin-dependent scattering probabilities from mostly spin-independent potentials, which are due to defects within the multilayer structure [Tsymbal96].

"Interfacial dusting" experiments provide strong evidence that the spin-dependent scattering arises at ferromagnet/nonmagnet interfaces rather than throughout the bulk of the ferromagnetic layers. A permalloy (Ni$_{80}$Fe$_{20}$)-copper spin-valve ordinarily has a magnetoresistance value approximately
one-half of that for a cobalt-copper spin-valve. However, 2.5 Å (approximately one monolayer) of cobalt inserted at permalloy-copper interfaces restores the magnetoresistance value to nearly that of the cobalt-copper spin-valve [Parkin93]. Furthermore, moving the 2.5 Å cobalt layer away from the permalloy/copper interfaces towards the interior of the permalloy layer results in a rapid decay of GMR to the original permalloy-copper value. This experiment indicates that knowledge of interface structure is highly important and could reveal the origin of spin-dependent scattering in magnetic multilayers.

1.3 Magnetic tunnel junctions

Magnetic tunnel junctions are made of two ferromagnetic electrodes separated by an insulating layer approximately 10 Å thick. As mentioned above, the conduction of electrons between two ferromagnetic layers depends on their relative magnetizations. Similar to spin valves, one ferromagnetic layer usually has its magnetization “pinned” by an adjacent antiferromagnetic layer. An applied field can change the orientation of the “free” magnetic layer to achieve parallel or anti-parallel alignment of the magnetic layers. Like GMR, the tunneling magnetoresistance (TMR) is defined as

$$TMR = \frac{R_{AP} - R_P}{R_P}$$

where $R_{AP}$ is the resistance with anti-parallel alignment of the ferromagnetic layers and $R_P$ is the resistance with parallel alignment. Figure 1.3 shows an example of a magnetoresistance measurement.
Figure 1.3: Magnetoresistance measurement of a cobalt-iron/alumina/cobalt magnetic tunnel junction. The individual ferromagnetic films show anisotropic magnetoresistance (AMR), which changes the resistance by less than 1%. The magnetoresistance of the tunnel junction is greater than 10%, clearly demonstrating its behavior cannot be explained by AMR. Arrows indicate relative alignment of layer magnetizations. (Figure reproduced from [Moodera96].)
performed on a cobalt-iron/alumina/cobalt magnetic tunnel junction. Note that the high resistance state is for anti-parallel alignment of the ferromagnetic layers while parallel alignment gives the low resistance state. Magnetic tunnel junctions can exhibit TMR values as high as 40% at 4.2 K and nearly 30% at room temperature [Lu98].

1.3.1 Simple magnetoresistance model

The Julliere model [Julliere75] predicts TMR values based on a simple density of states argument. It hypothesizes that tunneling conductance is proportional to the product of the densities of states at the Fermi energy on either side of the barrier. Further, it assumes that no spin-flip events occur during the tunneling process, and that up-spin (down-spin) electrons can only access unoccupied up-spin (down-spin) states on the opposite side of the barrier. Figure 1.4 shows a schematic drawing of the spin-polarized density of states of the magnetic tunnel junction for both parallel and anti-parallel alignment. The dashed arrows indicate allowed tunneling events. The bulge in the density of states represents the $d$-band.

The total tunneling current is the sum of up-spin and down-spin currents. Therefore,

$$I_P \propto n_{1\uparrow} n_{2\downarrow} + n_{1\downarrow} n_{2\uparrow}$$

$$I_{AP} \propto n_{1\uparrow} n_{2\downarrow} + n_{1\downarrow} n_{2\uparrow}$$

where $I_P$ and $I_{AP}$ are the tunnel conductances for parallel and anti-parallel alignment and $n_{xy}$ is the density of states at the Fermi energy for material $x$ and spin $y$. Using the above equations and the definition of spin-polarization $P = (n_{1\uparrow} - n_{1\downarrow})/(n_{1\uparrow} + n_{1\downarrow})$, the TMR can be written as
Figure 1.4: Diagrams for a simple theory of TMR. (above) The magnetic tunnel junction consists of ferromagnetic electrodes FM\textsubscript{1} and FM\textsubscript{2} separated by a thin tunnel barrier, shown for parallel and anti-parallel alignment of layer magnetizations. (below) A schematic representation shows the spin-polarized density of states for the above magnetic tunnel junction configurations. The spin-split d-band is represented by a "bulge" in the density of states for each spin direction. Dashed arrows show the allowed (i.e. spin-conserving) tunneling processes. For FM\textsubscript{1} = FM\textsubscript{2}, parallel alignment gives a greater tunnel conductance due to the large density of states at the Fermi energy (E\textsubscript{F}) for down-spin electrons on both sides of the barrier.
\[ TMR = \frac{R_{Ap} - R_p}{R_p} = \frac{I_p}{I_{Ap}} - 1 = \frac{2P_1P_2}{1 - P_1P_2}. \]

This is the Juliere prediction for TMR based on the spin-polarization of each ferromagnetic electrode.

### 1.3.2 Spin-polarized tunneling

After much work to improve junction quality, experimental agreement has more or less been achieved with the Juliere model [Moodera98, Lu98]. However, the spin-polarization values that work well with the Juliere model were measured using ferromagnet/alumina/superconductor structures [Meservey70, Meservey94], and the results of these experiments are not well understood. Nearly all spin polarizations measured with this technique are positive; however, negative values are expected in many cases based on density of states diagrams. For example, cobalt was measured to have a spin-polarization of +34% with the majority of electrons in the tunneling current aligned in the direction of its magnetic moment, even though there is a higher density of states at the Fermi energy for electrons anti-parallel to the magnetic moment.

Furthermore, experiment demonstrates that the spin-polarization of the tunneling current is not fundamentally determined by the ferromagnet alone. For example, positive spin polarization was observed tunneling from cobalt across an alumina barrier [Meservey94] while negative spin polarization was observed tunneling from cobalt across a strontium titanate barrier [Teresa99]. Thus, the most basic questions about spin-polarized tunneling remain unanswered. They include, “What is the spin polarization of
current in a ferromagnet?” and, “How does tunneling through a barrier affect this spin polarization?”

Many theoretical attempts have been made to understand the spin-polarized tunneling process. Calculations within a free-electron model show that barrier height influences the magnitude and sign of the spin polarization [Slonczewski89]. Spin polarization can also be affected by the barrier profile [Zhang99] and disorder within the barrier [Tsymbal98]. A multiband description of electron transport through a tunnel barrier shows that spin polarization depends strongly on the type of bonding at the ferromagnet/insulator interface [Tsymbal97]. Another multiband study makes the point that the evanescent Bloch waves in the barrier are characterized by different decay lengths, and thus barrier thickness can influence spin polarization [MacLaren99]. A first-principles calculation of electronic structure of a magnetic tunnel junction shows that the Fermi level within the barrier is sensitive to barrier termination [Oleinik00]. This controls barrier height as well as decay lengths associated with the spin-polarized density of states within the barrier.

All of these studies point to a need to understand the detailed structure of the tunnel barrier as well as its interfaces with adjacent ferromagnetic materials on an atomic scale. Very little experimental work exists in this regard, due to the combined requirements of atomic-scale spatial resolution and the ability to probe internal interfaces. Knowledge of the atomic-scale structure of magnetic tunnel junctions promises to lead to a much better understanding of the fundamental process of spin-polarized tunneling.
1.4 STEM as a tool to study magnetic interfaces

1.4.1 The STEM

A scanning transmission electron microscope (STEM) is a powerful tool for probing the physical and electronic structure of interfaces on an atomic scale. Figure 1.5 shows a schematic representation of a cross-section sample being probed by the STEM technique. 100 keV electrons are focussed to a 2 Å diameter beam that interacts with the sample. Various detectors collect the transmitted electrons, which provide much information about the sample. The annular dark field detector collects electrons scattered to high angles to provide Z-contrast imaging. Simultaneously, the electron energy loss spectrometer sorts transmitted electrons by energy and collects them to reveal the electron energy loss spectrum (EELS). There is also a bright field detector, which collects forward-scattered electrons to generate a phase-contrast signal.

1.4.2 Spatially resolved EELS

Electron energy loss spectroscopy was the main technique used to probe sample structure. Swift beam electrons lose energy by exciting electronic transitions within the sample. The EELS spectrum provides information on the local density of states as well as local element composition of the probed sample area. The inelastic scattering process is highly localized. For 100 keV electrons and energy losses greater than 400 eV, the radius of the inelastic scattering probability function is less than 1 Å greater than the probe radius at full-width half-maximum. At full-width tenth-maximum (appropriate for analytic work), the inelastic radius is less
2Å diameter beam is scanned across the sample in the x-y plane to form a two-dimensional image.

Figure 1.5: A schematic drawing of the STEM. Swift 100 keV electrons are focused to a 2 Å diameter beam, which is transmitted through a thin cross-section sample. Several detectors collect the transmitted electrons, including the annular dark field detector which gives a "Z-contrast" image and the EELS detector, which provides the spectrum of inelastically scattered electrons as a function of energy.
than 2 Å greater than the probe radius [Muller95]. Thus atomic-scale characterization of electronic and physical structure is possible.

The EELS spectrum is composed of the “zero-loss” peak due to electrons that have scattered only elastically (or have lost negligible energy from phonon scattering) and a tail due to electrons that have lost varying amounts of energy from inelastic scattering. The “low-loss” region from 5 to 40 eV contains electrons that have lost energy due to valence interband transitions and collective excitations; it dominates the inelastic scattering cross-section. At higher energy loss, the tails of the valence excitations decay with power law behavior [Bethe57]. Superimposed on the power-law background are “core-loss” edges, due to the excitation of atomic core-level electrons.

A theoretical description of the electron energy loss process is as follows: electrons in their ground state are excited to unoccupied states above the Fermi energy by swift beam electrons, which lose an energy $E$. The transition rate for this process is given by Fermi’s golden rule

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} \sum_f \left| \langle \psi_f | V | \psi_i \rangle \right|^2 \delta\left(E - (E_f - E_i)\right)$$

where the initial state $|\psi_i\rangle = |\phi_i\rangle |\phi_r\rangle$ is a product of the ground state wave-function of the target $|\phi_i\rangle$ and the probe wave-function $|\phi_r\rangle$. The final state $|\psi_f\rangle = |\phi_f\rangle |\phi_r\rangle$ is a product of the final state of the target electron wave-function $|\phi_f\rangle$ and the scattered probe wave-function $|\phi_r\rangle$, which can be treated as a plane wave. The interaction Hamiltonian $V$ is given by the Coulomb potential.

The matrix elements for the excitation of the specimen from its initial state to its final state factor out of the spatial variation and contain only
information about the specimen. Using the dipole approximation and omitting spatial information, the transition rate can be rewritten as

\[ \Gamma_{i \rightarrow f} \propto \sum_{f} |\langle \phi_i | \bar{r} | \phi_f \rangle |^2 \delta(E - (E_f - E_i)). \]

When the initial state \( |\phi_i \rangle \) is a core level state, this can be recognized as a local density of states where the final states \( |\phi_f \rangle \) are projected onto a localized basis of the form \( \bar{r} |\phi_i \rangle \). Since core electrons experience essentially a single-atom spherical potential and have wave-functions of definite angular momentum, dipole selection rules apply. Thus, the intensity of the EELS signal is proportional to the local density of states selected by angular momentum.

Figure 1.6 shows part of an energy loss spectrum containing a core-loss excitation for cobalt along with a schematic density of states diagram showing the electronic transitions. Dipole selection rules dictate that electrons from the 2p core levels of cobalt can only access d-like final states (transitions s-like states are also possible but are much weaker in this case). The density of states for cobalt contains a sp-band that is free-electron-like with a parabolic shape and large energy dispersion and a d-band with much lower dispersion and a higher density of states. The Fermi energy \( E_f \) lies near the top of the d-band. In the case of cobalt, the sharp peak corresponding to each 2p core-level reflects the shape of the unoccupied d-band above the Fermi energy.

Every element has a unique set of core level binding energies. Since a core-level excitation occurs at an energy \( E = E_f - E_i \) that is relative to a particular core level energy \( E_i \), each core edge is element specific. This
Figure 1.6: An example of a core excitation. (left) Part of the electron energy loss spectrum of cobalt shows the L_{3,2} core excitation. (right) A schematic diagram of the density of states of cobalt shows electronic transitions from the 2p core levels to unoccupied states of d-like symmetry above the Fermi energy (E_F), which are governed by dipole selection rules.
makes it possible to determine elemental composition from the ratio of measured core edge intensities.

To summarize, the spatially resolved EELS technique provides information on the local concentration of atomic species as well as the local density of states partitioned by site, element and angular momentum. The EELS technique is described in more detail in [Muller96, Egerton96].

1.4.3 Comparison of STEM with other techniques

The ability of the STEM to probe internal interfaces on an atomic scale is very powerful and is matched by few other techniques. This makes it uniquely suited for analyzing thin-film magnetic structures. Surface-sensitive techniques such as x-ray photoelectron spectroscopy, atomic or magnetic force microscopy, and scanning tunneling microscopy are complicated by the possibility of surface contamination of samples. More importantly, surfaces often have a different structure than bulk materials and internal interfaces.

Two techniques capable of probing internal interfaces are x-ray diffraction and nuclear magnetic resonance. However, these techniques lack spatial resolution, and information on interface structure must be extracted from the data based on models that typically contain several assumptions.

Conventional transmission electron microscopy can not perform atomic-scale EELS measurements and therefore can not detect electronic structure. Also, interpretation of TEM images can be difficult (see e.g. section 5.3.3).

There are some limitations to the STEM technique that also deserve mention. Unfortunately, since spin-polarization of electrons is very difficult to achieve, the STEM can not detect the spin-polarized local density of states. It only detects the average local density of states with EELS. (Operating the
STEM in Lorentz mode allows detection of local magnetization, but only on a nanometer length scale at best.) Photons are comparatively easy to polarize, and x-ray magnetic circular dichroism (XMCD) can detect the spin-polarized density of states. However, the best spatial resolution obtained with this technique is on the order of microns. Thus the two techniques can be viewed as complementary. Other limitations for the STEM technique include difficult sample preparation, radiation damage to sensitive materials, and diminished spatial resolution for rough interfaces. These issues are addressed where appropriate in this dissertation.

1.5 Types of interface structure

There are many answers to a question such as “How sharp is the interface?” In order to be precise in describing interfaces, what follows is a mini-glossary of the important terms used in classifying interface structure in magnetic thin-film structures. Equally important to the use of precise language is the realization that the same interface can have very different spatial parameters for different structural classifications. Illustrative examples are given under the appropriate headings.

Physical structure refers to spatial variations in the position of the interface. (Note that different criteria can result in different locations for the position of the interface.) The most common parameter is roughness, which describes deviation of interface position from the average plane of the interface. A related parameter is the wavelength of the roughness, which gives the average distance between two adjacent peaks or troughs of the interface profile.
Crystal structure refers to the physical order (or disorder) of atoms across an interface. It is considered a type of physical structure.

Chemical structure refers to the distribution of atomic species across an interface. Concentration profiles as well as chemical order or disorder can be important. For example, a titanium nitride layer placed between aluminum and tantalum oxide layers to act as an oxygen diffusion barrier appeared crystallographically sharp in TEM images but EELS analysis revealed substantial oxygen concentration throughout the entire structure [Jiang]. This led to the failure of the device.

Electronic structure refers to the local density of states across an interface. Theoretical calculations will often show a layer projected density of states for an ideal flat interface. An atomically abrupt semiconductor/insulator interface between silicon and silicon oxide was shown by spatially resolved EELS measurements to have a more diffuse electronic structure, due to the exponential decay of conducting states into the insulator [Muller98a]. This places a fundamental lower limit on the thickness of gate oxides in field-effect transistors.

Magnetic structure refers to direction, magnitude, and type (ferromagnetic, antiferromagnetic, etc.) of magnetization across an interface. For example, the magnetic roughness of a copper/cobalt interface as measured by x-ray scattering is much less than the physical roughness [MacKay96].
1.6 Overview

Sections 1.2 and 1.3 established that knowledge of atomic-scale structure was necessary for understanding spin-polarized transport in magnetic multilayers and magnetic tunnel junctions. In response to this need, STEM analysis was performed on copper/cobalt multilayers and cobalt/alumina/cobalt magnetic tunnel junctions. This provided information on the physical, chemical and electronic structure of interfaces in the magnetic thin-film systems considered. The implications of this information for spin-polarized transport were then determined as much as possible using theoretical calculations of spin-dependent band structure and spin-polarized transport in the current literature. In many cases, the results of the STEM analysis demonstrated a need for better theoretical calculations that are based on more realistic structures.

Chapter 2 details the experimental techniques used to make samples and analyze their structure. Chapter 3 presents the results of STEM analysis of copper/cobalt multilayers. Chapters 4 and 5 focus on STEM analysis of cobalt/alumina/cobalt magnetic tunnel junctions. Chapter 4 summarizes results from reference samples that are used to interpret the magnetic tunnel junction data in Chapter 5. Finally, Chapter 6 summarizes the main results and gives directions for future work.
Chapter 2

Experimental techniques

2.1 Thin film growth

DC magnetron sputtering was the deposition method used for fabricating the magnetic thin-film structures. This is because sputter deposition generally leads to quick success (i.e. high magnetoresistance values) compared to evaporation [Farrow93, Miyazaki95] and is the choice of most researchers and engineers in the field [Daughton99].

2.1.1 Physics of sputter deposition

In the sputtering process, a target is bombarded with high-energy ions. The ions, typically noble gas atoms missing one electron, are formed in a plasma near the target. The plasma is sustained by a potential difference between the target (held at negative potential) and a nearby ground shield. A magnetic field in the region of the plasma prevents electrons from leaving the plasma so that they cause more ionizing collisions; this allows a lower gas
pressure to sustain the plasma. Positively charged ions that leave the plasma are accelerated toward the target by the potential difference between the plasma and the target. This potential difference is nearly equal to the target-to-ground-shield potential difference, which is typically several hundreds of volts. The high-energy ions collide with the target, ejecting target atoms. Some of these atoms land on a substrate and accumulate to create a thin film.

Sputtering is an energetic process. The energy distribution of atoms leaving the target is generally peaked near 2 eV and has a higher energy tail, the extent of which depends on the energy of the incident ions. Collisions with the sputtering gas reduce the energy of the sputtered atoms. The target-to-substrate distance as well as the pressure of the sputtering gas determine the final energy distribution of atoms arriving at the substrate.

High-energy atoms arriving at the substrate have a substantial effect on film growth. Simulations of nickel-on-nickel growth [Gilmore92] show that atoms with energies in the range of 1 to 15 eV use their excess energy to increase the effective surface diffusion coefficient. This leads to films that are smoother and more dense than films grown with low-energy atoms, which generally contain more voids and are rougher (such as films grown by evaporation). Atoms arriving with energies greater than 15 eV cause transfer of atoms from one layer to another, typically over distances of 2 to 3 atomic planes.

The sputter deposition parameters for fabrication of samples in this dissertation include a target-to-substrate distance of 10 cm, an argon gas pressure of 1 to 2 mTorr, and a target voltage of -300 to -500 V. Monte-carlo simulations show that for an argon gas pressure of 1.5 mTorr and a target-to-substrate distance of 10.9 cm, the energy distribution of atoms arriving at the
substrate peaks at less than 1 eV and contains a high-energy tail that extends beyond 30 eV [Kools94]. As might be expected, permalloy-copper spin-valves fabricated under these conditions had fairly flat layers with a root-mean-square surface roughness of 3 Å (for 10 mTorr argon the roughness increased to 5 Å). These spin-valves also had interdiffused zones at interfaces with 3.5 Å of magnetically dead permalloy per interface (for 10 mTorr argon the magnetically dead permalloy dropped to 1.5 Å).

