ELECTRONIC STRUCTURE OF OXIDE TUNNEL BARRIERS AND GAAS – FERROMAGNET INTERFACES

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
Phillip G Mather
January 2006
In this thesis, I have used scanning tunneling spectroscopy (STS) to examine the density of states (DOS) at oxide tunnel barrier surfaces and ballistic electron emission microscopy (BEEM) to determine how these states couple through the oxide layer. I have also employed BEEM to understand the nature of ballistic electron transport at Ferromagnet - Semiconductor interfaces.

The DOS of the uncovered and oxygen covered AlO$_x$ surface changes when chemisorbed oxygen ions are moved into the oxide by either electron bombardment (EB) or by thermal annealing. Both treatments increase the oxide band gap, however EB, which has similarities in effect to depositing a metallic overlayer with a high work function, has different effect on the oxide states than anneals. The former, if sufficiently energetic, results in locally well defined conduction band onsets at $\sim$1 V, while the latter results in a progressively higher local conduction band onset, exceeding 2.3 V for 500° and 600° C thermal anneals.

I have grown (001) textured MgO barrier layers through several deposition techniques. While bulk MgO has a band gap of $\sim$ 7 eV, fits to IVs from fully formed devices typically exhibit a barrier height of $\sim$ 0.5 eV. Measuring the band structure as the full band gap degenerates in the transition from 30 Å to 15 Å films lends insight into how these fits can be explained. Initially sparsely populated
distinctly resolvable defect states due to both oxygen and magnesium vacancies are present. These states gradually meld together as the films become thinner, forming band tails that extend to $\sim 500$ mV both above and below the Fermi level in the 15 Å films.

I also have utilized BEEM to measure scattering at the interface between GaAs and sputtered Fe, Co$_{50}$Fe$_{50}$, Ni$_{81}$Fe$_{19}$, and Molecular Beam Epitaxially (MBE) deposited Fe. For the sputtered films, NiFe has the least amount of scattering and the highest hot electron transfer ratio, while MBE (001) oriented Fe has minimal scattering. I attribute this behavior both to the presence of a thin oxide layer at the interface between the Fe and GaAs, and to interfacial alloying in the sputtered films.
BIOGRAPHICAL SKETCH

Phil Mather was born in Kalamazoo, MI in September of 1976, where after an initial four year stint in Westchester, PA, he stayed in the area until the conclusion of college. After working through initial complaints that kindergarten was cutting too much into his play time, his parents fostered an early interest in Math and Science. This was facilitated through his fathers establishment and direction of Adventures in Spaces, a program designed to stimulate interest in science elementary and middle school students.

While, in his youth, Phil thoroughly enjoyed making devices to blow things up. However, a senior internship while attending KAMSC (a math and science magnet school for high school students) was instrumental in demonstrating that chemistry was not where his interests were. He went on to attend Kalamazoo College in 1995, majoring in Physics and some other things, and managed to get away to Quito, Ecuador for a six month study abroad program. A few months after leaning over to make some comments about the overly energetic professor of a class on Chinese Philosophy to Natalia, the student next to him, Phil adjusted his classes to enable a full year of study abroad. They were married in October of the following year. One year later upon graduation, they came to Cortland, NY to pursue graduate studies at Cornell and Syracuse Universities. Phil received his Masters Degree in 2003, and after ∼6\(\frac{1}{2}\) years at Cornell, Phil received his Ph.D in Applied Physics. They are now journeying out into the sunset to the Southwest.
Para Natalia
ACKNOWLEDGEMENTS

Many people have contributed both to this work and to my sanity both during the long hours and late nights when some piece of equipment decided things had been going smoothly for long enough, or when the data was particularly confusing. Without them, this thesis would be a shadow of what you are holding today.

First and foremost, I would like to thank my advisor Bob Buhrman whose support, insightful comments, and incredible ability to pull together ideas from widely dispersed areas of physics proved invaluable to both interpreting results and trouble shooting misbehaving equipment. He has been a constant source of information and ideas during my last six years here. I would also like to thank Dan Ralph and Clif Pollock for serving on my committee and reviewing this work.

All of the members of the D7 peninsula of Buhrmania have been especially helpful. When I joined the group, the BEEM section of the lab consisted of one microscope (old BEEM) and one sample preparation chamber. As well as teaching me about the operation (and troubleshooting) of old BEEM, and BEEM principles in general, Andrew Perrella helped greatly in working through many of the problems of bringing a second microscope and sample preparation chamber on line. His positive attitude in the face of impediments continues to amaze me. John Read joined the lab a few years ago, and now has become sole occupant of D7. He is the source of the MgO XPS data lending insight into the physical structure of the different MgO films. We have spent many late nights together swearing at broken equipment, and discussing data, Art, Music, and Politics. He has been a great source of support through the years, and it with great confidence that I leave the lab to him. Ei-leen Tan is responsible for bringing the XPS system back into operation after years of neglect, as well as taking all of the XPS data on AlO$_x$ that
is mentioned in this thesis.

I would also like to thank other members and ex-members of the Buhrman group, with whom I embarked upon many enjoyable discussions: Ozhan Ozatay, Nate Emley, Pat Braganca, Aycan Yurtsever, Juting Zhai, Eric Ryan, Greg Fuchs, and Preeti Chalsani.

The individuals in both the student and Pro Shop were an excellent support for helping with the various difficult machining projects I embarked upon, as well as providing timely emergency welding repair jobs: Bob Snedeker, Nate Ellis, Stan Carpenter, Jeff Koski, Rodney Bowman, Chris Cowulich, and Stan Mcfall. Ron Kemp was a wonderful resource in the facilities of the Technical Operations Lab.