In principle, neutral gas atoms reflected from the target could arrive at the substrate as well. However, for the bombardment of 3d metals with argon only a very small fraction of the incident energy is converted in reflected neutrals due to the relatively small mass difference, and the effect of reflected neutrals on film growth is low [Kools94].

2.1.2 Sputter deposition chamber

The vacuum chamber used for sputter deposition was pumped on by a 330 L/s turbo pump. The base pressure was 1 × 10⁻⁸ Torr. A load lock expedited sample transfer in and out of the chamber. The load lock was pumped out by a smaller 70 L/s turbo pump. A gate valve separated the main chamber from the load lock.

The main chamber was equipped with four AJA International A320 dc magnetron sputter guns. For sputter deposition of magnetic materials, the magnet configuration of the guns was changed to counteract the tendency of magnetic targets to “short out” the plasma-confining magnetic field. Sputter deposition rates were calibrated by depositing a film under known conditions for an interval of time, typically 1000 seconds. The film thickness was
measured by a surface profilometer and the deposition rate computed by dividing the film thickness by the time interval of deposition.

Precise control of individual layer thickness to within ±1 Å was critical for most samples. Therefore, it was important to make sputter deposition conditions as reproducible as possible. Flow of 99.998% argon to the sputter guns was maintained at constant rates by an MKS Instruments 254A flow ratio controller. Pneumatically operated shutters on the guns were computer controlled to give precise deposition times for each material. Low power (less than 100 W) to each gun produced relatively slow deposition rates on the order of 1 Å/s to provide additional accuracy.

Fabrication of magnetic tunnel junction samples required the sputter deposition chamber to have an additional capability of maintaining molecular oxygen at a relatively high pressure of 100 mTorr. The flow controller was used to maintain a steady flow of 99.998% oxygen into the chamber during the oxidation step. Since turbo pumps can maintain full speed only up to a few millitorr, a throttle valve was inserted between the main chamber and the turbo pump. When closed down, this allowed a large pressure difference to be maintained between the chamber and the pump. A fromblin oil backing pump to the turbo pump was used to safely remove oxygen from the system.

2.1.3 Magnetoresistance characterization

Magnetoresistance of multilayer samples was measured at room temperature and at 4.2 K (attempts to measure magnetoresistance of magnetic tunnel junction samples have been unsuccessful to date). At room temperature, a large electromagnet with an iron core was used to sweep the magnetic field. The electromagnet was capable of producing a field of up to
1.5 T. At 4.2 K, a superconducting solenoid was used to sweep the magnetic field. The superconducting solenoid was capable of producing a field of several tesla.

Figure 2.1 contains a schematic of the magneto-resistance characterization setup. Resistance was measured with a four point method. A row of equally spaced spring-loaded pins was pressed into the multilayer film. Current was passed between the outer two pins while voltage was detected between the inner two pins. To reduce noise in the resistance measurement, an ac lock-in technique was used. Ac current at a frequency of 1000 Hz was generated by passing the output voltage of a EG&G Princeton Applied Research 5210 lock-in amplifier through a 1000 Ω resistor. Variation of the low (~1 Ω) resistance of the sample in series with the 1000 Ω resistor had a negligible effect on the current. The voltage across the sample was measured by the lock-in amplifier, which selected the 1000 Hz component. Resistance was computed as the magnitude of the ac voltage divided by the magnitude of the ac current.

The magneto-resistance measurement process was automated by use of a computer with analog-to-digital (ADC) inputs for reading sample voltage and digital-to-analog (DAC) outputs for controlling the magnet power supplies. The magnet power supplies were programmable using analog signals. The measurement program was written in LabView.
Figure 2.1: Schematic drawing of magnetoresistance characterization setup for magnetic multilayer samples. Resistance was measured with a four point method. To reduce noise in the resistance measurement, an ac lock-in technique was used. The magnetoresistance measurement process was automated by use of a computer, with analog-to-digital (ADC) inputs for reading sample voltage and digital-to-analog (DAC) outputs for controlling the magnet power supply.
2.2 STEM instrumentation

Scanning transmission electron microscopy (STEM) of the thin-film samples was undertaken at the Cornell Center for Materials Research UHV-STEM laboratory. The STEM model is VG-HB501A with an accelerating voltage of 100 kV. The STEM is located within a shielded room to ensure the high mechanical and electrical stability needed to obtain atomic resolution [Silcox92]. In addition, a number of modifications have been made to reduce drift rates so that the spatial drift rate is less than 0.5 Å/min and the energy drift rate is less than 0.06 eV/min [Muller96]. The most important detectors used in this study were the annular dark field detector and the parallel electron energy loss spectrometer, both of which were upgrades from the original instrumentation. The annular dark field (ADF) detector is described in [Kirkland96]. The McMullan-style parallel electron energy loss spectrometer (PEELS) is described in [McMullan92, Muller96]. Data acquisition is computer controlled as described in [Kirkland94].

2.3 Sample preparation

Preparation of cross-section samples for STEM analysis has been referred to as “electron microscopy’s dirty little secret” [Silcox]. The goal is to thin a bulk material to a thickness of less than approximately 400 Å (ideally near 200 Å) with as little damage as possible in order to make the specimen transparent to the 100 keV electrons in the STEM. Various thinning techniques include mechanical polishing, electrochemical polishing, cleaving and ion milling, and the optimal method depends on the material to be
thinned. The structures examined in this dissertation are mostly thin (less than 1000 Å total thickness) metallic films on silicon, and the best method for this class of materials was found to be the “wedge-polishing” technique.

2.3.1 Wedge-polishing technique

The general wedge-polishing technique is described in [Klepeis88] and [Benedict92]. The particular procedure described below is the result of a trial and error process in which the wedge-polishing technique was optimized for the metal-on-silicon samples in this study. This procedure consistently produced high quality, very thin cross-sections for STEM analysis that required no additional ion milling.

First, the sample was cleaved into two pieces approximately 2 × 3 mm in size. They were glued together with metal layers facing using two-part epoxy by Allied High Tech Products. The epoxy was cured at a low temperature of 100 C for two hours to avoid any question of altering sample structure. During the curing step, the sample was placed in a spring-loaded vice to give a very thin glue layer, typically 500 Å thick. A thin glue layer results in better mechanical stability of the sample, which is critical during mechanical polishing.

After bonding, the sample was mounted on to a tripod polishing jig [Klepeis88], which allowed precise orientation of the polishing surface. First, a smooth surface was mechanically polished perpendicular to the layers using progressively finer grit diamond lapping sheets from Allied High Tech Products. Then, a second surface also perpendicular to the layers was polished at a low angle to the first, using the same method as for the first surface. The resulting wedge-shaped sample provided thin areas near the tip for STEM
analysis. Figure 2.2 shows the wedge sample geometry. A wedge angle (\(\alpha\)) of 100 mrad resulted in specimens with good mechanical stability and sufficient thin areas for study.

For both sides of the wedge, the final polish was with a 0.1 \(\mu\)m diamond sheet using methanol as the lubricant. While the cause is unknown, using methanol results in a much smoother finish than using water [Thomas]. Scratches are fewer in number and much less deep, allowing the thinnest regions at tip of the wedge to remain intact. This is critical for producing thin specimens that do not require any ion milling.

Mechanical integrity is also very important for preparing a high quality wedge-polished specimen. A dramatic difference was seen between samples in which the first cobalt layer was deposited on bare silicon versus silicon with a native oxide layer. Cobalt does not adhere well to silicon oxide, and delamination of the metallic layers at the silicon oxide/cobalt interface always occurred in thin parts of the sample. Not only does this delamination introduce uncertainty in the alignment of the metal layers with respect to the silicon lattice (see section 2.4.1 below), it allows the thin, ductile strip of metal layers to be separated from its rigid silicon support and incur substantial mechanical damage. In almost all cases, the metal layers were severely damaged up to a cross-section thickness on the order of 1000 \(\AA\). In contrast, deposition of cobalt on bare silicon at room temperature resulted in a 20 \(\AA\) thick cobalt-silicide reaction layer [van der Veen89], which greatly promoted adhesion. No delamination at the silicon/cobalt interface was observed in these samples. In all such samples
Figure 2.2: Diagram of wedge-polished cross-section sample. Two metal-on-silicon pieces were glued together with metal layers facing and then polished along two planes perpendicular to the metal/silicon interfaces. The two finely polished surfaces meet at a small angle $\alpha \ll 1$. The tip of the wedge provides thin cross-section areas ($< 400$ Å thick) suitable for STEM analysis.
examined to date, thin cross-section regions with no observable mechanical
damage were found suitable for STEM analysis.

To remove the native oxide layer from a silicon wafer and uncover
bare silicon, the wafer was spin-etched with hydrofluoric acid. The spin-etch
sequence was 25 drops of reagent alcohol, 40 drops of 1 part 49% HF to 5
parts reagent alcohol, and 25 drops of reagent alcohol. The rotation speed of
the wafer chuck was about 3000 r.p.m.

2.3.2 Ion milling

Wedge-polished samples that did not have sufficiently thin cross-
section areas for STEM analysis were further thinned in a Bal-Tec RES 010 ion
miller. A low incident angle (less than 5°) of the beam with respect to the
wedge surface was chosen to give uniform thinning across different materials
[Anderson92]. Low-angle milling also results in less surface damage and
heating of the sample. Ion beam settings were typically within the ranges of 1
- 4 kV and 1 - 3 mA. Milling times varied from 5 minutes to more than an
hour.

Optical alignment of the overall wedge surface can be achieved to
within ±1°. However, at the thinnest parts the wedge, convergent beam
electron diffraction revealed that the orientation of the silicon lattice varies by
several degrees as function of position. This warping introduces a relatively
large uncertainty in the local angle between the sample surface and the ion
beam. This can lead to ion beam induced artifacts in some areas, such as
localized heating or preferential milling of softer materials.

In an attempt to reduce localized heating of the sample by the beam,
the milling stage was cooled via a copper braid attached to a liquid-nitrogen-
cooled copper block. However, cooling by this method was inefficient at best. Measurement by a thermocouple attached by carbon paint to the central rotary part of the stage revealed that its temperature never dropped below -30 C in more than 3 hours of cooling [Thomas]. In addition, a thin cross-section sample that is mostly silicon is expected to be inefficient at conducting heat away from areas exposed to the ion beam. Since the local temperature of the sample in areas of interest was very difficult to measure, it was nearly impossible to guarantee that the sample has not been significantly altered as a result of milling.

The inherent uncertainties of the ion milling process make it a questionable technique for thinning cross-section samples that are heat sensitive, such as the magnetic thin-film structures considered in this dissertation. Therefore, it was avoided whenever possible.

2.3.3 “Float-off” method

The “float-off” method is simple and requires little time; however, it is only applicable to a thin-film sample deposited on a sodium chloride substrate (or similarly dissolvable substrate). Furthermore, samples can only be examined with the electron beam more-or-less parallel to the growth direction of the film. Generally, the float-off method was used for making reference samples of uniform composition.

The float-off method was used to transfer thin-film samples on a sodium chloride substrate to a TEM support grid. The sodium chloride substrate was held at the surface of HPLC grade water in a large beaker. As the salt crystal substrate dissolved in the water, the thin film remained floating on the surface. After the substrate completely dissolved, the thin film was
transferred to another large beaker of HPLC grade water to reduce salt content. Finally, the thin film was swept out of the water on a TEM support grid and left to dry before loading in the microscope.

2.4 Imaging techniques

2.4.1 Sample alignment

Alignment of the metal layer interfaces with respect to the electron beam direction is important since misalignment effectively causes loss of spatial resolution. To expedite the alignment process, silicon wafers with a surface polished to within ±0.25° of (100) were used as substrates for the metallic layer systems analyzed in this study. Thus alignment of the electron beam to the (110) direction of the silicon lattice using electron diffraction resulted in an error of less than 1 Å between the top and bottom surfaces of a 200 Å thick cross-section. This error is less than the resolution of the STEM.

Alignment to the silicon lattice with convergent beam electron diffraction was used to correct local misalignment of the sample resulting from warping of the silicon lattice in regions with a very thin cross-section thickness. This was achieved by aligning to the silicon lattice nearest the region of interest. An additional advantage of this alignment method was that the silicon lattice provided a known regular object with small wavelength (3.3 Å) features that allowed for quick stigmation of the objective lens.

On a final note, the above alignment procedure describes how to achieve the best average alignment of layer interfaces with respect to the electron beam. The best local alignment varied from the best average alignment by up to a few degrees due to roughness of the (100) silicon surface
as well as layer roughness induced by grain structure and other factors. Cross-section areas with good local alignment were identified by sharp annular dark field profiles, and STEM analysis of sample structure was generally confined to such regions.

2.4.2 Through-focal series

Taking through-focal series of images allows accurate determination of best focus as well as providing additional information regarding sample structure [Ross91]. Since a calibration of the objective lens was unavailable, images were taken at equal steps of the objective lens current, usually three clicks of the "vernier" focus knob. Since the objective lens exhibited hysteresis and travel of the focus knob was limited, only a section of the through-focal series could be completed for one full turn of the "vernier" knob. After that, the "vernier" knob was returned to its original position, the "fine" knob moved one click over, and a new sub-series was taken. The sub-series were patched into a single series afterwards by finding images from the end of one sub-series that matched best with images from the beginning of an adjacent sub-series.

2.5 Electron energy loss spectroscopy

2.5.1 Acquisition techniques

Acquisition of electron energy loss spectra was generally done with the 100 keV electrons focussed to a 2 Å diameter beam. However, for materials highly sensitive to radiation damage such as alumina, the beam was spread into a line or even a rectangle to reduce the radiation dose to acceptable levels.
Radiation dose was also controlled by adjusting the current of the electron beam. Figure 2.3 shows beam current measured as a function of tip extraction voltage. Current decreased exponentially with decreasing extraction voltage, halving approximately every 0.12 kV.

2.5.2 Background subtraction from core-loss edges

Accurate background subtraction was important when comparing core-loss spectra to search for similarities or differences. It was also important for quantitative elemental analysis, which involved integration of area under background-subtracted spectra. Spectra read from the PEELS spectrometer were distorted from the true shape of the energy loss spectrum. When these distortions were corrected, more accurate background subtraction is possible. This sub-section describes the two most important corrections as determined empirically.

First, all data points in the PEELS spectrum had a constant offset of approximately 600 counts. The offset was determined by measuring a spectrum with no electron beam present and averaging the data points. This constant offset was subtracted from all PEELS spectra before background fitting and subtraction.

Second, channels near the edges of the PEELS detector had a lower gain than channels at the center. Figure 2.4 illustrates this effect by comparing parallel and serial EELS spectra taken from the same sample (at the same location). In the serial EELS technique (SEELS), each data point is taken with the same physical detector. Therefore, there is no possibility of gain variation; indeed, a power-law function (the expected form of the
Figure 2.3: STEM beam current as a function of tip extraction voltage. Lowering the tip extraction voltage exponentially reduces beam current, which halves approximately every 0.12 kV. Reduction of beam current was sometimes necessary to avoid radiation damage to sensitive samples.
Figure 2.4: Example showing PEELS detector spectral distortion. Serial and parallel EELS spectra taken from the same location are progressively divergent towards the edge of the PEELS spectrum. This is due to channel gain variation in the PEELS detector, which distorts the shape of the EELS spectrum. Correcting this gain variation results in improved background subtraction for core-loss edges.
background [Egerton96]) describes the SEELS data very well. Thus, the SEELS spectrum provided a standard against which the PEELS spectrum can be compared to detect channel gain variation. In Figure 2.4 the parallel and serial EELS spectra matched well near the center of the PEELS spectrum. However, towards the left edge of the PEELS spectrum there was an increasing gap between the two spectra, indicating a decreasing gain for channels in the PEELS detector. This decreasing gain for channels near the edge of the PEELS detector was a geometrical consequence of a rectangular CCD array and a circular scintillator.

Correction for channel gain variation in the PEELS detector was accomplished in a number of ways. The most accurate method was to take a SEELS spectrum from the same location and divide the SEELS spectrum by the PEELS spectrum to generate a weighting function that can be used to adjust other PEELS spectra. If SEELS spectra were not available, then a power law was fit to the central region of PEELS spectrum showing no core loss edges. Division of the power law fit by the PEELS spectrum generated a weighting function that also worked well.

After corrections to the PEELS spectra were accomplished, a power-law background was fit to pre-edge part of the spectrum using a least-squares fitting algorithm [Egerton96]. The general form of the background was $Ae^{-r}$ where $A$ is a constant and $r$ typically ranges from 2 to 6. Subtraction of the background then yielded the core-loss intensity.

2.5.3 Removal of plural scattering

Plural scattering can greatly affect the shape of a core-loss edge beginning at approximately one plasmon energy loss beyond edge onset.
Plural scattering occurs when one or more inelastic collisions of low energy loss occur in addition to the core-loss collision. Removal of plural scattering from core-loss edges was accomplished by deconvolution of the core-loss spectrum with the measured low loss spectrum. This step was performed after correcting the spectrum for PEELS spectrometer distortion (section 2.5.2) and before background subtraction. Deconvolution also had the effect of removing instrumental spread from the PEELS spectrum. Richardson-Lucy deconvolution [Richardson72, Lucy74] as described in [Hanisch96] was used to perform the deconvolutions.

2.5.4 Cross-section thickness

Knowledge of cross-section thickness was important when interpreting spatially resolved measurements. It allowed estimation of beam-sample interactions such as beam spreading and channeling effects. Cross-section thickness was determined from the low loss part of the PEELS spectrum using the log-ratio method as described in [Egerton96].
Chapter 3

Copper/cobalt multilayers

3.1 Introduction

STEM analysis of copper/cobalt multilayers was performed with the goal of understanding the microscopic origin of giant magnetoresistance. As discussed in section 1.2.2, experiment has shown that spin-dependent scattering occurs at interfaces; therefore, the STEM analysis focussed on interface structure. The physical, chemical and electronic structures of copper/cobalt interfaces were characterized and the relevance of these structures to the giant magnetoresistance effect was evaluated.

Two different types of copper/cobalt multilayers are discussed in this chapter. They are labeled as “first-maximum” and “second-maximum” multilayers in reference to their copper layer thicknesses (9 Å and 19 Å, respectively). The first- and second-maximum multilayers were grown with copper layer thicknesses corresponding to the first and second antiferromagnetic coupling maxima (see section 1.2).
Magnetic multilayers serve as an illustration of what types of structures do not easily lend themselves to characterization by the STEM technique. Arguably, the two greatest assets of the STEM technique are atomic-scale spatial resolution (in two dimensions) and parallel electron energy loss spectroscopy. Copper/cobalt multilayers manage to simultaneously evade much of the potential power of both of these assets, limiting what can be learned about their structure.

3.2 Fabrication

3.2.1 Sputter deposition

The first- and second-maximum multilayer samples were sputter deposited onto silicon wafers with a native oxide layer. During sputter deposition, pressure in the chamber was 2 mTorr of argon. Power to both cobalt and copper guns was 80 W, except during deposition of the first-maximum sample when the copper gun was set to 40 W. These conditions resulted in 4.1 and 1.8 Å/s deposition rates for copper and cobalt, except during first-maximum sample deposition when the copper rate was 2.2 Å/s. The first-maximum multilayer had the layer deposition sequence Si(111)/Co 50 Å/(Cu 9 Å/ Co 13 Å)$_x$. The second-maximum multilayer had the layer deposition sequence Si(100)/Co 35 Å/(Co 11.5 Å/Cu 19 Å)$_x$.

A pure copper reference sample was also fabricated. It was coated with chromium to prevent oxidation at its surfaces. It was sputter deposited onto a sodium chloride crystal, which was cleaved just prior to mounting in the chamber. During deposition both copper and chromium guns received 80 W power and the argon pressure was 2 mTorr. These conditions resulted in 4.0
and 1.74 Å/s deposition rates for copper and chromium, respectively. The layer deposition sequence was Cr 40 Å/Cu 250 Å/Cr 40 Å.

3.2.2 Magnetoresistance characterization

Figure 3.1 shows the magnetoresistance measurement for the second-maximum sample at room temperature. (The magnetoresistance characterization method is described in section 2.1.3.) It had a GMR of 28%, with a field of approximately 0.1 T required to break the RKKY anti-parallel coupling and bring all cobalt layers into parallel alignment. At 4.2 K, the magnetoresistances of the first- and second-maximum samples were 85% and 49%, respectively. These magnetoresistance values are typical for such multilayer structures [Barthelemy94], and establish that they are high-quality samples.

3.2.3 Cross-section preparation

The wedge-polish method was used to make thin cross-sections of both multilayer samples for STEM analysis (see section 2.3.1). Syton (colloidal silica) was used during the final polish on all multilayer samples. The first-maximum sample received no ion milling. The second-maximum sample was milled at 3° with respect to each surface for 30 minutes at 4.0 kV and 2.0 mA (see section 2.3.2). It was cooled with liquid nitrogen during milling.

The "float off" method was used to transfer the thin chromium-coated copper film onto a standard TEM support grid (see section 2.3.3). It received no ion milling.
Figure 3.1: Magnetoresistance measurement of the "second-maximum" multilayer at room temperature. The GMR was 28% and a field of approximately 0.1 T required to break the RKKY anti-parallel coupling and bring all cobalt layers into parallel alignment.
3.3 Data acquisition

For the element maps, the cobalt L edge (onset at 779 eV) and copper L edge (onset at 931 eV) were measured simultaneously using the “PEELS4” dispersion setting, which gives roughly a 300 eV window of the energy loss spectrum. A point beam was electronically stepped across the cobalt and copper layers. Collection times ranged from 3 to 10 s at each point. No change in the energy loss spectrum was observed even for a collection time of 30 s; therefore, radiation damage was not a concern in these samples.

The areas under the cobalt L$_3$ and copper L$_3$ edges were integrated to generate cobalt and copper signals. Very small, if any, changes were observed in near edge fine structure across the layers; therefore, any integration window was valid. To avoid large background subtraction errors, integration windows near edge onset were chosen. The copper signal was generally much noisier than the cobalt signal due to its greater energy loss and smaller area under near edge fine structure. Therefore, in all element maps the copper signal has been replaced by the inverted and appropriately offset cobalt signal. The offset of the “copper” signal was determined by assuming the ratio of each average signal is equal to the ratio of the respective layer thicknesses. This is reasonable since sputtering rates can easily be determined to within 5% and remain constant over many sample depositions.

For accurate comparison of near edge fine structure, all core-loss spectra were deconvolved with respective low loss spectra to remove plural scattering. The copper L edge fine structure for bulk copper was measured from the chromium-coated copper film. It served as a reference for spectra from multilayer structures. The copper L edge spectrum was acquired for a
total of 200 s in imaging mode at ×2M magnification (320 Å square). The shape of the spectrum matched well with a x-ray absorption spectrum from bulk f.c.c. copper [Ebert96].

3.4 Physical structure

3.4.1 Grain structure

Figure 3.2 shows bright field and annular dark field images of the second-maximum structure. Grain structure is more evident in bright field, which is a phase-contrast image and shows diffraction effects. This image shows columnar growth of hetero-epitaxial grains. Individual hetero-epitaxial regions can be identified by a similar contrast between copper and cobalt layers and an overall similar intensity. Some of the borders between neighboring hetero-epitaxial regions have been marked with dashed lines in the bright field image. The width of the columns ranges from 100 to 200 Å. Such hetero-epitaxial growth has been previously observed in conventional TEM [Smith93, Bayle-Guillemaud96] and scanning tunneling microscopy studies [Minvielle96]. The lattice mismatch between close-packed copper and cobalt is less than 2%, enabling coherent crystallographic growth across interfaces.

Figure 3.3 shows an atomic force microscope (AFM) image of the surface of a multilayer that was very similar to the second-maximum sample discussed above. It was deposited on (100) silicon wafer which retained its native oxide layer; the layer deposition sequence was Si/Co 50 Å/(Cu 20 Å/Co 10 Å)$_{26}$/Cu 20 Å. The line-scan below the image was taken
Figure 3.2: Bright field and annular dark field images of the "second-maximum" multilayer. The growth direction is from right to left, with the silicon substrate visible on the far right of each image. The bright field image shows columnar growth of hetero-epitaxial grains. Some of the borders between neighboring hetero-epitaxial regions have been marked with dashed lines. In the annular dark field image contrast has been enhanced to increase the visibility of individual copper and cobalt layers. The actual contrast was at most 5%, which was much less than the predicted 12% contrast for pure copper and cobalt.
Figure 3.3: An atomic force microscope (AFM) image of the surface of a multilayer similar to the “second-maximum” multilayer. (top) Many large dome-shaped grains are apparent, which are the top surfaces of heteroepitaxial columns. (below) The line-scan below the image was taken from the position of the white line within the image. (top, inset) A schematic of a cross-section of thickness $t$ shows layers with a radius of curvature $r$ that are tilted at an angle $\theta$ with respect to the electron beam.
from the position of the white line within the image. Many large dome-shaped grains are apparent, which have an average diameter of 280 Å. These are the top surfaces of the hetero-epitaxial columns noted above in Figure 3.2. The average diameter is wider in the AFM image since the cross-section STEM image likely does not show the widest part of any particular column. Also, the hetero-epitaxial columns tend to become wider towards the top of the film.

3.4.2 Long-wavelength roughness

The layers of the multilayer structure are highly visible in the bright field image of Figure 3.2. This is due to the presence of Fresnel fringes, which enhance contrast near interfaces and give them a sharp-looking appearance. (The Fresnel fringe effect is discussed in more depth in section 5.3.) Some layer roughness is evident. Careful examination of Figure 3.2 shows that within most hetero-epitaxial regions the layers have a slight positive curvature with respect to the substrate. This indicates that layer roughness is induced by the hetero-epitaxial grain structure, whereby each layer grows conformal to the surfaces of the dome-shaped grains. Thus the wavelength of the roughness is the same as the diameter of the grains, which is 280 Å. The root-mean-square magnitude of the roughness is also the same as the hetero-epitaxial grains, which is 4.2 Å.

Such roughness can significantly affect STEM measurements since the electron beam samples the entire thickness of the cross-section sample. If the position of the interface with respect to the beam varies, a blurred interface profile will result even if there is an atomically sharp chemical transition at the interface. For example, the inset to Figure 3.3 shows a schematic of a cross-section of thickness \( t \) with atomically sharp layers that have a radius of
curvature $r$. It is apparent that no matter what angle $\theta$ the electron beam is with respect to the layers, the element profiles of the interfaces will not show atomically sharp transitions and will instead appear diffuse.

To estimate how long-wavelength layer roughness might affect STEM profiling of interfaces, atomic force microscopy (AFM) was performed on several multilayer samples. Since the growth of layers within the heteroepitaxial grains is conformal, the surface topology of the multilayer should be a good approximation to the structure of the layers below.

High quality cross-section samples are only 200 Å thick, which is smaller than the 280 Å wavelength of the layer roughness. The roughness within a 200 Å thick cross-section can be estimated by doing a linear fit to 200 Å sections of the AFM profile and calculating the standard deviation of the AFM profile from the linear fit. For the surface imaged in Figure 3.3, 55% of the 200Å sections have root-mean-square deviation of less than 1Å. For a sine-wave distribution, this translates to a peak-to-peak roughness of 2.8 Å, which is only slightly greater than the diameter of the probe. Thus, more than half of the regions in a 200 Å thick STEM cross-section sample can be accurately profiled assuming that the region is at optimal tilt with respect to the beam.

In conclusion, long-wavelength roughness was not an absolute limitation to accurate measurement of layer profiles in the copper/cobalt multilayer samples considered in this chapter. Rather, a strategy of measuring several element profiles from different regions of the cross-section and selecting profiles with the highest contrast was adapted for getting an accurate element map across the layers.
3.4.3 Short-wavelength roughness

The annular dark field image in Figure 3.2 shows the structure of individual layers. This incoherent image is sensitive primarily to atomic number and is not complicated by phase-contrast effects, such as in bright field. The annular dark field signal is approximately proportional to $Z^{1.7}$ [Kirkland96]; thus, copper ($Z = 29$) appears brighter than cobalt ($Z = 27$). Contrast has been highly enhanced to make the individual copper and cobalt layers visible in the annular dark field image. The actual contrast was at most 5% for the highest contrast regions, which was much less than the predicted 12% contrast for pure copper and cobalt. This indicated that the beam was sampling both copper and cobalt at all locations.

Figure 3.4 shows the sharpest concentration profile measured for the second-maximum multilayer sample shown in Figure 3.2. Shaded regions indicate the nominal locations of cobalt layers. The cross-section thickness for this sample was approximately 250 Å. The profile appears quite diffuse with 36% copper signal in the center of the cobalt layer and 16% cobalt in the center of the copper layer. This was consistent with the annular dark field observations.

To confirm that the layers were at optimal tilt with respect to the beam, layer profiles of the same region were taken as a function of tilt angle with respect to the electron beam. Figure 3.5 shows cobalt profiles of a 230 Å thick region for angles $\theta = 0, \pm 100$ mrad (see Figure 3.3 inset). The profile for $\theta = 0$ mrad had the highest contrast in cobalt signal while the
Figure 3.4: A concentration profile for the second-maximum multilayer. Shaded regions indicate the nominal locations of cobalt layers. The profile appears quite diffuse, consistent with the annular dark field observations. The diffuse profile is evidence of a large-amplitude interface roughness with a wavelength much less than the thickness of the cross-section sample, which was 250 Å.
Figure 3.5: Cobalt profiles of a "second-maximum" multilayer as a function of angle with respect to the electron beam. The profile for $\theta = 0$ mrad had the highest contrast in cobalt signal while the two profiles at $\theta = \pm 100$ mrad had equally diminished contrast. This shows that $\theta = 0$ mrad was the optimal tilt for this region and that mistilt of the layers with respect to the beam could not explain the diffuse concentration profile of Figure 3.4. Error bars are representative for all profiles.
two profiles at $\theta = \pm 100$ mrad had equally diminished contrast. This shows that $\theta = 0$ mrad was the optimal tilt for this region. Note that it had similar contrast to the profile shown in Figure 3.4, demonstrating it was from a region with relatively flat layers. This confirmed that mistilt of the layers with respect to the beam could not explain the mixed concentration profiles.

The concentration profile for the first-maximum multilayer shown in Figure 3.6 was similarly diffuse. It was typical of the sharpest profiles measured from several different areas of the sample. Shaded regions indicate the nominal locations of cobalt layers. Note that the composition was 44% cobalt even in the center of a 9-Å-wide copper layer. As stated above, this sample received no ion milling, so redeposition of sputtered material was not a possible source of artifacts in this measurement.

Beam spreading was minimal and also could not account for the diffuse layer profiles. Figure 3.6 shows that the initial probe intensity profile fits almost entirely within the copper layer, with only 5% of the total intensity outside of it. The initial probe shape was determined by integrating the calculated probe intensity function [Kirkland98] in the dimension parallel to the interface, since spreading in this dimension does not affect the resolution of the measurement. For a 200 Å thick cross-sections measured in off-axis conditions, beam spreading in Ni$_3$Al (which has a similar atomic number to copper and cobalt) is calculated to increase the average probe radius by only 1.5 Å [Muller96].

To confirm experimentally that beam spreading could not explain the concentration profile result, several profiles were measured at two different cross-section thicknesses of 180 Å and 320 Å, a variation of nearly
Figure 3.6: A concentration profile for the "first-maximum" multilayer. Shaded regions indicate the nominal locations of cobalt layers. The diffuse profile is similar to that of the second-maximum multilayer. The initial probe intensity profile (labeled "probe") fits almost entirely within the copper layer, with only 5% of the total intensity outside of it. For a 200 Å thick cross-section, beam spreading is small and cannot explain the diffuse profile.
a factor of two. These profiles showed very similar contrast in the cobalt signal. Since beam spreading is proportional to $t^{3/2}$ where $t$ is cross-section thickness [Goldstein77], a large difference in the two profiles would be expected if beam spreading were a substantial effect. This result also rules out significant surface damage during mechanical polishing, since such an effect would give a sharper profile for the thicker cross-section.

It was highly unlikely that the diffuse layer profiles indicated a chemically diffuse structure for the multilayer since cobalt and copper are immiscible in bulk. Furthermore, copper-cobalt surface alloys are observed not to occur experimentally [Pederson97] and such surface alloys are predicted to be energetically unfavorable [Christensen97]. A more likely explanation for the diffuse profiles was a large-amplitude interface roughness with a wavelength smaller than the thickness of the cross-section sample, distinct from the long-wavelength roughness induced by hetero-epitaxial grain structure (see section 3.4.2).

The cobalt profile in Figure 3.3 was very regular over several periods of the multilayer. From the uniformity of the concentration profile across several multilayer periods, it was concluded that the wavelength of the roughness was much less than the cross-section thickness of 250 Å. The peak-to-peak magnitude of the roughness was determined by measuring the highest concentration gradient at an interface and calculating the distance it would take to change completely from one atomic species to the other. Using this method, the peak-to-peak roughness was $20\pm 1$ Å. This implied a root-mean-square value of 5 Å assuming the peak-to-peak value spans $\pm 2\sigma$, where $\sigma$ is the standard deviation.
There is experimental evidence for such roughness. Less than one monolayer (ML) of cobalt evaporated onto an atomically flat single crystal copper (111) surface at 150 K forms cobalt islands 3 ML thick, 1 ML of which is buried in the copper substrate [Pederson97]. Cobalt evaporated at a relatively fast rate of 0.1 ML/s forms dendritic islands with features approximately 50 Å wide (a rate of 0.001 ML/s results in triangular islands). When brought up to room temperature a copper brim of equal height surrounds the cobalt islands, and holes 1 ML deep in the copper substrate appear. This initial three-dimensional growth and burrowing of cobalt particles is driven by the much lower free surface energy of copper (1.934 J/m²) relative to cobalt (2.709 J/m²) [Mezey82] as well as the high mobility of copper atoms on the (111) copper surface. The study of [Pederson97] describes growth of a very rough copper/cobalt interface with a wavelength much less than the typical STEM cross-section thickness.

Evaporation at 0.1 ML/s onto a flat copper substrate at 150 K in the above study describes a somewhat different deposition process than sputtering at approximately 1 ML/s onto a multilayer substrate at room temperature. However, the more energetic sputtering process likely produces a similar structure since this growth mode is predicted to be an equilibrium surface configuration [Christensen97].

In fact, there are studies of sputter deposited copper/cobalt multilayers exhibiting giant magnetoresistance that indicate a similar growth occurs during standard sputtering conditions. A Lorentz microscopy study observed ferromagnetically coupled regions within the nominal antiferromagnetic state, which was attributed to variation in copper layer thickness [Zweck97]. Nuclear magnetic resonance studies [Meny92, Jedryka97], which detect the
nearest-neighbor environment of cobalt atoms, show 1.7 ML of pure cobalt per multilayer interface. This is consistent with a large amplitude, short wavelength roughness at the interfaces. While a large 70% increase in interface area due to roughness is somewhat unlikely, the amount of interfacial cobalt is probably an overestimate since cobalt atoms at defects can not be distinguished from cobalt atoms at interfaces. The study instead interprets the data to mean that 1 to 3 ML at each interface is a random two-dimensional copper-cobalt alloy, which is unrealistic for reasons given above.

3.5 Chemical structure

The near edge fine structure of a core-loss edge reflects the local environment of a particular type of atom. It is sensitive to nearest-neighbor bonding and can be useful in distinguishing a rough but chemically sharp interface from a chemically diffuse interface.

Figure 3.7 shows a comparison of the average copper L\textsubscript{1} edge from the first-maximum multilayer with the spectrum from bulk copper. The multilayer and bulk copper spectra are nearly identical in shape. This indicates that most copper atoms in the multilayer are in a bulk-like f.c.c. copper environment with only copper nearest neighbors and are not alloyed on an atomic scale with cobalt atoms (as the concentration profile in Figure 3.6 might seem to imply). This adds strong support to the conclusion of rough, but chemically sharp copper/cobalt interfaces put forward in section 3.4.3.
Figure 3.7: A comparison of the average copper L₃ edge from the “first-maximum” multilayer with that from bulk copper. The two spectra are nearly identical in shape. This indicates that most copper atoms in the multilayer are in a bulk-like f.c.c. copper environment with only copper nearest neighbors and are not alloyed on an atomic scale with cobalt atoms. The changes were a result of d-d hybridization between copper and cobalt d-states.
In general it was very difficult to detect any change in the copper near edge fine structure as a function of position within the first- and second-maximum multilayer structures. This was partly due to the small-wavelength interface roughness (see section 3.4.3), which caused dilution of the interface signal with the bulk signal and spatially distributed the interface signal. In addition, there was a very low signal-to-noise ratio for such measurements due to the low intensity of the energy loss spectrum at the copper L edge and the small magnitude of the observable changes. The fine structure changes were inherently small due to the nature of $d-d$ hybridization (see section 3.6), which involves states with small spatial overlap. Finally, the less than ideal 0.8 eV energy resolution (determined by the full-width at half maximum of the zero loss peak) further reduced the ability to observe changes in copper L edge fine structure.

3.6 Electronic structure

The near edge fine structure of a core-loss edge also reveals the shape of the local density of states and thus gives information on local electronic structure. Specifically, the copper L\textsubscript{3} edge is a result of transitions from the 2p\textsubscript{3/2} core level of copper atoms to unoccupied states above the Fermi energy. It reflects the shape of the unoccupied density of states with $d$-symmetry near copper atoms.

The spectrum labeled "multilayer Cu" in Figure 3.7 showed the $d$-density of states for copper atoms at a copper/cobalt interface averaged with that of bulk copper. The changes from the bulk copper spectrum included an increase in height of the first peak and an increase in energy for the second
peak; such changes were consistent with x-ray absorption spectroscopy of copper/cobalt multilayers [Samant94, Nilsson96]. They were a result of d-d hybridization between copper and cobalt d-states [Nilsson96]. This hybridization resulted in a larger density of d-states at the Fermi energy for interfacial copper atoms. It also implied an increased magnetic moment for interface copper atoms, which was observed with the x-ray magnetic circular dichroism (XMCD) technique [Nilsson96].

3.7 Conclusions

STEM analysis has shown that copper/cobalt interfaces are chemically sharp and very rough. The roughness is characterized by a large root-mean-square amplitude of 5 Å and short wavelength of much less than 250 Å. The short-wavelength roughness indicates a high density of spin-dependent scattering potentials at interfaces, which according to some theoretical predictions will create the giant magnetoresistance effect [Zhang92]. However, this conclusion is debatable. A theoretical evaluation of the resistance contribution due to roughness at a chemically sharp copper/cobalt interface concluded that such roughness produces only a secondary contribution to the giant magnetoresistance effect [Todorov96], which is generated mostly from spin-independent scattering potentials [Tsymbal96]. Also, large-amplitude short-wavelength physical roughness does not imply a corresponding magnetic roughness at interfaces. X-ray resonant magnetic scattering experiments show that the magnetic structure of sputtered copper/cobalt interfaces has both a smaller amplitude and longer wavelength roughness than the physical structure [MacKay96].
In addition to the short-wavelength roughness, the copper/cobalt multilayers also exhibited a long-wavelength roughness with a wavelength of 280 Å and a root-mean-square amplitude of 4.2 Å. This roughness was related to the hetero-epitaxial grain structure. Such roughness where layers are conformal can lead to “orange-peel” ferromagnetic coupling of the cobalt layers [Neel62] and has been shown to diminish giant magnetoresistance values [Misra95].

Hybridization between copper d-states and cobalt d-states was observed at copper/cobalt interfaces; this resulted in a larger density of d-states at the Fermi energy for interface copper atoms. It also implied an increased magnetic moment for interfacial copper atoms, which has been ascribed importance in understanding the interlayer exchange coupling effect [Samant94].

It might be interesting to repeat this study with structures grown using a surfactant. It has been shown that a few monolayers of silver deposited within the first cobalt layer of a copper/cobalt spin valve promote smoother growth and enhance magnetoresistance values [Yang]. It would be interesting to compare interface structure of spin valves grown with and without surfactants. Also, smoother interfaces would effectively improve spatial resolution during measurement of interface properties and reduce dilution of interface signals with bulk signals. Furthermore, recent improvements in the Cornell STEM instrumentation promise to make measurement of changes in the copper L edge spectrum less difficult to detect. They include a better energy resolution of 0.5 eV and a new CCD camera for the PEELS detector with a four-fold increase in efficiency.
Chapter 4

Reference samples for magnetic tunnel junction study

4.1 Introduction

In order to interpret data from the magnetic tunnel junction sample (see Chapter 5), four reference structures were characterized with EELS. The cobalt/aluminum and cobalt/cobalt oxide multilayer samples provide a better understanding of magnetic tunnel junction growth. The sapphire and amorphous alumina samples provide a calibration of the ratio of aluminum-to-oxygen content. All samples provide EELS spectra for comparison with the magnetic tunnel junction data. Since EELS spectra reflect the local atomic environment of a particular type of atom, spectra from known samples can be used to identify local structures in unknown samples. Each section of this chapter is treated as a separate entity with its own set of conclusions.
4.2 Cobalt/aluminum multilayers

Two different types of cobalt/aluminum structures were investigated in this study. "Bilayer" structures consisted of one aluminum and one cobalt layer, each of which were relatively thick. The "multilayer" structure consisted of a series of aluminum layers of varying thickness, each separated by a cobalt layer 50 Å thick. The bilayer structures provided isolated cobalt/aluminum interfaces for study. The multilayer structure provided insight to the growth process of thin aluminum layers on cobalt as a function of aluminum thickness.

4.2.1 Fabrication

All samples were grown on silicon substrates that retained their native oxide layer. Two bilayer samples were evaporated with layer sequences of Co 200Å/Al 200 Å and Al 200 Å/Co 200Å. Base pressure in the evaporation chamber was 8×10⁻⁶ Torr, and evaporation rates were approximately 3 Å/s. The two bilayer structures were made into a single wedge-polished cross-section sample. The final polish was with syton, and no ion milling was used on this sample.

The multilayer structure was grown by dc magnetron sputter deposition. Cobalt was deposited in 2.7 mTorr Ar at 80W power to give 1.8Å/s deposition rate. Aluminum was deposited in 2.3 mTorr Ar at 20W power to give 0.4 Å/s deposition rate. The layer deposition sequence was Si/Co 75Å/(Al 12Å/Co 50Å),/Al 25Å/Co 50Å/Al 50Å/Co 50Å/Al 100Å/Co 100Å.
The multilayer structure was cross-sectioned using the wedge-polishing method. The final polish was with syton. Ion milling was used for additional thinning. Each side was milled for 20 minutes at ion beam settings of 3.5 kV and 2 mA. The beam was at 4° with respect to the surface and a sector rotation angle of 30° was used. The stage was cooled with liquid nitrogen while milling. The final mill on each side was for 5 minutes at 1.5 kV and 2 mA.

4.2.2 Data processing

For element maps, the cobalt signal was determined by integrating the area under the cobalt L edge from -7 to 14 eV relative to the edge onset. This avoids substantial background subtraction errors. While the near edge fine structure for the cobalt L3 edge varies significantly across the interface, the area under the L3 edge remains constant since there is no charge transfer in metals and the total number of unoccupied states is conserved for metals [Muller98b]. The aluminum signal was determined by integrating the aluminum K edge from -10 to +50 eV beyond edge onset. Since the shape of the aluminum K edge did not vary significantly across interfaces, any integration window was valid.

For near edge fine structure analysis, all cobalt L edge spectra have been deconvolved with the zero-loss peak and normalized with respect to L3 edge area. Background subtraction of the aluminum L edge was difficult due to overlap with the cobalt M edge. A power-law background was fit to a narrow energy window in the region after the cobalt M edge onset and before the aluminum L edge onset. Thus, only the near edge spectrum within approximately 10 eV of the edge onset is accurate.
4.2.3 Physical structure

Figure 4.1a shows bright field and annular dark field images of two bilayer samples. The left half of each image shows a Si/Co/Al structure (growth direction from left to right), and the right half a Si/Al/Co structure (growth direction from right to left). Between the two structures is a layer of glue. Cobalt is the lightest (darkest) layer in dark (bright) field. The cobalt/aluminum interface is much rougher for the structure in which aluminum is deposited first. This is due to the relative three-dimensional growth of aluminum compared to cobalt.

Figure 4.1b shows bright field and annular dark field images of the cobalt/aluminum multilayer structure described above. From left to right in each image is silicon/multilayer/glue. Cobalt appears bright (dark) in dark (bright) field. The 12 Å and 25 Å aluminum layers appear relatively uniform in thickness compared to the 50 Å and 100 Å aluminum layers. This suggests a transition in growth mode for aluminum on cobalt as a function of aluminum layer thickness. Thin aluminum layers grow smoothly up to a certain thickness and then switch to three-dimensional growth beyond it. The 25 Å aluminum layer shows an isolated bulge near the bottom of the image. This indicates that the transition in growth mode is sudden and occurs at a thickness slightly less than 25 Å for sputter-deposited layers.

4.2.4 Chemical structure

Figure 4.2 shows element profiles across the interface in a cobalt/aluminum bilayer structure. The width of the annular dark field profile in Figure 4.2 is 30 Å (for 20% to 80% change in signal). This
Figure 4.1: Images of cobalt/aluminum multilayers. (a) "Bilayer" images and (b) "multilayer" images show bright field on the left and annular dark field on the right. Cobalt appears as the darkest (brightest) layers in bright (dark) field. See text for more details.
Figure 4.2: Element map of cobalt/aluminum interface in bilayer structure. Note that for this thick cross-section sample beam spreading and interface roughness have probably caused significant broadening of the interface profile.
represents an upper bound on the true width of the interface since for this thick cross-section sample beam spreading and interface roughness have probably caused significant broadening of the interface profile. The long decay of the cobalt signal into the aluminum layer is likely an effect of substantial probe tails that develop due to beam spreading rather than a true measurement. Note that the center of the cobalt profile is shifted by +10 Å from the center of the annular dark field profile. This is due to large variation in elastic scattering between aluminum and cobalt layers, which affects the amount of signal collected by the PEELS detector (see sections 4.3.3 and 5.4.4 for further discussion). Due to this effect, the most accurate measurement of the location of the interface is the center of the annular dark field profile, which is at 0 Å in Figure 4.2.

Figure 4.3 shows cobalt L\textsubscript{3} edge fine structure as a function of position across the bilayer interface. The spectra labeled “region a” and “region b” correspond to the areas labeled as such in Figure 4.2. The cobalt L\textsubscript{3} peak becomes shorter and wider towards the aluminum layer. Note that substantial changes in the shape of the cobalt L\textsubscript{3} edge occur over a distance of greater than 30 Å across the cobalt/aluminum interface. This indicates that there is a reaction layer several angstroms thick at the cobalt/aluminum interface in which cobalt and aluminum are mixed on an atomic scale. A chemically abrupt interface would only have a single plane of cobalt atoms generating an interface signal whereas a chemically diffuse interface would have several atomic planes of cobalt atoms generating an interface signal.

The fine structure of the “region b” spectrum closest to the aluminum layer is similar to that of bulk CoAl. This might be expected
Figure 4.3: Cobalt L edge across cobalt/aluminum interface in bilayer structure. The spectra labeled “region a” and “region b” correspond to the areas labeled as such in Figure 4.2. Substantial changes in the shape of the cobalt L₃ edge occur over a large width of the cobalt/aluminum interface, indicating there is a reaction layer several angstroms thick at the interface. Note that the fine structure of the “region b” spectrum is similar to that of bulk CoAl. Error bars are equal to the height of markers.
since CoAl is the most stable bulk cobalt-aluminum alloy [Hultgren73]. The two distinct peaks of the CoAl spectrum are not present in the “region b” spectrum; this is likely a result of disorder. The bulk CoAl spectrum was taken from [Button96]. It has been convolved with the point spread function of the PEELS detector in order to approximate the resolution of the other spectra.

The amount of cobalt in the reaction layer can be estimated by integrating the area under the cobalt concentration profile over which an interface signal is observed. As noted above, the annular dark field profile gives a more accurate interface profile; therefore, it will be used in place of the cobalt concentration profile. Region “b” likely contains only interface atoms, since it is closest to the aluminum layer. Region “a” may contain only interface atoms, but it is also possible that the spectrum is simply a linear combination of those from region “a” and bulk cobalt. In latter case, only about half of the atoms in region “a” are interface atoms. Taking into account both of these extreme cases and taking the average concentration of cobalt in regions “a” and “b” as 0.45 and 0.16 respectively, an estimated 6 to 10 Å of pure cobalt is mixed with aluminum. This implies that three to five atomic planes of cobalt are mixed with aluminum at the cobalt/aluminum interface.

This estimate of the amount of reacted cobalt at the cobalt/aluminum interface is in agreement with a previous study of evaporated multilayer thin films [Mitsuzuka90]. This study identifies the presence of a CoAl phase through X-ray diffraction and estimates based on saturation magnetization measurements that there is 5.6 Å of non-magnetic cobalt at each interface.

There is a relatively large positive shift for the onset of the cobalt L₁₃ edge of “region b” (closest to the aluminum layer) compared to that of bulk
cobalt. This shows that cobalt in the cobalt-aluminum interfacial alloy is much more energetically stable than bulk cobalt, which would explain the substantial chemical mixing observed at the cobalt/aluminum interface. In metals, a downward shift in energy of the $2p_{3/2}$ core level results in a corresponding increase in the energy of $L_3$ edge onset. Since core level shifts track changes in binding energy very closely [Muller98], the positive shift in edge onset can be interpreted as an increase in binding energy.

The best measure of edge onset is at its inflection point [Muller96]; unfortunately, the spectra were too noisy for an accurate determination of this point. One estimate of edge onset to use the position at one-half of the $L_3$ peak height; in this case the spectrum from region "b" was shifted $+0.35$ eV with respect to that of bulk cobalt. The shift in onset was $+0.8$ eV when edge onset was determined using a constant signal of 0.05. Averaging the two estimates, the shift in edge onset of the "region b" spectrum with respect to bulk cobalt was $0.6 \pm 0.3$ eV. This value agrees within error with the 0.56 eV per atom released during formation of bulk CoAl [Hultgren73].

Figure 4.4 shows element profiles across the interface between the 100 Å aluminum and 100 Å cobalt layer in the multilayer structure described above. The position of 0 Å is set at the center of the aluminum layer. At this location, the cobalt signal is still 23% of its maximum signal within the cobalt layer, which is 40 Å from the edge of either adjacent cobalt layer. This degree of mixing is very unexpected. This cannot be explained by beam spreading, since the cross-section is only about 250 Å thick. Severe mistilt of the layers with respect to the beam can also be
Figure 4.4: Element map of aluminum/cobalt interface in multilayer structure. The map was from the interface between the 100 Å aluminum and 100 Å cobalt layer. The position of 0 Å was set at the center of the aluminum layer. The substantial amount of chemical mixing was unexpected, and it is likely that ion milling severely modified the original structure. This sample was still useful since it allowed measurement of near edge fine structure of core-loss edges as a function of cobalt-aluminum alloy composition.
ruled out, since analysis of the cobalt L edge fine structure (see below) shows that cobalt and aluminum are highly mixed on an atomic level at this location. While cobalt-aluminum alloys have large negative heats of formation [Hultgren73], they are at most only half of that for cobalt-silicides [Knacke91]. Room-temperature deposition of cobalt on silicon forms only a 20 Å thick cobalt-silicide reaction layer at the interface [van der Veen89]. Thus, the aluminum/cobalt interface is expected to be less than 20 Å wide.

A very likely explanation is that ion milling has severely modified the original structure. Either substantial redeposition of sputtered material or localized heating of the sample (to 350° C or greater [Colgan89]) during ion milling induced additional mixing of cobalt and aluminum layers. This invalidates detailed quantitative conclusions based on this sample regarding the growth of aluminum on cobalt. However, this sample did provide a good opportunity to measure near edge fine structure of core-loss edges as a function of cobalt-aluminum alloy composition.

Figure 4.5 shows cobalt L₃ edge fine structure as a function of position across the multilayer interface shown in Figure 4.4. Note its similarity to Figure 4.3. The spectra labeled "Co", "Co > Al" and "Co < Al" are from the regions labeled as such in Figure 4.4. Note that there is a positive core level shift for the "Co < Al" spectrum relative to the bulk cobalt spectrum, similar to the shift observed in the bilayer system.

### 4.2.5 Electronic structure

Cobalt L₃ fine structure reflects the shape of the unoccupied d-density-of-states. The changes in its shape are due to s-d hybridization between cobalt d-states and aluminum s-states [Muller98b]. This is
Figure 4.5: Cobalt L-edge across aluminum/cobalt interface in multilayer structure. (top) The spectra labeled "Co", "Co > Al" and "Co < Al" are from the regions labeled as such in Figure 4.4. Note its similarity to Figure 4.3. (bottom) s-d hybridization causes the d-band to broaden in energy, which is reflected in the broadening of the cobalt L₃ peak.
illustrated schematically by the diagram in the lower part of Figure 4.5. \textit{s-d} hybridization causes the \textit{d}-band to broaden in energy, which is reflected in the broadening of the cobalt L$_3$ peak. The area under the L$_3$ edge remains constant since the total number of unoccupied states is conserved; therefore, the increase in peak width implies a decrease in peak height.

\textit{s-d} hybridization also affects the electronic structure near aluminum atoms. Figure 4.6 shows the aluminum L edge for two different positions relative to a cobalt/aluminum interface in the multilayer structure. For each spectrum, there is a "knee" near the aluminum L edge onset. The energy of the "knee" feature increases from 77.5 to 81.0 eV for cobalt composition increase from 30\% to 70\%. It is very similar to the increase in pseudogap energy in the aluminum density of states observed for increasing nickel concentration in bulk nickel-aluminum alloys [Muller98b]. The pseudogap is a consequence of \textit{s-d} hybridization between cobalt \textit{d}-states and aluminum \textit{s}-states. \textit{s-d} hybridization scoops aluminum \textit{s}-states out of energy regions with high density of cobalt \textit{d}-states and piles them up outside of such regions [Muller98b]. Due to disorder and possibly sample quality, the "pseudogap" feature in the aluminum L edges from the cobalt/aluminum interface is less distinct than in the aluminum L edge spectrum reported for CoAl [Button96].

4.2.6 Conclusions

Aluminum sputter-deposited on cobalt wets the cobalt surface well and grows relatively smooth up to a thickness of approximately 25 Å. At 25 Å of aluminum, there is a sudden transition to a three-dimensional growth mode. The initial wetting and smooth growth of aluminum on
Figure 4.6: Aluminum L edge across aluminum/cobalt interface in multilayer structure. For each spectrum, there is a “knee” (indicated by the arrows), which increases in energy for cobalt composition increase. It is due to the increase in pseudogap energy in the aluminum density of states, which is caused by s-d hybridization between cobalt d-states and aluminum s-states.
cobalt is an important step in forming a uniform pinhole-free barrier in a magnetic tunnel junction.

Aluminum deposited on cobalt by evaporation reacts with an estimated 4±1 atomic layers of the cobalt surface to form a cobalt-aluminum interfacial alloy. The reaction is driven by a large favorable mixing energy, measured as 0.6 ± 0.3 eV per atom. It was not possible to conclude how much interfacial mixing occurred at sputtered cobalt/aluminum interfaces, although some is expected based on the large cobalt-aluminum mixing energy.

Interfacial mixing has interesting implications for growth of magnetic tunnel junctions, which are formed by oxidizing an aluminum layer as thin as 6 Å that has been deposited on a ferromagnetic layer. Since nickel-, iron- and cobalt-aluminides all have large negative heats of formation [Hultgren73], it is possible that a large fraction of this aluminum is mixed with the underlying ferromagnetic layer. This raises several questions about the structure of the tunnel barrier.

The near edge fine structures of the cobalt L and aluminum L edges were characterized as a function of cobalt-aluminum alloy composition. Shape changes in each of these edges can be understood in terms of s-δ hybridization between cobalt δ-states and aluminum s-states. These spectra can be used for identification of cobalt-aluminum bonding in other structures.

Repeating this study could give a more accurate measurement of cobalt/aluminum interface width and interface alloy composition for both sputtered and evaporated systems. High quality, thin cross-section samples are possible without ion milling using the techniques described in section 2.3.1. It would be interesting to look for differences between such systems. For example, one study on sputtered multilayer thin films did not find any
evidence of interfacial CoAl formation [Cui91]. This may help to understand differences between magnetic tunnel junctions grown by evaporation as opposed to sputter deposition.

4.3 Cobalt/cobalt oxide layers

The purpose of this study was to characterize the structure of cobalt oxide that was formed under the same conditions used for oxidation of the aluminum layer in the magnetic tunnel junction structure. This was to aid in identification of possible cobalt oxide formation in the vicinity of the tunnel barrier.

4.3.1 Fabrication

The cobalt/cobalt oxide/cobalt structure was grown very similar to the magnetic tunnel junction structure described in section 5.2.1. The layer deposition sequence was Si/Co 60Å/O2 exposure/Co 200Å. The Si substrate retained its native oxide layer. Cobalt was deposited in 2.7 mTorr Ar with a 1.8Å/s deposition rate. During the oxygen exposure 99.998% pure O2 was let into the chamber to maintain a pressure of 100 mTorr for 15 minutes. The oxygen was pumped out before the final cobalt layer was deposited.

The cross-section sample was prepared using the wedge-polish method. The final polish on each side was with the 0.1 μm grit diamond sheet using methanol as a lubricant. Due to delamination of the metal layers from the silicon oxide, the thinnest regions of the sample were unusable. The sample was ion milled for 20 minutes at a 3° angle to each surface of the
wedge. The ion beam voltage and current settings were 3 kV and 2 mA respectively. The ion mill stage was liquid nitrogen cooled during milling.

4.3.2 Data acquisition and processing

The ion milling damaged the cobalt oxide layer. Thinner regions of the cross-section sample (approximately less than 300 Å) showed very little oxygen at the location of the cobalt oxide layer, even though the annular dark field signal decreased substantially. Either the cobalt oxide was preferentially milled away or localized heating in the thinnest regions of the sample due to the milling caused the oxygen to migrate into the cobalt on either side. In either case, this indicates that ion milling is not a desirable thinning technique for this kind of sample. Due to milling damage to thinner regions of the sample, only very thick regions (greater than 600 Å) could be examined.

Element maps for cobalt and oxygen were generated by electronically stepping a 0.2 nA point beam in 2.7 Å increments across the cobalt oxide layer. For each data point, the oxygen K and cobalt L edges were acquired for 3 s each. All spectra were integrated from 50 to 75 eV beyond edge onset. This was to avoid substantial near edge fine structure variation observed in the case of cobalt L edge.

4.3.3 Physical structure

A typical element map is shown in Figure 4.7. The width of the cobalt oxide layer as determined from the oxygen profile is 13 Å (full width
Figure 4.7: Element map across cobalt oxide layer. The width of the cobalt oxide layer as determined from the oxygen profile is 13 Å. The anomalous increase in cobalt signal in the center of the cobalt oxide layer can be explained by differences in elastic scattering of the beam within the cobalt oxide layer compared to the cobalt layers.
at half maximum). The cobalt profile strangely shows a 20% increase in signal in the region of the cobalt oxide layer. It is not physically possible for the cobalt to become more densely packed than pure cobalt since it already grows in a close-packed structure. Furthermore, sample thickness remains constant across the oxide layer, so the increase can not be explained by a thicker cobalt oxide layer parallel to the beam. The increase in signal can be explained by differences in elastic scattering of the beam within the cobalt oxide layer compared to the cobalt layers. (See section 5.4.4 for more discussion of this effect.) The apparent increase in cobalt is an artifact and illustrates the importance of understanding sample-beam interactions when interpreting PEELS data.

4.3.4 Chemical structure

Figures 4.8 and 4.9 show the cobalt L and oxygen K edges measured at the center of the cobalt oxide layer. The “center” spectra are an average of spectra taken within ±2 Å of the cobalt oxide layer center where the largest changes were observed. The near edge fine structures of both the oxygen K and cobalt L edges match well with those of CoO and are very different from those of Co₃O₄ [Bentley93]. Both of these spectra can serve as fingerprints to help identify the presence of CoO in other samples.

4.3.5 Electronic structure

The ratio of the area under the L₃ edge to the area under the L₂ edge increases 22% for the cobalt oxide compared to the cobalt. The area of each peak was computed by integrating the spectrum in a 17 eV window beginning at the onset of each edge. (The shape of the low loss spectrum
Figure 4.8: Cobalt L edge across cobalt oxide layer. The near edge fine structure of the cobalt L edges matches well with that of CoO. The ratio of the area under the L$_3$ edge to the area under the L$_2$ edge increases 22% for the cobalt oxide compared to the cobalt, indicating the origin of the changes in electronic structure are atomic rather than solid-state in nature.
Figure 4.9: Oxygen K edge in center of cobalt oxide layer. The near edge fine structure of the oxygen K edge matches well with that of CoO and is very different from that of Co$_3$O$_4$. 
was observed to remain constant across the cobalt oxide layer, so the change in relative peak areas cannot be attributed to differences in plural scattering.) In general, solid state effects result in similar changes for both L₁ and L₂ edges while atomic effects such as Coulomb repulsion and exchange effects may cause differences between these edges [Krivanek90]. The L₁ edge is a result of electronic transitions from the 2p₀/₂ core level to unoccupied states whereas the L₂ edge is due to transitions from the 2p₁/₂ level.

4.3.5 Conclusions

A cobalt surface exposed to molecular oxygen forms a CoO layer approximately 13 Å thick. CoO in bulk is an antiferromagnet, and it could strongly affect spin-polarized tunneling if present in a tunnel junction.

A much better sample is possible using the techniques described in section 2.3.1. Such a sample could provide a more accurate profile of the cobalt oxide layer. It could also make possible detection of interfacial spectra, which may be more appropriate for identification of interfacial cobalt oxide in the magnetic tunnel junction.

4.4 Sapphire

The primary goals of this study were (1) to measure the ratio of the atomic cross-sections for oxygen and aluminum, and (2) to obtain EELS fine structure edges for comparison with the aluminum oxide barrier in a magnetic tunnel junction.
4.4.1 Data acquisition and processing

To avoid radiation damage, all measurements were taken in imaging mode at two-million-times magnification (approximately 315 Å square) and were exposed to a 0.3 nA beam for no more than 120 s. At this dose there was no visible change in annular dark field. Radiation damage in sapphire is a linear process in which the beam mills away the sample at exposed surfaces [Humphreys90]. Radiation-damaged areas can be easily identified as regions that appear darker upon exposure to the beam.

All measurements were deliberately taken with the sample tilted away from zone axis. This was to avoid channeling effects in which the beam intensity can preferentially sample one type of atom more than another, resulting in an inaccurate measurement of the atomic cross-section ratio. A number of regions of different thickness were sampled in order to confirm that the cross-section ratio measurements were independent of thickness. Note that for sample thickness determination, the plasmon scattering length was taken as 1060 Å [Egerton92]. Two different dispersion settings of the PEELS detector were used to confirm independence from this factor as well. At each region, the aluminum K, oxygen K, aluminum L and low loss spectra were measured for a total of 50, 20, 1.5, and 1.5 seconds each. The aluminum L and low loss spectra were taken with the beam at reduced intensities of 0.06 and 0.004 nA respectively to avoid saturating the PEELS detector.

In the following sub-sections, spectra designated as "raw" have simply had a power law background fit and subtracted. Spectra designated as "deconvolved" have been deconvolved with corresponding low loss spectra to remove plural scattering effects. Then a power law background is fit and subtracted.
Accurate deconvolution of the aluminum L edge was not possible due to a highly sloped pre-edge background. In addition, peaks due to multiple plasmon scattering made background subtraction difficult. Empirically, the best background was found to be a linear combination of power law and exponential fits to the pre-edge spectrum.

4.4.2 Aluminum-to-oxygen atomic cross-section ratio

In a perfect sapphire crystal, there are exactly three oxygen atoms for every two aluminum atoms. This allows an accurate calibration of the ratio of the atomic cross-sections of oxygen and aluminum. For the cross-section measurement, the aluminum K edge was chosen rather than the aluminum L edge because it is possible to make a more accurate background subtraction of the aluminum K edge. The aluminum L edge onset is near 80 eV in the energy loss spectrum, which means that its background can deviate from simple power law behavior due to multiple plasmon scattering or due to overlap with the cobalt M edge in the case of the magnetic tunnel junction measurements. Since an integration window must be chosen beginning at greater than 50 eV beyond edge onset in order to avoid near edge fine structure variations, accurate background subtraction is crucial to avoid introducing a large error in the measurement.

The raw oxygen K and aluminum K edge spectra are shown in Figure 4.10. All spectra have been scaled to match at their first peak. Note that well beyond the edge onset within the integration window for
Figure 4.10: "Raw" oxygen K and aluminum K edges from sapphire. Spectra were measured as a function of sample thickness. The integration window used to determine the atomic cross-section ratio is indicated in each plot. Error bars are equal to the height of markers for O K edge spectra.
determining atomic cross-section, there is considerable variation in the height of the spectra. This is due to differences in plural scattering from plasmons, and is a function of the sample thickness at the location of the measurement. Deconvolution removed this effect, which is considerable for the thick samples measured in this study. Figure 4.11 shows that when the height of the deconvolved spectra were normalized, they all collapsed to a single spectrum. This is expected since the core-loss spectrum should be the same everywhere in a perfect crystal. This result gives confidence that the data analysis was accurately performed.

Figure 4.12 shows the aluminum-to-oxygen atomic cross-section ratio as a function of cross-section thickness for both raw and deconvolved spectra. For each data point, the integrated area from 50 to 75 eV beyond edge onset of the aluminum K edge was divided by that of the oxygen K edge (see Figures 4.10 and 4.11 for positions of integration windows). The data from the deconvolved spectra show that the measured cross-section ratio is independent of cross-section thickness, as would be expected for an accurate study. Note that the data point from the thickest cross-section is not included due to difficulty in deconvolving the aluminum K edge spectrum (Figure 4.11 shows this spectrum does not match as well with other deconvolved spectra). The average aluminum-to-oxygen cross-section ratio is 0.037±0.001.

The data from the raw spectra show some variation with cross-section thickness. Note that the data point taken with the “PEELS4” dispersion setting (0.6 eV per pixel) falls on the linear fit for the data taken with the “PEELS1” dispersion setting (0.4 eV per pixel), showing that the measurement is independent of PEELS detector setting. When the linear
Figure 4.11: “Deconvolved” oxygen K and aluminum K edges from sapphire. These plots show the spectra from Figure 4.11 with plural scattering removed. The spectra collapsed to a single shape as expected for a uniform sample. The integration window used to determine the atomic cross-section ratio is indicated in each plot. Error bars are equal to the height of markers for O K edge spectra.
Figure 4.12: Aluminum-to-oxygen atomic cross-section ratio. The atomic cross-section ratio is plotted as a function of cross-section thickness for both raw and deconvolved spectra. Points labeled "P1" and "P4" refer to measurements taken with the "PEELS1" and "PEELS4" dispersions settings of the PEELS detector. (See text for more details.) The atomic cross-section ratios determined from the deconvolved spectra are independent of thickness as expected.
fit to the raw data is extrapolated to zero cross-section thickness, it equals the average cross-section ratio for the deconvolved spectra (within the uncertainty of the measurement), as expected.

4.4.3 Crystal structure

The highly ordered crystalline structure of sapphire is reflected in the sharp features of the oxygen K edge (see Figure 4.11). In the multiple scattering description, intensity modulations in near edge fine structure are determined by interference of the outgoing electron wave of the ejected electron with the electron wave that has been backscattered from atoms surrounding the excited atom. Since the physical structure of sapphire is highly symmetric, there are many sharp peaks and troughs in the "interference spectrum" as a function of ejected electron energy.

Figure 4.13 shows the near edge fine structure for the aluminum L edge. In sapphire, all aluminum atoms are octahedrally coordinated with their oxygen nearest neighbors. Indeed, a multiple scattering theory calculation for aluminum in octahedral coordination with oxygen [Brydson96] compares well with the spectrum in Figure 4.13. This coordination fingerprint can be used to investigate the structure of other aluminum oxides.

4.4.4 Electronic structure

From an electronic structure viewpoint, the oxygen K edge reveals the shape of the unoccupied density of states with $p$-symmetry. The sharp onset of the oxygen K edge reflects the well-defined energy gap of sapphire. Note that calculations of the oxygen K edge in sapphire show no significant
Figure 4.13: Aluminum L edge from sapphire. This spectrum provides a coordination fingerprint for aluminum atoms octahedrally coordinated with oxygen nearest neighbors.
core-hole effects [Brydson96], validating the single-particle interpretation of its fine structure.

4.4.5 Conclusions

The aluminum-to-oxygen atomic cross-section ratio for the aluminum K and oxygen K edges was measured to be $0.037 \pm 0.001$. Aluminum L, aluminum K and oxygen K edges were characterized for comparison with other aluminum oxides. The sharp features of the oxygen K edge reflect its well-ordered crystalline structure and the sharp onset reflects a well-defined band gap. The shape of the aluminum L edge is a coordination fingerprint for aluminum in octahedral coordination with nearest oxygen neighbors. Finally, a thinner sample could give a more accurate aluminum-to-oxygen cross-section ratio as well as a more accurate measurement of the aluminum L edge spectrum.

4.5 Amorphous alumina

The purpose of this study was to gain a better understanding of the properties of amorphous alumina, which forms the thin tunnel barrier in the magnetic tunnel junction sample. While there are many ways to create an amorphous structure, it will be shown that this sample has a structure that is identical to the structure of the aluminum oxide barrier of the magnetic tunnel junction. Therefore, the results of this study are of great interest.
4.5.1 Fabrication

The amorphous alumina sample was evaporated from powdered alumina. A sodium chloride crystal, which was cleaved just prior to mounting in the evaporation chamber, was used as a substrate. The evaporation chamber had a base pressure of $7.7 \times 10^{-8}$ Torr. In order to ensure that the evaporated alumina film was fully oxidized, molecular oxygen was bled into the chamber to an initial pressure of $10^{-3}$ Torr. Just before evaporation began, oxygen flow was stopped and pumping on the chamber was resumed. Alumina was deposited at a rate of 5 Å/s and continued until the film was 270 Å thick, as measured by a surface profilometer. Finally, the "float off" method was used to transfer the thin film onto a standard TEM support grid.

4.5.2 Data acquisition and processing

To avoid radiation damage, all PEELS measurements were taken in imaging mode. Lack of radiation damage was confirmed by no visible change in annular dark field (see section 4.5.6 for more details). Spectra for measurement of aluminum-to-oxygen ratio were acquired with a 0.2 nA beam at $\times 100k$ magnification ($6300 \times 6300$ Å). The oxygen K edge was acquired for 10 s and the aluminum K edge for 20 s in the same region. The relatively high beam current yields a large signal for accurate measurement. However, some distortion of the PEELS spectrum shape occurs at the $\times 100k$ magnification setting (it was confirmed that this distortion does not affect the aluminum-to-oxygen ratio measurement). The oxygen K edge fine structure was measured with a 0.017 nA beam at $\times 200k$ magnification for 20 s each in six different regions. The aluminum L edge fine structure was measured with a 0.017 nA beam at $\times 1M$ magnification ($630 \times 630$ Å) for 1.5 s in three separate regions.
For both edges, all spectra were averaged to give a final spectrum. The “PEELS4” dispersion setting (0.6 eV per pixel) of the PEELS detector was used for all measurements.

In the following sub-sections, oxygen K and aluminium K edge spectra designated as “raw” have simply had a power law background fit and subtracted. Spectra designated as “deconvolved” have been deconvolved with the low loss spectrum to remove plural scattering. Then a power law background fit and subtracted.

Accurate deconvolution of the aluminum L edge was not possible due to a highly sloped pre-edge background. These spectra were corrected for PEELS detector distortion and fit with a power law background.

4.5.3 Aluminum-to-oxygen ratio

The ratio of aluminum atoms to oxygen atoms in the amorphous alumina film was determined using the aluminum-to-oxygen cross-section ratio measured from sapphire (see section 4.4.2). Both raw and deconvolved spectra were integrated from 50 to 75 eV beyond edge onset. The integration windows are shown in Figures 4.14 and 4.15. The raw spectra had an aluminum-to-oxygen area ratio of $0.027 \pm 0.002$ while the deconvolved spectra had an area ratio of $0.026 \pm 0.002$. It is not surprising that these two measurements give the same result, since the oxygen K and aluminum K edges have the same shape within the integration window for both raw and deconvolved spectra. This implies that deconvolution is unnecessary when determining the aluminum-to-oxygen ratio in other
Figure 4.14: Oxygen K edge from amorphous alumina. Both “raw” and “deconvolved” spectra were integrated in the window indicated to determine the ratio of aluminum atoms to oxygen atoms in the amorphous sample. In contrast to the sharp features of the sapphire spectrum, the spectrum from amorphous alumina has dull features indicating it is physically disordered. The gradual onset of the oxygen K edge reflects a less well-defined energy gap in amorphous alumina compared to sapphire. Error bars are equal to height of the spectrum markers.
Figure 4.15: Aluminum K edge from amorphous alumina. Both “raw” and “deconvolved” spectra were integrated in the window indicated to determine the ratio of aluminum atoms to oxygen atoms in the amorphous sample. In contrast to the sharp features of the sapphire spectrum, the spectrum from amorphous alumina has dull features indicating it is physically disordered. Error bars are equal to the height of spectrum markers.
amorphous aluminum oxide samples that have similar (or thinner) thickness. Using the sapphire cross-section ratio to interpret the area ratio, there are 2.8±0.2 oxygen atoms for every two aluminum atoms in the amorphous alumina film. Fully oxidized alumina would be (like sapphire) three oxygen atoms for every two aluminum atoms; therefore, the amorphous alumina film is fully or near fully oxidized.

4.5.4 Crystal structure

Figure 4.16 shows a selected area diffraction pattern from the evaporated alumina film. It was acquired with a 50 μm selected-area-diffraction aperture, 300 μm collector aperture and 1 m camera length. The image shows a series of diffuse concentric rings, which shows that the structure of the film is amorphous [Cowley92]. A perfect crystal would show an ordered array of well-defined spots, and a poly-crystalline film would show a series of sharp concentric rings (that may have additional spots if the grains have a preferred orientation).

The near edge fine structures for the oxygen K and aluminum K edges are already given in Figures 4.14 and 4.15. In contrast to the sharp features of the sapphire spectra, the spectra from amorphous alumina show relatively dull features. This is a consequence of the physical disorder of the amorphous alumina. (See section 4.4.3 for further explanation.)

Figure 4.17 shows the Al L edge. The shape of the aluminum L edge is primarily a function of its nearest-neighbor oxygen environment [Brydson96]. It matches well with the calculated structure for aluminum in tetrahedral coordination with its nearest oxygen neighbors [Brydson96]. It
Figure 4.16: Selected area diffraction pattern from amorphous alumina. The plot shows the azimuthally integrated intensity of the diffraction pattern in the inset image. The image shows a series of diffuse concentric rings, which confirms that the structure of the film is amorphous.
Figure 4.17: Aluminum L edge from amorphous alumina. It matches well with the calculated structure for aluminum in tetrahedral coordination with its nearest oxygen neighbors, showing that amorphous alumina has some short-range order.
is very different from the sapphire aluminum L edge, which reflects aluminum in octahedral coordination with its nearest oxygen neighbors. The strong tetrahedral coordination fingerprint of the aluminum L edge is in agreement with an x-ray diffraction study. The study [Manaila84] of evaporated alumina thin films showed that for films evaporated at 3.3 Å/s, aluminum atoms occupied exclusively tetrahedral sites within a randomly close-packed oxygen sub-lattice (films evaporated at 12 Å/s showed some octahedral-site occupation by aluminum atoms).

While the amorphous alumina has no long-range crystalline order, the aluminum L edge result shows that it does have some short-range order. In fact, x-ray diffraction studies of amorphous alumina thin films evaporated under various conditions show that such structures generally exhibit a relatively high degree of local order [Manaila84]. This and other studies [Finney81] show that amorphous alumina structures can be pictured as a dense random packing of the larger oxygen anions that create mostly tetrahedral and some octahedral interstitial sites. The smaller aluminum cations fill interstitial sites not randomly, but in a way that minimizes electrostatic repulsion among the cations. This has been observed to lead to local spinel-type ordering [Manaila84].

4.5.5 Electronic structure

From an electronic structure viewpoint, the oxygen K edge reveals the shape of the unoccupied density of states with p-symmetry. The gradual onset of the oxygen K edge reflects a less well-defined energy gap in amorphous alumina compared to sapphire. Note that calculations of the oxygen K edge in sapphire and γ-alumina show no significant core hole effects [Brydson96].
indicating that the single-particle interpretation of the fine structure is likely valid. Also, core-hole effects tend to sharpen rather than broaden the edge onset.

4.5.6 Radiation damage

Amorphous alumina damages very easily. For example, Figure 4.18a shows part of an annular dark field image originally taken with a 0.2 nA beam at ×200k magnification. Figure 4.18b shows that after scanning in imaging mode for 10 s at ×5M magnification (130 Å × 130 Å), the same region had a darker rectangle approximately the size of a ×5M image. The darker region had a 15% lower annular dark field signal than surrounding regions that have not received the intense radiation dose. A study of radiation damage in amorphous alumina [Humphreys90] showed that aluminum is lost from intensely irradiated areas, which is consistent with these regions appearing darker in annular dark field. Interestingly, Figure 4.18c shows that damaged areas can be healed, a result also noted in [Humphreys90]. Exposure to smaller radiation dose, in this case scanning the beam in imaging mode at ×1M magnification for 10 s, once again gives a fairly uniform annular dark field image.

Figure 4.18d shows the oxygen K edge as a function of time during the ×5M irradiation procedure described above. A sharp pre-peak at 532 eV shows the presence of molecular oxygen in the irradiated region. This is a sign that radiation damage has occurred. Molecular oxygen forms a result of ionization damage. High-energy electron irradiation causes oxygen ions lose electrons and the ionic bonds become destabilized. Large radial electric fields that occur in bulk insulators due to beam exposure cause bulk Al³⁻.
Figure 4.18: Radiation damage to amorphous alumina. The annular dark field sequence at the top shows (a) undamaged alumina, (b) damage after ×5M exposure and (c) healing after ×1M exposure. The scale bar in (a) is 100 Å. The plot (d) shows the oxygen K edge as a function of time during the ×5M irradiation procedure. The sharp pre-peak at 532 eV is a signature of molecular oxygen. Error bars are shown on the legend when greater than the thickness of the line.
ion migration away from the irradiated area. The remaining oxygen atoms form molecular oxygen in that same area [Humphreys90].

It is important to note that the pre-peak at 532 eV can appear similar to observations of gap states, such as in [Muller98a]. Thus, care must be taken that radiation damage is not mistaken for detection of gap states.

4.5.7 Conclusions

There are $2.8\pm0.2$ oxygen atoms for every two aluminum atoms in the amorphous alumina film, which shows that it is fully or near fully oxidized. The amorphous alumina has no long-range crystalline order, but it does have some short-range order. All or nearly all aluminum atoms are in tetrahedral coordination with its nearest oxygen neighbors. More information on the short-range structure of the amorphous alumina could be determined by analysis of extended edge fine structure and better electron diffraction measurements, which would yield radial distribution functions.

Amorphous alumina has a less well-defined energy gap in comparison with sapphire. This has important consequences for conduction through an amorphous tunnel barrier.

Bulk amorphous alumina damages very easily with a radiation dose of 12 fA/Å$^2$ causing significant damage in less than one second. Signs of radiation damage include darkening of exposed regions in the annular dark field image and the appearance of a pre-peak at 532 eV on the oxygen K edge.
Chapter 5

Cobalt/alumina/cobalt magnetic tunnel junctions

5.1 Introduction

STEM analysis of a cobalt/alumina/cobalt magnetic tunnel junction was performed with the ultimate goal of gaining a better understanding of the fundamental process of spin-polarized tunneling. As discussed in section 1.3.2, while the spin-polarization of the tunneling current depends on the band structure of the ferromagnetic material in which it originates, it is also highly sensitive to the detailed structure of the tunnel barrier. Since very little is known experimentally about the atomic-scale structure of magnetic tunnel junctions, the goal was to map the structure of one particular tunnel junction in as much detail as possible and relate this structure to spin-polarized transport.
5.2 Fabrication

The results in this chapter are based primarily on a single magnetic tunnel junction cross-section sample. This particular cross-section sample was made with the best sample preparation technique and was far superior to many previous attempts. Unless otherwise noted, it should be assumed that this sample is being referred to.

5.2.1 Magnetic tunnel junction growth

The magnetic tunnel junction for this study consisted of a “single” barrier and a “double” barrier. The single barrier was fabricated by depositing 12 Å of aluminum and oxidizing it; the double barrier was fabricated by repeating the single barrier twice. The single barrier was of primary interest as this was expected to give the best magnetoresistance value. The layer deposition sequence was Si/Co 60Å/Al 12Å/O₂ exposure/Co 60Å/(Al 12Å/O₂ exposure)₂/Co 100Å. The native oxide layer of the silicon substrate was removed prior to deposition of the layers.

The magnetic tunnel junction was grown by sputter deposition. Cobalt was deposited in 2.7 mTorr Ar at 80W power to give 1.8Å/s deposition rate. Aluminum was deposited in 2.3 mTorr Ar at 20W power to give 0.4 Å/s deposition rate. During the oxygen exposure 99.998% pure O₂ was let into the chamber to maintain a pressure of 100 mTorr for 15 minutes. The oxygen was pumped out before subsequent layers were deposited.
5.2.2 Cross-section preparation

A cross-section sample of the magnetic tunnel junction was prepared using the wedge-polish method. The final polish on each side was with the 0.1 μm grit diamond sheet using methanol as a lubricant. No ion milling or further treatment was given to the sample after polishing. This was to limit possible sources of artifacts to mechanical damage of the cross-section surfaces.

5.3 Physical structure

5.3.1 Barrier roughness

Figure 5.1 shows low-resolution bright field and annular dark field images of two different magnetic tunnel junction samples. In both samples the growth direction is from left to right and the thin bright (dark) vertical regions in the bright (dark) field image are the alumina barriers. The sample in Figure 5.1a shows the first attempt to examine a magnetic tunnel junction structure. It had the layer deposition sequence Si (100) + native oxide/Co 200Å/Al 12Å/O₂ exposure/Co 200Å. The sample in Figure 5.1b is the sample described in section 5.2.

Note that in Figure 5.1a the barrier appears rough whereas in Figure 5.1b the single barrier appears relatively smooth. It has been shown that barrier layer roughness can reduce magnetoresistance due to “orange-peel” magnetostatic coupling, especially in ultra-thin (< 10Å) tunnel barriers [Fujikata01]. Furthermore, roughness is of concern from a microscopy standpoint since the transmitted electron beam samples positions throughout the entire thickness of the cross-section sample. Thus,
Figure 5.1: Low resolution images of magnetic tunnel junctions. (a) Bright field (left) and annular dark field (right) images of Si/Co 200Å/Al 12Å/O₂ exposure/Co 200Å. (b) Bright field (left) and annular dark field (right) images of Si/Co 60Å/Al 12Å/O₂ exposure/Co 60Å/(Al 12Å/O₂ exposure)₂/Co 100Å. In both samples the growth direction is from left to right and the thin bright (dark) vertical regions in the bright (dark) field image are the alumina barriers.
variations in interface position with respect to the beam effectively reduce the spatial resolution. For both of these reasons it is important to understand and control barrier roughness.

Barrier roughness is correlated with the grain structure of the underlying cobalt layer. Grain structure is most apparent in bright field where strongly diffracting grains appear dark. For example, the very dark region in the center of the bright field image in Figure 5.1a is likely from a single grain. This grain’s dome-shaped surface creates a bulge (i.e. region of positive curvature with respect to the substrate) in the aluminum oxide layer. On careful examination, other dome-shaped grains that cause such bulges are also visible in this image. Thus, both the magnitude of the barrier roughness and its correlation length are determined by grain size in the underlying cobalt layer.

In order to limit cobalt grain size and thereby limit barrier roughness, the magnetic tunnel junction in Figure 5.1a was redesigned with a thinner cobalt under-layer. The redesigned magnetic tunnel junction was the one shown in Figure 5.1b. Indeed, as the cobalt under-layer thickness was decreased from 200 Å to 60 Å, the average grain size diminished and the root-mean-square roughness of the barrier dropped from 3.6 Å to 1.7 Å.

5.3.2 Barrier thickness

Figure 5.2 shows a high-resolution annular dark field image of the same magnetic tunnel junction sample shown in Figure 5.1b. Note the (110) projected silicon lattice is visible in dark field on the left side of the image. The thickness of the alumina barrier is about 15 Å (full width at
Figure 5.2: High resolution annular dark field image of a magnetic tunnel junction. The image is of the same sample shown in Figure 5.1b. Note the (110) projected silicon lattice is visible on the left side of the image. The barrier thickness appears very uniform, indicating that the alumina barrier is free of pinholes. The cobalt/alumina interfaces appear diffuse partly due to roughness of the barrier, which is visible in the image.
half maximum). Thus oxidation has expanded the thickness of the original 12 Å aluminum layer by approximately 25%.

The barrier thickness appears very uniform throughout the image in Figure 5.2. The magnetic tunnel junctions in Figure 5.1 also show very uniform barriers despite differences in layer roughness. Uniform thickness indicates that the alumina barrier is free of pinholes, which is essential for a high quality tunnel junction.

An interesting contrast to the uniformity of the single barrier is the substantial variation in the thickness of the double barrier shown in Figure 5.1b. While the bottom (left, in images) cobalt/alumina interface is relatively smooth like the single barrier interfaces, the top (right, in images) alumina/cobalt interface is very rough. It appears that the first aluminum layer grows smoothly on cobalt. However, the second aluminum layer balls up on the alumina, creating a very rough layer.

This shows that attempting to grow a thick alumina barrier by repeatedly depositing a thin aluminum layer and then oxidizing it is a poor strategy. More importantly, the uniform thickness of the single barrier demonstrates that aluminum has a strong tendency to wet a cobalt surface, which explains why aluminum works so well for ultra-thin tunnel barriers [Moodera00]. As discussed in section 4.2, cobalt aluminides (and other transition metal aluminides) have large negative heats of formation, which leads to good wetting behavior.
5.4 Barrier profile

5.4.1 Data acquisition and processing

The oxygen K, cobalt L, and aluminum K edges were chosen to map element profiles across the barrier. The aluminum K and cobalt L edges were chosen rather than the higher intensity aluminum L and cobalt M edges in order to give higher spatial resolution [Muller95]. Also, integrating the area under the aluminum L edge involves a very difficult background subtraction (see section 5.6.1) which introduces a large uncertainty. In contrast, the aluminum K and cobalt L edges have very sharp onsets with no edge overlap and therefore give clear signals.

For all element profiles, a 0.074 nA, 2 Å diameter beam was shifted electronically in steps of 2.7 Å across the barrier. The cobalt and oxygen spectra were collected for 1 s each, while the aluminum spectra were collected for a total of 7 s each. As discussed below in section 5.7.2, radiation damage was negligible for element profile measurements taken with these beam parameters.

To achieve high signal-to-noise ratios, cobalt and oxygen spectra were integrated from edge onset to 40 eV beyond edge onset; aluminum spectra were integrated from onset to 75 eV beyond onset. Such a strategy minimized background subtraction errors while including the portion of the spectrum with greatest signal. The near edge fine structure of the core-loss edges remained constant within uncertainty, confirming the validity of such measures.
5.4.2 Raw element map

Figure 5.3 shows an element map of oxygen, cobalt, and aluminum across the magnetic tunnel junction. The profile appears highly mixed, with substantial cobalt in the center of the junction. However, this is a combined result of barrier layer roughness, elastic scattering effects that enhance signals in the barrier center, and broad beam tails. EELS near edge fine structure measurements (see section 5.5.2), which are very sensitive to the local environment of an atom, show there is no cobalt in the center of the alumina barrier.

Some important information can be determined from the element profiles of the barrier, despite its roughness. At the bottom cobalt/alumina interface the aluminum-to-oxygen ratio increases compared to the center of the junction, indicating an aluminum-rich region. It is probable that the top interface is also aluminum-rich, but this can not be stated conclusively due to the large uncertainty of the aluminum profile. Comparison of the less noisy cobalt and oxygen profiles shows that the width of the cobalt profile is 1.2 Å greater than the oxygen profile (measuring full width at half maximum). This is consistent with aluminum-rich edges to the alumina barrier. EELS fine structure measurements discussed in section 5.6.2 also indicate aluminum-rich edges to the barrier.

5.4.3 Oxygen-to-aluminum ratio

The oxidation state of aluminum in the barrier was determined by comparing its oxygen and aluminum signals to those from the amorphous alumina standard described in section 4.5. Spectra taken within ±3 Å of the center of the barrier were used to determine the oxygen-to-aluminum
Figure 5.3: Raw element map across tunnel barrier. The profile appears highly mixed; however, this is a result of barrier layer roughness and other effects. The profiles indicate aluminum-rich regions at the top and bottom cobalt/alumina interfaces. Note that the aluminum signal has been scaled to match the oxygen signal where the oxygen-to-aluminum ratio was 1.5. The oxygen-to-aluminum ratio in the center of the barrier was 1.4±0.1, indicating that the aluminum was fully or near-fully oxidized.
ratio. The fine structures of both the oxygen K and aluminum K edges from the barrier were the same (within uncertainty) as those from the amorphous alumina. Therefore, to improve the signal-to-noise ratio all edges were integrated from onset to 75 eV beyond the onset. The ratios of the oxygen K edge areas to the aluminum K edge areas matched exactly, indicating that the barrier had the same stoichiometry as the amorphous alumina standard. Therefore, the oxygen-to-aluminum ratio in the center of the barrier was 1.4±0.1, indicating that the aluminum was fully or near-fully oxidized. This is reflected in the element map (Figure 5.3), where the aluminum signal has been scaled to match the oxygen signal where the oxygen-to-aluminum ratio was 1.5.

5.4.4 Elastic scattering correction

The electron beam undergoes elastic (and inelastic) scattering within the sample, which causes it to spread and deviate from its original direction. Thus the exiting probe can have a very different size and momentum spread compared to its original parameters. The PEELS detector only collects electrons within 12 mrad of the original beam direction; this is the half-angle of the entrance to the spectrometer. Since cobalt scatters more strongly than aluminum oxide due to its higher atomic number, it is expected that fewer electrons will enter the spectrometer for cobalt than for aluminum oxide.

The total number of electrons reaching the PEELS detector is proportional to the entire energy loss spectrum integrated up to 100 eV¹. Figure 5.4 shows the total integrated PEELS signal across the barrier. Note the

¹ The power law decay of the EELS background and exponential decay of core loss edges ensures the area under the remaining spectrum is negligible.
large variation in signal, with nearly twice as many electrons reaching the PEELS detector in the center of the aluminum oxide layer compared to in the flanking cobalt layers. The variation in total integrated PEELS signal matches the variation in annular dark field signal. This reveals that the source of the scattering is Rutherford-type scattering, which is the source of the dark field signal. This is only true in the absence of any coherent scattering effects, which are avoided here by choosing off-axis conditions for the cobalt grains.

Figure 5.5 shows the element map of Figure 5.3 corrected for variation in the total number of electrons reaching the PEELS detector due to elastic scattering. Each data point has been normalized by dividing by the total integrated PEELS signal measured at its location. Quantitatively, the normalized data is quite different from the raw data. In general, the widths of the profiles increase in the normalized data. The width of the cobalt profile jumps from 13.8 to 17.4 Å while the width of the oxygen profile increases from 12.6 to 14.0 Å. This makes the cobalt profile 3.4 Å wider than the oxygen profile, compared to 1.2 Å wider in the raw data. Note that the widths of the element profiles in the normalized map are more consistent with the 16.0 Å width of the barrier from the annular dark field profile at this location.

Figure 5.5 also shows that signals at the barrier center are smaller relative to those at the barrier edges. The cobalt signal in the center of the barrier is only 11% of the maximum bulk cobalt signal compared to 21% in the raw data. This normalized profile makes it more believable that there is no cobalt in the center of the barrier. Residual signals at the 10% level
Figure 5.4: Variation in elastic scattering across the tunnel barrier. The PEELS detector only collects electrons within 12 mrad of the original beam direction and is therefore sensitive to variation in elastic scattering. Note there was a large variation in the total number of electrons reaching the PEELS detector across the alumina tunnel barrier. This variation matched the shape of the annular dark field signal, revealing that the source of the scattering was Rutherford-type scattering. This only holds true in the absence of strong diffraction effects.
Figure 5.5: Element map across the barrier corrected for elastic scattering. Each raw data point in Figure 5.3 has been normalized by dividing by the total integrated PEELS signal shown in Figure 5.4. Quantitatively, the normalized data is quite different from the raw data. In general, the widths of the profiles increase in the corrected data. Also, signals at the barrier center are smaller relative to those at the barrier edges.
are generally ignored since the long tails of the probe contain approximately of 10% of the total beam intensity [Hillyard96].

5.5 Barrier center

TEM images have been used to determine that the aluminum oxide barrier is amorphous [Parkin99]. However, there are many ways that a structure can be amorphous and simply identifying a structure as such reveals very little. EELS analysis provides much more information about the physical and electronic structure of the barrier on an atomic scale. As discussed in section 1.3.2, understanding barrier structure is critical for understanding spin-polarized tunneling.

5.5.1 Data acquisition and processing

PEELS spectra across the aluminum oxide barrier were acquired for the oxygen K edge and aluminum L edge. The oxygen K edge spectra were taken with a 0.074 nA beam spread into a 64 Å × 2 Å line parallel to the barrier in order to avoid radiation damage (see section 5.7.2 below). Each spectrum was acquired for 4 seconds after which the beam was manually shifted approximately 2 Å perpendicular to the barrier. The much greater intensity of the energy loss spectrum near the aluminum L edge allowed spectra to be taken with a 0.0074 nA beam focussed to a 2Å diameter spot. Spectra were acquired for 1 second each after which the beam was electronically shifted 2.7 Å perpendicular to the barrier. The resulting radiation dose was slightly less than the dose sustained by the sample during oxygen K edge measurements and should not have caused any damage.
Similar spectra from the barrier center were averaged to increase signal-to-noise ratios. The resulting aluminum L and oxygen K edge spectra represents a 7 Å wide region centered on the barrier.

The oxygen K edge spectrum was deconvolved with the low loss spectrum from the same area of the sample to remove plural scattering. Deconvolution of the aluminum L edge spectrum could not be performed due to its strongly sloping background. The aluminum L edge (onset at 81 eV) overlapped with the cobalt M edge (onset at 63 eV), making background subtraction somewhat difficult since the exact shape of the cobalt M edge was unknown. However, in the center of the barrier, the cobalt M edge composed less than 20% of the total background intensity to the aluminum L edge, and a power law fit was a good approximation to the pre-edge background.

5.5.2 Physical structure

EELS fingerprinting analysis showed conclusively that the alumina in the center of the tunnel barrier had a noncrystalline structure. Figure 5.6 compares oxygen K edges from the barrier center with those from sapphire and amorphous alumina. For best comparison, plural scattering has been removed from all spectra. The shape of the oxygen K edge from the barrier center matches that of amorphous alumina at all energies and is very different from that of sapphire. The small differences that remain between the barrier and the amorphous alumina spectra are due to differences in data acquisition technique and are not meaningful.
Figure 5.6: Oxygen K edge from center of tunnel barrier. The shape of the oxygen K edge from the barrier center matches that of amorphous alumina at all energies and is very different from that of sapphire. This shows that the barrier is amorphous in structure. The error bars for each data point are equal to height of data markers.
A further confirmation of the amorphous nature of the barrier is given in Figure 5.7, which is a comparison of aluminum L_{32} edges. Again, the shape of the aluminum L_{32} edge from the barrier center matched well with that from amorphous alumina. The difference at energies greater than 20 eV beyond the edge onset was due to difference in plural scattering and was not significant.

Note that the aluminum L_{32} and oxygen K edge fine structure matches with the spectra from pure amorphous alumina show that the barrier center contains only alumina. There is no cobalt as the concentration profile in Figure 5.3 might imply. Otherwise the spectra would have a different fine structure that reflected bonds with cobalt atoms.

5.5.3 Barrier height

The electronic structure of the barrier is reflected in the oxygen K edge fine structure, which shows the shape of the unoccupied density of states with p-symmetry. Figure 5.8 details the oxygen K edge onset shown in Figure 5.6. Note that the oxygen K edge from amorphous alumina has a much more gradual onset than the edge from sapphire\(^2\). The gradual onset indicates that the conduction band in the tunnel barrier has a significant band tail. The effect of this band tail is to lower the barrier height. Indeed, ballistic conduction through an alumina barrier in a cobalt/alumina/cobalt magnetic tunnel junction is observed to turn on at only 1.25 eV above the Fermi energy [Rippard01]. For comparison,

\(^2\) Note the energy offsets of the spectra in figure T were chosen for ease of comparison and do not reflect their exact positions in the energy loss spectrum.
Figure 5.7: Aluminum L edge from center of tunnel barrier. The shape of the aluminum L$_{3,2}$ edge from the barrier center matched well with that from amorphous alumina, confirming the amorphous structure of the barrier. However, the barrier did have some short-range order as evidenced by the shape of the aluminum L$_{3,2}$ edge, which matched a calculation for aluminum in tetrahedral coordination with its oxygen nearest neighbors. The magnitudes of the error bars for each spectrum are shown on the legend.
Figure 5.8: Oxygen K edge onset from center of tunnel barrier. The oxygen K edge from amorphous alumina had a much more gradual onset than the edge from sapphire. The oxygen K edge fine structure shows the shape of the unoccupied density of states with $p$-symmetry in the barrier. Thus the gradual onset indicated that the conduction band in the tunnel barrier has a significant band tail. The magnitudes of the error bars are equal to heights of data markers.
sapphire has a measured band gap of 8.8 eV [French90], which leads to an expected barrier height of 4.4 eV assuming the Fermi energy is centered in the gap.

It should be noted that in insulators the core hole that is created by removing a core electron can sometimes significantly modify the local density of states. In such a case the interpretation taken above for the oxygen K edge would not be entirely correct. However, the oxygen K edges calculated for two crystalline forms of alumina (γ-alumina and α-alumina) [Brydson96] as well as for amorphous silica [Neaton00] show no significant core-hole effects. (The amorphous silica result is relevant since the oxygen K edge is more sensitive to oxygen second-nearest neighbors than to silicon nearest neighbors [Wallis95].) Also core-hole effects tend to sharpen the edge onset rather than blur it; clearly there are no sharp features at the edge onset for the spectrum of amorphous alumina in Figure 5.8.

5.5.4 Barrier disorder

Disorder in the barrier is predicted to have a large effect on the spin polarization of the tunneling current [Tsymbal98]. Using a tight-binding approach, Tsymbal and Pettifor parameterized the amount of disorder in the barrier as the width of an assumed random gaussian distribution of on-site energies for atoms in the barrier. The results showed that tunneling occurs through a few localized resonant channels that have a lower effective barrier than surrounding channels\(^3\). Barriers with greater disorder were predicted to transmit current with less spin polarization due to a lower effective barrier.

\(^3\) BEEM measurements of barrier height will likely not be sensitive to these resonant channels which do not in general conserve momentum direction.
This was due to resonant channels with very low barriers that allowed coupling of electronic states through the barrier.

While the alumina barrier was disordered, it was not completely random on a local scale as assumed in Tsymbal and Pettifor’s theory. It had some short-range order as evidenced by the shape of the aluminum L$_{3,2}$ edge (Figure 5.7), which matched a calculation for aluminum in tetrahedral coordination with its oxygen nearest neighbors [Brydson96]. See section 4.5.4 for further discussion of local ordering in amorphous alumina.

Short-range order plays a very important role in determining electronic structure [Sutton93]. For example, a study of amorphous silica showed that the local band gap in the vicinity of a particular oxygen atom depends explicitly on the number of its oxygen second-nearest neighbors [Neaton00]. Thus it is order or disorder on a local scale that will have the largest effect on electronic structure; the fact that the barrier is disordered on a long-range scale reveals very little. Additional studies promise to reveal the precise nature of short-range structure of the aluminum oxide barrier, which could aid greatly in understanding spin-polarized transport through such barriers (see section 6.3.3).

5.6 Barrier edges

The barrier edges are of great interest since tunneling is expected to occur between the first few atomic layers on either side of the barrier. Since the materials fabrication process is not well understood on an atomic scale, it is very possible that the composition of these layers is different from the bulk ferromagnet. This could cause magnetization at the interface to deviate from
the bulk value or introduce (spin-sensitive) scatterers. Even if the chemical
transition between ferromagnet and insulator were atomically abrupt, very
different magnetic and electronic properties could result depending on
whether the barrier were aluminum-terminated, oxygen-terminated or a
combination of both. Very little experimental work exists which addresses
these important questions.

5.6.1 Data acquisition and processing

PEELS spectra across the alumina barrier were acquired for the oxygen
K, aluminum L and cobalt L edges. The oxygen and aluminum spectra were
taken as described in section 5.5.1. The cobalt spectra were acquired in the
same manner as the oxygen spectra. The aluminum L edge spectra were
processed as described in section 5.5.1. The cobalt L edge spectra were
deconvolved with the zero-loss spectrum to remove the detector point spread
function.

The largest change in the cobalt L₃ edge fine structure was actually
measured near the center of the barrier, despite the fact there was no cobalt in
the center of the barrier (see section 5.5.2). This was due to interfacial
roughness which resulted in the averaging of bulk and interface spectra,
except near the barrier “center” where the beam was sampling mostly
interface cobalt atoms. The greater beam spreading in cobalt versus in the
alumina amplified this effect. The interfacial cobalt spectrum was determined
by averaging over a 12 Å wide region approximately centered on the barrier.

As noted in section 5.5.1, the cobalt M and aluminum L edges overlap,
which made accurate background subtraction of the aluminum L edge
difficult. This was especially true towards the edges of the barrier, where
cobalt M edge intensity increased while aluminum L edge intensity decreased. It was further complicated by the fact that the aluminum L edge onset became more sloped at the barrier edges, making it difficult to determine where the edge began. Therefore, measurement of aluminum L edge fine structure was limited to spectra nearest the barrier center. The changes in aluminum L edge fine structure were symmetric across the barrier, so to reduce noise they were averaged as a function of absolute distance from the barrier center.

5.6.2 Physical structure

Figure 5.9 shows the averaged aluminum L edge as a function of absolute distance from the barrier center. At the edges of the barrier, the aluminum L edge onset became lower in energy and more sloped in comparison with the spectrum from the center of the barrier. In contrast, the oxygen K edge fine structure showed no observable change across the barrier.

The large change observed in the aluminum L edge and not the oxygen K edge near both cobalt/alumina interfaces strongly indicated that both barrier edges were aluminum terminated. In general, the near edge fine structure of core-loss edge is highly sensitive to nearest-neighbor atomic arrangements, and a change in fine structure indicates a change in nearest-neighbor bonding. This was confirmed by a layer-projected density of states calculation based on a cobalt/sapphire/cobalt magnetic tunnel junction [Oleinik00]. It predicted that for an aluminum- (oxygen-) terminated sapphire barrier, the interfacial aluminum (oxygen) layer had a
Figure 5.9: Aluminum L edge at cobalt/alumina interfaces. At the edges of the barrier, the aluminum L edge onset became lower in energy and more sloped in comparison with the spectrum from the center of the barrier. The large change observed in the aluminum L edge and not the oxygen K edge near both cobalt/alumina interfaces strongly indicated that both barrier edges were aluminum terminated. Also, the much lower onset of the interfacial aluminum L edge likely indicated the presence of metal-induced states within the band gap of the alumina.
very different layer density of states than other aluminum (oxygen) layers
within the interior of the barrier. In contrast the oxygen (aluminum) layers all
had very similar layer densities of states.

Note that some change in the oxygen K edge fine structure was
expected at the barrier edge, even though none could be observed. The
height of the first peak of the oxygen K edge is sensitive to the number of
oxygen second-nearest neighbors [Wallis95, Neaton00], which must decrease
at the interface. This change was also apparent in the layer-projected density
of states calculated for the oxygen layer nearest an interface in aluminum-
terminated cobalt/sapphire/cobalt structure [Oleinik00]. It was likely that
interface roughness resulted in averaging the interface signal with the bulk
signal so that the changes were smaller than the noise and thus hidden.

Figure 5.10 shows the interfacial cobalt L₃ edge. Compared to the bulk
cobalt spectrum, the interfacial cobalt had a shorter and wider L₃ peak. This
interfacial cobalt spectrum matched a spectrum from cobalt at a
cobalt/aluminum interface, indicating that interfacial cobalt atoms had some
aluminum nearest neighbors. This was consistent with the conclusion that the
barrier was aluminum terminated.

Formation of cobalt oxide was not observed at either interface. CoO
had an L₃ peak that was taller and narrower with a slightly lower onset than
that of bulk cobalt (see Figure 5.10). All of these changes were opposite from
what was observed in the interfacial cobalt spectrum. Also, the oxygen K
dge fine structure for CoO was very different than that observed at either
barrier edge. The lack of interfacial cobalt oxide at both barrier edges was also
consistent with an aluminum-terminated barrier.
Figure 5.10: Cobalt L edge at cobalt/alumina interfaces. The interfacial cobalt spectrum matched a spectrum from cobalt at a cobalt/aluminum interface, indicating that interfacial cobalt atoms had some aluminum nearest neighbors. No evidence of cobalt-oxygen bonds was observed. The interfacial cobalt spectrum also showed evidence of s-d hybridization, which causes the cobalt d-band spread in energy. The L$_3$ edge which reflected the empty d-DOS became broader as well. Error bars are equal to the heights of the data markers.
Aluminum termination of the barrier at the first interface was expected based on growth conditions. As shown in section 4.2, aluminum deposited on cobalt mixed at the interface due to a large favorable mixing energy. Since the 12 Å aluminum layer was probably slightly too thick for complete thermal oxidation [Knechten01], thermal oxidation was not expected to significantly rearrange this structure.

Aluminum termination of the barrier at the second interface was somewhat surprising. The formation of bulk CoAl releases 0.56 eV per atom [Hultgren73] which is much less than the 2.47 eV per atom released for bulk CoO [Knacke91]. This led to the expectation that a significant fraction of the interfacial bonds should be cobalt-oxygen bonds. However, no evidence of such bonds was seen at the top interface.

A first-principles density functional theory calculation [Jennison00] of metal/alumina/metal structures indicated that cobalt-aluminum bonds may indeed be strongly favored at the top interface. This study showed that when an ultra-thin alumina film was supported by aluminum, the addition of copper, platinum or palladium overlayers caused oxide-surface aluminum atoms to rise so only they contacted the overlayer. This resulted in a greater than 1 eV increase in binding energy per atom in the first atomic overlayer. While a detailed physical mechanism is not given for the preferred aluminum contact, it was suggested that elements to the far right of the periodic table might prefer cation rather than anion contact.

5.6.3 Electronic structure

The cobalt L\textsubscript{3} edge from cobalt/alumina interfaces (see Figure 5.10) showed evidence of s-d hybridization between cobalt d-states and aluminum
s-states. As a result of the s-d hybridization the cobalt d-band spread in energy, and the L₂ edge which reflected the empty d-DOS becomes broader as well (see [Muller98b] for an example with nickel-aluminum alloys). A theoretical calculation predicts that strong s-d hybridization between cobalt and aluminum atoms at a cobalt/alumina interface results in a positive spin-polarization for the tunneling current in the alumina, despite a negative spin-polarization of the density of states at the Fermi energy in cobalt [Nguyenmanh98]. Positive spin-polarization was observed experimentally for electrons tunneling from cobalt across an alumina barrier [Meservey94].

The aluminum L edge from cobalt/alumina interfaces (Figure 5.9) had a much lower onset than that from the barrier center. In fact the onset of the interfacial spectrum approached that of aluminum at a cobalt/aluminum interface. This likely indicated the presence of metal-induced states within the band gap of the insulating alumina. Such gap states are the tails of the metal wave functions that decay exponentially into the insulating side of the interface [Finnis96]. As a result of the gap states interfacial aluminum layers had a substantial density of states at the Fermi energy and were effectively metallic. This conclusions was supported by a layer-projected density of states calculation, which predicted that the interfacial aluminum layer in a cobalt/sapphire/cobalt structure would be metallic [Oleinik00]. Unfortunately, the aluminum L edge from alumina exhibits a substantial core-hole effect [Brydson96], which would necessitate the use of computer simulation for a more rigorous interpretation of its fine structure.

Finally, aluminum-termination of the barrier is predicted to affect the position of the Fermi energy relative to the band gap of the alumina. This depends on the strength of the dipole layer at the metal/insulator interface
[Bordier91]. This dipole layer forms due to charge transfer between the metal and the insulator, which in turn depends on the atomic structure of the interface. First principles calculations based on cobalt/sapphire/cobalt structures show that the Fermi energy is approximately 3.5 eV below the conduction band of sapphire with oxygen-terminated interfaces but only 1.5 eV below for aluminum-terminated interfaces⁴ [Oleinik00].

5.7 Sample damage

5.7.1 Damage during cross-section preparation

The polishing process used to make a cross-section sample for STEM study caused significant mechanical damage to the thinnest (approximately less than 150Å thick) areas of the wedge-shaped sample. The magnetic tunnel junction samples tended to separate at the alumina layer, which apparently had the weakest mechanical cohesion. This damage was avoided by choosing areas of study towards the thicker part of the wedge-shaped cross-section at least 500Å away from any obviously damaged region.

Over-polishing or under-polishing of the aluminum oxide layer relative to the nearby cobalt layers did not appear to be a problem. The relative thinness of the layer (~15Å) compared with the typical cross-section thickness (~200Å) tended to prevent significant variation in cross-section thickness due to differences in layer composition. EELS spectra across alumina barrier showed that the ratio of the zero loss peak area to the plasmon peak area remained constant, indicating uniform thickness of the cross-section sample.

⁴ The local density approximation used for these calculations tends to underestimate energies. The band gap in the sapphire layer is calculated to be 6.2 eV, which is 2.6 eV lower than the experimental value.
5.7.2 Radiation damage

Radiation damage to the aluminum oxide layer was a serious concern since “bulk” amorphous alumina damaged very easily (see section 4.5.6). Indeed, it was the reason this study of magnetic tunnel junctions was not attempted sooner. Fortunately, it was discovered that the thin alumina barrier in the magnetic tunnel junctions was comparatively highly resistant to radiation damage, due to the flanking cobalt layers.

Both knockout damage and ionization damage were potential forms of radiation damage to the alumina layer. Knockout damage causes loss of both aluminum and oxygen whereas ionization damage causes loss of only aluminum from the irradiated area [Humphreys90]. To test for such losses, the center of the alumina layer was exposed to a 0.074 nA, 2Å diameter beam for 60 seconds. Over this time period, no oxygen or aluminum loss was detected within the uncertainty of the measurements. This showed that neither damage mechanism had a large effect on the alumina layer and demonstrated that element concentration profile measurements could easily be performed with such a point beam.

During the above point beam exposure, the oxygen K edge developed a small pre-peak at 532 eV (Figure 5.11). This indicated that a
Figure 5.11: Radiation damage to amorphous alumina barrier. A pre-peak at 532 eV on the oxygen K edge indicates formation molecular oxygen, which is a result of ionization damage. Point beam exposure of amorphous alumina in the tunnel barrier caused much less damage than in bulk amorphous alumina, as shown by the much smaller pre-peak. Spreading the beam to a 60 Å line completely avoided damage to the barrier. Error bars are equal to the heights of the data markers.
small fraction of the exposed volume of oxygen atoms had formed molecular oxygen as a result to ionization damage. It was estimated that only 2.4% of the irradiated alumina barrier become molecular oxygen during sustained point beam exposure to a 230 Å thick cross-section. This fraction increased to 4% for a thinner, 170 Å cross-section. These estimates were made assuming that the relative height of the peak at 532 eV corresponded to the fraction of irradiated oxygen that was molecular oxygen. It was also assumed that the oxygen K edge from the point beam exposure of amorphous alumina corresponded to 100% molecular oxygen.

The dramatic reduction in molecular oxygen formation in the alumina barrier compared to bulk amorphous alumina was due to the flanking cobalt layers, which prevented the buildup of large radial electric fields that occur in bulk insulators during exposure to the electron beam. These large field gradients cause bulk aluminum cation migration away from the irradiated area and subsequent molecular oxygen formation [Humphreys90].

This small amount of radiation damage to the alumina barrier could be avoided completely by spreading the 2 Å diameter beam into a 60Å × 2Å line. Under the same conditions as for the point beam exposure described above, the alumina layer was exposed to a line beam for more than 30 seconds. During this time, the oxygen K edge fine structure remained the same as that of undamaged amorphous alumina, indicating no significant ionization damage had occurred. Thus, core-loss fine structure measurements on the alumina barrier could be successfully performed with the beam spread to a 60 Å wide line.
5.8 Limitations of bright field imaging

Images are an intuitive way to examine sample structure and can provide direct, localized measurements of layer roughness, interface sharpness, etc. in a way that other methods such as x-ray cannot. However, the very fact that electron microscope images look like common photographs can make it easy to draw false conclusions. The human eye uses a simple lens system to image light that is almost always from incoherent, reflective and localized scattering processes. In an electron microscope a wide range of imaging conditions and scattering processes are possible, most of which are unfamiliar to the human eye. Thus it is extremely important to know the imaging conditions when using an electron microscope and understand the effects of probe-sample interactions.

5.8.1 Bright field contrast

Low-angle scattering is a coherent, dynamical process. It generates a phase-contrast signal that is highly sensitive to diffraction effects as well as many other factors [Williams96]. Thus the bright field intensity can be difficult to interpret, especially in a quantitative manner.

One source of contrast in bright field imaging of the tunnel barrier is "mass-thickness" contrast, which results from differences in elastic scattering. Electrons elastically scatter to higher angles in cobalt than in aluminum oxide, and as a result fewer make it through the collector aperture to the bright field detector. This aperture-dependent amplitude contrast is similar to annular dark field in that it is a "Z-contrast" signal, and it has potential to accurately
reflect the barrier profile. However, other sources of contrast often add to the mass-thickness contrast and complicate the interpretation of the data.

A second source of bright field contrast when imaging the magnetic tunnel junction is Fresnel fringes. They are very pronounced due to the large difference in average electrostatic potential between cobalt and aluminum oxide. Although measurements of the average forward scattering potentials are not available for cobalt or aluminum oxide, an estimate can be made with copper and aluminum which have potentials of 19 V and 12 V respectively [Ross89]. The relative phase change in the weak phase object approximation is $\phi = \sigma \Delta U \times t$ where the constant $\sigma = 9.248 \times 10^6 \text{ V}^{-1} \text{ m}^{-1}$ (for 100 keV accelerating voltage), $\Delta U$ is the change in potential, and $t$ is cross-section thickness [Reimer84]. Assuming a cross-section thickness of 200 Å and estimating the potential change as 7 V, the relative phase change is 1.3 radians or nearly one-quarter of a wavelength. Since the intensity of the fringes scales linearly with $\phi$ (approximation best for small $\phi$) [Rasmussen90], this demonstrates that the Fresnel fringes will be pronounced even for very thin cross-sections.

5.8.2 Fresnel fringes in STEM bright field

High-resolution images of the magnetic tunnel junction sample were taken with a 40 μm objective aperture and 50 μm collector aperture. This corresponds to a $\alpha = 10.4$ mrad semi-angle acceptance into the objective lens and a $\beta = 0.45$ mrad semi-angle acceptance into the bright field collector. Under these imaging conditions the criterion for coherent imaging $\beta << 0.16\alpha$ is satisfied [Kirkland98] and the bright field image will be almost entirely coherent.
Figure 5.12 shows images and profiles of the alumina barrier selected from a through-focal series of the sample shown in Figure 5.2. Slight changes in defocus result in very different profile shapes in bright field. This is due to the strong presence of Fresnel fringes. They create deceptively sharp-looking cobalt/alumina interfaces in the “under-focussed” image. They also change the apparent width of the barrier from 12.3 Å in the “under-focussed” image to 14.4 Å in the “best focus” image (measuring full width at half maximum).

Fresnel fringes have least intensity when the focus is in the object plane (the criterion for “best” focus here). However, due to a finite cross-section thickness they never entirely disappear as seen from the “best focus” barrier profile. Note that when inverted and scaled properly the “best focus” bright field profile matches the annular dark field profile with the exception of the residual Fresnel fringes (see Figure 5.13). This is because the barrier profile contains primarily mass-thickness contrast.

The appearance of Fresnel fringes makes it very difficult to determine barrier width or chemical interface sharpness from a single bright field image, although models exist for extracting this information from a through-focal series of images [Ross91, Rasmussen90]. The reciprocity theorem [Pogany68] guarantees that this conclusion also holds for single TEM bright field images, as demonstrated in the following section.
Figure 5.12: Fresnel fringes at tunnel barrier in STEM bright field. The images and profiles of the alumina barrier were selected from a through-focal series of the magnetic tunnel junction shown in Figure 5.2. Slight changes in defocus resulted in very different barrier profiles in bright field. This was due to the strong presence of Fresnel fringes.
Figure 5.13: Comparison of barrier profiles from STEM bright field and annular dark field at best focus. Fresnel fringes had least intensity when the focus was in the object plane (the criterion for "best" focus here). However, due to a finite cross-section thickness they never entirely disappeared. Note that when inverted and scaled properly the "best focus" bright field profile matched the annular dark field profile with the exception of the residual Fresnel fringes. This was because the bright field barrier profile contained primarily mass-thickness contrast.
5.8.3 Fresnel fringes in TEM bright field

Images of a magnetic tunnel junction sample were taken on a conventional TEM since this is a common method of atomic-scale structural analysis. TEM bright field imaging confirmed the conclusions drawn in the previous section regarding the limitations of bright field imaging to reveal meaningful structural information. Dr. Nan Jiang, a TEM expert, took images on the JEOL 4000 EX at Cornell University. It is a 400 keV analytical TEM specified to have 1.4Å information limit.

Figure 5.14 shows a TEM image of the magnetic tunnel junction. Fresnel fringes are visible at many interfaces that are well-aligned with respect to the illumination direction. Their signature is a dark line at the edge of the cobalt next to a bright line at the edge of the alumina. The Fresnel fringes create the appearance of interfaces with atomically-sharp changes in chemical composition, similar to the “under-focussed” image in STEM bright field (see Figure 5.12). The width of the alumina layer appears to be about 13Å as calibrated from the silicon lattice. The Fresnel fringes are likely responsible for the 2 Å narrower appearance of the alumina layer compared to STEM annular dark field.

In many cases the Fresnel fringe signature noted above is not readily visible to the eye; however, Fresnel fringes can still strongly affect interface appearance. For example, the top inset to Figure 5.14 shows an enlarged 30 Å section of the barrier indicated by the white arrowheads. The cobalt/alumina interfaces appear sharp and there is no obvious Fresnel fringe signature. In Figure 5.15, averaging the barrier profile along a 1.5 Å length shows random oscillations in the barrier intensity mainly due to its amorphous structure. However, averaging the barrier profile along the
Figure 5.14: TEM bright field image of magnetic tunnel junction. The top inset shows an enlarged 30 Å section of the barrier from the region indicated by the white arrowheads. The bottom inset shows a STEM annular dark field image taken at exactly the same location. Note that the cobalt/alumina interfaces appear sharp in TEM and diffuse in STEM annular dark field.
Figure 5.15: Comparison of barrier profiles from TEM bright field and STEM annular dark field. The barrier profiles are taken from the inset images in Figure 5.14. In TEM the intensity profile 1.5 Å section of the barrier shows random oscillation due to its amorphous structure, which hide the presence of Fresnel fringes. However, averaging the barrier profile along the entire 30 Å section removes the random oscillations and reveals the presence of Fresnel fringes. These Fresnel fringes create the appearance of atomically sharp cobalt/alumina interfaces. Annular dark field shows that the interfaces should appear diffuse in a transmission image due to barrier roughness.
entire 30 Å section removes the random oscillations reveals the presence of Fresnel fringes.

As a result of these fringes, the apparent width of the top (right, in images and plot) interface is only 1.6 Å (measuring 20% to 80% change in signal). This value is not very believable since barrier roughness should cause the profile to appear blurred in a transmission image. This can be easily visualized by noting the image in Figure 5.14 shows a 300Å section of the alumina barrier, which is also the thickness of the cross-section sample. Indeed, a STEM annular dark field image taken at exactly the same location (Figure 5.14, bottom inset) shows diffuse-looking interfaces. Averaging the annular dark field barrier profile along the same 30 Å length shows the top interface having a 6.0 Å width (see Figure 5.15), four times wider than in TEM.

Since there is no unique best focus in high-resolution TEM imaging [Kirkland98] and lattice fringes appear over a wide range of focal values, it is likely that a TEM operator will choose the focus that gives the sharpest-looking interfaces. Such an image will almost certainly contain Fresnel fringes. Attempts to get a truer image, such as one showing only "mass-thickness contrast," require careful examination of a through-focal series to identify the defocus at which the fringes are weakest. In practice this may be very laborious if the TEM has instabilities or has only photographic recording equipment (both are true of the TEM used in this study). Furthermore, such attempts will be met with only limited success since as demonstrated in STEM bright field the Fresnel fringes never completely disappear for any focus, even with thin cross-sections.

In conclusion, TEM is of limited use in revealing structural information about magnetic tunnel junction barriers. Strong Fresnel fringes, which are not
always readily visible to the naked eye, can cause deceptively sharp-looking interfaces and change the apparent thickness of the barrier. Unfortunately, single TEM images have often been used as evidence of atomically abrupt interfaces in magnetic tunnel junctions and have even been used to ascribe significance to an apparent 2Å change in barrier thickness [Smith98, Parkin99, Dunin-Borkowski99]. Fresnel fringes are clearly visible in most of these images, which makes their conclusions highly questionable.

5.8 Conclusions

Some important physical and electronic features in the magnetic tunnel junctions were identified that were expected to affect the spin-polarization transport. The overall structure of the magnetic tunnel junction was characterized by a remarkably uniform width of the alumina barrier. This demonstrated that aluminum wets cobalt very well, which is important for forming a pinhole-free tunnel barrier. The roughness of the alumina layer was correlated with the grain structure of the underlying cobalt layer. Roughness, which was undesirable for magnetic tunnel junction performance as well as STEM analysis, was reduced by decreasing grain size.

The central region of the barrier was identified as amorphous alumina, which contained fully or near-fully oxidized aluminum. Physical disorder resulted in a band tail in the alumina barrier conduction band. This extensive band tail lowered the height of the barrier relative to the expected value for a perfect crystalline sapphire barrier, in agreement with experimental observation.
Theory predicts that random disorder creates resonant channels through the barrier and lowers the spin-polarization of the tunneling current. However, the amorphous alumina barrier was observed to have some short-range order, which made the validity of the theory questionable. Further studies promise to reveal the precise nature of short-range structure of the alumina barrier, which could aid greatly in understanding spin-polarized transport through such barriers.

Both edges of the barrier were aluminum-terminated. The interfacial aluminum layers had a very different electronic structure than aluminum layers in the center of the barrier and were probably metallic. Each electrode of the magnetic tunnel junction should be thought of as cobalt terminated by a monolayer of aluminum rather than pure cobalt.

$s$-$d$ hybridization was observed in cobalt-aluminum interfacial bonds. This type of bonding is predicted to strongly affect the spin-polarization of the tunneling current, reversing its polarity relative to that of bulk cobalt. This would provide an explanation for experimental observations of a positively spin-polarized tunneling current from cobalt across an alumina barrier.

There was no evidence of cobalt oxide at either interface, which if present would allow strong coupling to magnons at higher bias voltages. Such an effect has been used to explain the universal reduction of magnetoresistance values with increasing bias voltage in magnetic tunnel junctions. The observed lack of cobalt oxide calls this theory into question.

TEM was shown to be of limited value in analyzing magnetic tunnel junctions. Strong Fresnel fringes in the vicinity of the barrier complicated the interpretation of coherent bright field STEM and TEM images. Due to their presence, a single under-focussed image could show cobalt/alumina interfaces
that falsely appeared to be atomically sharp. In addition, TEM can not give any information regarding short-range order in thin layers, which is very important in understanding electronic structure.
Chapter 6

Conclusions

6.1 Structure of magnetic thin-film systems

This section summarizes the main experimental results regarding the structure of cobalt/ alumina/ cobalt magnetic tunnel junctions and copper/ cobalt multilayers. It puts these results in perspective with other work in the field.

6.1.1 Magnetic tunnel junctions

STEM has proved to be a powerful probe of tunnel barrier structure, allowing a more sophisticated and realistic understanding of its structure. Often the tunnel barrier is assumed to be a simple rectangular barrier, and current-voltage curves are fitted to extract barrier height and width [Simmon63]. However, a rectangular barrier is only appropriate for a perfectly crystalline barrier with atomically sharp, smooth edges. STEM analysis has shown that the barrier is amorphous. This disorder creates a tail
in the conduction band and has several consequences for spin-polarized transport through the barrier. First, the conduction band tail lowers the average barrier height compared to a perfect crystalline $\alpha$-alumina barrier; this explains ballistic electron emission microscopy measurements of a relatively low barrier height [Rippard01]. Second, disorder implies a spatially non-uniform barrier height. When disorder is modeled as a random gaussian distribution of on-site energies for barrier atoms, channels with very low barriers dominate barrier transport and reduce spin-polarization by allowing coupling of states through the barrier [Tsymbal98]. This model is likely inappropriate, since the amorphous alumina barrier was shown to have short-range order and likely can not be modeled by such an energy distribution. However, a focus on the energy associated with local barrier structural arrangements is useful, and further studies promise to reveal more (see section 6.3.3).

Electrons tunneling from cobalt through an alumina barrier have positive spin-polarization, despite a greater negative density of states for cobalt at the Fermi energy [Meservey94]. Theorists have long attempted to explain this result. One school of thought predicts that spin-polarization is very sensitive to structure and bonding at ferromagnet/insulator interfaces [Tsymbal97]. STEM characterization of cobalt/alumina/cobalt tunnel junction provides the first experimental evidence in support of this theory. Observation of strong $s$-$d$ hybridization between cobalt and aluminum atoms at cobalt/alumina interfaces is consistent with a first-principles calculation that predicts a positively spin-polarized tunneling current for such a structure [Nguyen-Manh98]. Basically, the Fermi energy of cobalt lies above the majority $d$-band, but in the middle of the minority $d$-band, implying a negative
spin-polarization for $d$-states at the Fermi energy. Hybridization of the $d$-states of cobalt with the $s$-states of the interfacial aluminum layer induces a positive spin-polarization for the aluminum $s$-states at the Fermi energy. This positive spin-polarization in the density of states was shown to extend well into the alumina barrier, and implies a positive spin-polarized tunneling current.

A common explanation for the universal drop in magnetoresistance observed with increasing bias voltage is excitation of magnons, which can lead to spin-flip scattering and a reduction in spin-polarization. In order to achieve quantitative agreement with experiment, most theories assume the existence of an antiferromagnetic oxide at tunnel barrier edges. Such an oxide would allow strong excitation of the magnon spectrum by electrons tunneling through the barrier. However, no cobalt oxide formation was observed in the magnetic tunnel junction structure. Thus, another explanation for the bias voltage effect is necessary, such as a different physical mechanism for the generation of magnons or another effect entirely.

### 6.1.2 Copper/cobalt multilayers

There has been much debate about the physical structure of copper/cobalt interfaces. STEM analysis has shown that copper/cobalt interfaces are chemically sharp. They have a large amplitude ($5 \, \text{Å} \text{ root-mean-square}$), short-wavelength ($<< 250 \, \text{Å}$) roughness. The short wavelength roughness indicates a high density of spin-dependent scattering potentials that according to some theoretical calculations will create or at least contribute to the giant magnetoresistance effect [Zhang92, Todorov96]. In addition, there is a long-wavelength ($280 \, \text{Å}$) roughness of large amplitude ($4.2 \, \text{Å} \text{ root-mean-}
square) associated with heteroepitaxial grain structure. This long wavelength roughness is correlated from layer to layer which leads to Neel orange-peel coupling which diminishes giant magnetoresistance values [Misra95].

Low angle x-ray diffraction is a very common technique for measuring interface roughness. Such studies typically report values for root-mean-square roughness of 1 - 4 Å [Ueda94, MacKay96], which are somewhat smaller than the values indicated from STEM analysis. However, it is often overlooked that the Fresnel formalism used extensively to interpret x-ray data only gives qualitative predictions and that a quantitative understanding is lacking [Falicov90]. Furthermore, such theories often assume that roughness is uncorrelated, which is clearly not the case for the large-wavelength roughness.

There has been much debate about the relationship between the structure of copper/cobalt interfaces in multilayers and the giant magnetoresistance phenomenon. Often conflicting conclusions are drawn by x-ray diffraction studies. For example some studies report decrease in magnetoresistance with increasing interface roughness [Ueda94] while others report the opposite trend []. A possible explanation for these confusing results is that low-angle x-ray diffraction is insensitive to roughness correlation lengths. As revealed by STEM analysis, there are two different kinds of roughness, one which leads to an increase in GMR and the other which leads to a decrease. Since low angle x-ray diffraction cannot distinguish between these two types of roughness, it is not surprising that seemingly conflicting conclusions might be drawn. This demonstrates that x-ray diffraction is a poor technique for probing magnetic multilayer structure.
6.2 STEM technique

This section summarizes the main techniques used for STEM characterization of thin-film magnetic structures. It describes what was found to be effective for sample preparation, imaging, and EELS analysis.

6.2.1 Sample preparation

A high quality cross-section sample was essential for getting high quality STEM data. This was achieved by growing interfaces with as little roughness as possible, since in most cases roughness effectively reduces spatial resolution. It was demonstrated that limiting film thickness limits grain size and reduces interface roughness. Other methods proposed for reducing roughness were use of a surfactant such as silver during copper/cobalt multilayer growth [Yang] and growth of films on an atomically flat silicon substrate [Huang98].

Another critical factor for making successful wedge-polished samples was mechanical integrity. Films with poor adhesion, such as cobalt on silicon oxide, delaminated during mechanical polishing. This almost always led to poor quality samples that required extensive ion milling. However, films with good adhesion, such as cobalt on silicon, remained intact during polishing. This has consistently lead to high quality samples that require no ion milling.

Finally, ion milling was shown to be an undesirable method for additional thinning of many of the cross-section samples examined in this dissertation. Extensive ion milling of cobalt/aluminum multilayers very likely modified their structure. Heating or substantial redeposition of sputtered material led to cobalt/aluminum interfaces that were atomically mixed over
more than 50 Å. Ion milling of cobalt oxide layers in cobalt also caused substantial damage, allowing the release of oxygen so that the thinnest cross-section regions contained no oxygen.

6.2.2 Imaging

Annular dark field imaging was superior to bright field imaging for examining sample structure. Bright field imaging, including conventional TEM imaging, easily led to deceptively sharp-looking cobalt/alumina interfaces in a magnetic tunnel junction sample. This was due to the presence of Fresnel fringes. Annular dark field images were simpler to interpret, since this imaging mode has a unique best focus and is sensitive primarily to atomic number.

Image resolution was limited by interface roughness. The diffuse appearance of the annular dark field profile of cobalt/alumina interfaces in magnetic tunnel junctions was partly due to interface roughness. It was difficult to determine the level of atomic-scale mixing from imaging alone.

6.2.3 EELS technique

In many cases, very thin (200 Å or less) cross-sections were critical for collecting core-loss EELS spectra with high signal-to-noise ratios. Elastic scattering of the beam within the cross-section sample causes beam broadening. Beam broadening reduces the flux of electrons entering the EELS spectrometer. Thus, for close-packed, high-Z materials that scatter strongly (e.g. cobalt and copper) or core-loss edges with low intensity (e.g. copper L edge and aluminum L edge), thin cross-sections were especially important.
Near edge fine-structure analysis of core-loss EELS spectra was a powerful technique for revealing atomic-scale structure. Fine-structure analysis was able to distinguish between rough, chemically sharp interfaces in copper/cobalt multilayers and chemically diffuse interfaces in cobalt/aluminum multilayers. It also identified the phase of the alumina forming a tunnel barrier as amorphous rather than crystalline. Finally, fine-structure analysis gave important information on electronic structure, such as showing that the conduction band in the amorphous alumina tunnel barrier had a band tail.

Quantitative EELS analysis required a good understanding of beam-sample interactions. Differences in elastic scattering between materials of different atomic number led to substantial variation in the flux of electrons entering the EELS spectrometer. Raw EELS signals had to be adjusted by as much as a factor of two to make a quantitatively accurate element map across a cobalt/alumina/cobalt magnetic tunnel junction. Channeling, which also can affect quantitative EELS measurements, was avoided by deliberately choosing off-axis conditions for all measurements.

6.3 Future work

Many atomic-scale structural features that are likely important for understanding spin-polarized transport have been identified in a single magnetic tunnel junction sample. A comparison with other magnetic tunnel junctions that have been slightly modified would strengthen this study and help put the initial results in perspective. Such studies could help identify which features magnetoresistance is most sensitive to, and answer questions
regarding barrier formation. For these studies, the capability to measure the magnetoresistance of the magnetic tunnel junctions would be highly desirable.

6.3.1 Annealing studies of magnetic tunnel junctions

It would be interesting to examine magnetic tunnel junctions that have been annealed to improve magnetoresistance. One study [Sousa99] showed that increase in magnetoresistance is correlated with increase in barrier height, as determined by fits to I-V curves. While this was attributed to an increase in symmetry of oxygen distribution across the barrier as revealed by Rutherford back-scattering measurements, this is also consistent with the barrier becoming more ordered. Oxygen K edge fine structure will show an increase in order through a general sharpening of its features. This includes a taller, narrower first peak and a sharpening of the edge onset. The aluminum L edge should also be monitored for any coordination changes.

6.3.2 Tunnel barrier formation studies

It was shown that for evaporated cobalt/aluminum layers, an estimated 4±1 monolayers of pure cobalt mix with aluminum at the interface. Sputtering likely produces interfacial mixing of a similar or even greater extent due to its more energetic process. This means that most or all of a 7 Å aluminum layer deposited on cobalt, which is typical for magnetic tunnel junctions, will be mixed with the cobalt. The extensive mixing raises the question of how oxygen reacts with the mixed cobalt-aluminum region to form an alumina tunnel barrier. It was established that the barrier contains no cobalt, and therefore that oxygen reacts selectively with the aluminum. One possibility is that the oxygen only reacts with pure aluminum and not the
mixed cobalt-aluminum region. However, in this case the bottom cobalt electrode would contain substantial aluminum, which would probably reduce or even eliminate its interfacial magnetic moment and consequently the magnetoresistance. The other possibility is that the oxygen pulls aluminum out of the mixed cobalt-aluminum region to a greater or lesser extent. It is known that oxidation of the (111) surface of bulk CoAl causes the aluminum atoms in the first atomic layer to react with oxygen to form a 5 Å alumina layer [Franchy00].

To address the question raised above, it would be interesting to characterize interfacial mixing in sputtered cobalt/aluminum layers. A quantitative comparison of the amount of cobalt-aluminum alloy in an oxidized versus an unoxidized cobalt/aluminum layer structure would reveal whether the oxygen interacts with the cobalt-aluminum alloy and give a more detailed understanding of the barrier formation process.

Barrier oxidation conditions are another approach to studying barrier formation. Ballistic electron emission microscope studies of alumina barrier formation reveal that below a certain threshold, low oxygen doses result in barriers with weak areas that allow greater ballistic conduction. STEM characterization of such incomplete barriers to reveal their physical and electronic structure could give insight into the barrier formation process. Another possible study involves using plasma oxidation rather than thermal oxidation to form the alumina barrier. Magnetoresistance is very sensitive to oxygen plasma dose. It is believed that too little oxygen leaves metallic aluminum while too much oxygen causes oxidation of the bottom cobalt electrode. STEM could be used to characterize a magnetic tunnel junction that has been plasma oxidized to give the maximum magnetoresistance. This
would reveal the optimal structure for the bottom cobalt/alumina interface, and possibly give insight into the spin-polarized tunneling process.

6.3.3 Structure of amorphous tunnel barrier

A better structural determination of the amorphous aluminum oxide barrier would allow a realistic model of barrier electronic structure. This would give a better understanding of spin-polarized transport through the barrier and show if e.g. resonant channels [Tsymbal98] are an important feature for such transport. This would likely involve collaboration with theorists who could use density functional theory to generate a realistic electronic structure and examine the consequences of realistic defects, as determined by STEM characterization.

Amorphous alumina generally has a high degree order (see section 4.5.5). With more careful EELS measurements, it would be possible to determine quite a bit about its local atomic structure. As discussed earlier, the aluminum L edge fine structure reflects the average aluminum coordination. Decomposition of the shape based on octahedral- and tetrahedral-coordination fingerprints could give the fractional occupation of both kinds of sites. A more precise determination of the aluminum to oxygen ratio to within 5% error is possible with better measurements. The oxygen K edge fine structure, which is mainly determined by oxygen neighbors [Wallis95], could be used to determine the degree of order in the oxygen sublattice. Finally, since the evaporated alumina sample was shown by EELS fingerprint identification to have the same structure as the barrier oxide, a precise radial distribution function can be determined from better electron diffraction measurements of this film (see section 4.5 for first results). Also, micro-
diffraction has the potential to reveal three- and four-body correlation functions using a fluctuation statistics approach [Voyles]. This information can also be determined from the extended fine structure of the EELS core-loss edges.
References


[Voyles] P. Voyles, D.A. Muller, unpublished.