Finally, I’d like to thank my parents for encouraging and supporting me in my pursuits of science. A special appreciation goes to my wife, Natalia Alvear for putting up with all those late nights (and early mornings) that I have put in over the years.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>References for Chapter 1</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>Magneto-electronic Measurements and Devices</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>2.1 Tunneling Models</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>2.1.1 Normal Metallic Systems</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>2.1.2 Spin Polarized Tunneling</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>2.2 Magnetic Tunnel Junctions</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>2.2.1 AlO&lt;sub&gt;x&lt;/sub&gt; Based MTJs</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>2.2.2 MgO Based MTJs</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>2.2.3 Devices</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>2.3 Other Uses for Thin Insulating Oxide Layers</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>2.3.1 Josephson Junctions</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>2.3.2 Gate Dielectrics</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>2.4 Spin Injection into Semiconductors</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>References for Chapter 2</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>Scanning Tunneling and Ballistic Electron Emission Microscopies</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>3.1 STM Techniques</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>3.1.1 Measuring Local Work Function</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>3.1.2 Measuring Local Density of States</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>3.2 Ballistic Electron Emission Microscopy</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>3.2.1 Bell Kaiser Model of BEEM Transport</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>3.2.2 Ludeke Bauer Model of BEEM Transport</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>3.2.3 Modelling Interfacial Scattering</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>References for Chapter 3</td>
<td>73</td>
</tr>
<tr>
<td>4</td>
<td>Experimental Procedures</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>4.1 Old BEEM</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>4.2 Prep I</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>4.3 Load Lock</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>4.4 Prep II</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>4.4.1 Sample Transfer</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>4.4.2 Evaporation Flange</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>4.4.3 Atom Source</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>4.4.4 Sputter System</td>
<td>88</td>
</tr>
</tbody>
</table>

References for Chapter 1:
6
References for Chapter 2:
46
References for Chapter 3:
73
References for Chapter 4:
75
References for Chapter 6

ix
# LIST OF TABLES

<table>
<thead>
<tr>
<th></th>
<th>Table Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Comparison of current memory types</td>
<td>34</td>
</tr>
<tr>
<td>4.1</td>
<td>Deposit SiO$_2$ in IPE PECVD</td>
<td>114</td>
</tr>
<tr>
<td>4.2</td>
<td>Spin photoresist</td>
<td>115</td>
</tr>
<tr>
<td>4.3</td>
<td>Expose photoresist</td>
<td>115</td>
</tr>
<tr>
<td>4.4</td>
<td>Develop photoresist</td>
<td>116</td>
</tr>
<tr>
<td>4.5</td>
<td>Etch SiO$_2$</td>
<td>116</td>
</tr>
<tr>
<td>4.6</td>
<td>Prepare ohmic contact</td>
<td>117</td>
</tr>
<tr>
<td>4.7</td>
<td>Prepare sample dice</td>
<td>118</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

2.1 Simple model for electron tunneling ............................................ 9  
2.2 Fe DOS .......................................................... 13  
2.3 Generic ferromagnetic "Nickel" DOS ........................................... 13  
2.4 Allowed tunneling processes for MTJs ......................................... 15  
2.5 Demonstration of large TMR at room temperature ......................... 19  
2.6 Fe band structure ....................................................... 23  
2.7 Tunneling DOS of Fe(001)/MgO(001)/Fe(001) system ..................... 24  
2.8 Impact of anneal temperature on tunnel junction performance ........... 27  
2.9 Technology as a function of resistance area product ........................ 30  
2.10 Bias dependance of TMR .................................................. 30  
2.11 Individual MRAM bit and arrays ............................................ 36  
2.12 MRAM resistance distributions .............................................. 37  
2.13 Charge based JJ qubit ..................................................... 42  

3.1 Topographic and DOS images; conventional IV and direct $\frac{dI}{dV}$ measurements ................................................ 56  
3.2 Experimental and energy diagram for BEEM ................................. 58  
3.3 BEEM, STM, DOS, and local workfunction images of 135 Å Au film .... 60  
3.4 Energy levels of interest for BK model ..................................... 62  
3.5 Conduction band minima for GaAs (100) ................................... 65  
3.6 Projection of electron beam upon GaAs CBM ................................ 66  
3.7 BK and LB calculations for BEEM current .................................. 71  

4.1 Layout of D7, past and present ................................................. 77  
4.2 Inverting current to voltage preamplifier ................................... 81  
4.3 Vacuum annealing oven ...................................................... 83  
4.4 Prep II ........................................................................ 85  
4.5 Wobble stick jaws ............................................................... 89  
4.6 Sample staging area ............................................................ 91  
4.7 New BEEM .................................................................. 93  
4.8 Beetle scan head design ......................................................... 95  
4.9 RHK bottom flange ............................................................. 98  
4.10 Floating preamp design ......................................................... 111  
4.11 External STM preamp .......................................................... 112  
4.12 X-ray diffraction ............................................................... 120  
4.13 XRD data of Fe grown on GaAs .............................................. 121  
4.14 X-ray photoelectron spectroscopy .......................................... 123  
4.15 XPS survey scan ................................................................ 125  
4.16 XPS high resolution scans of Al and O regions ............................ 126  

5.1 STM and BEEM images of Al(111) and randomly oriented Al .......... 132  
5.2 STM and BEEM images of 10 Å AlO$_x$ film ................................. 134  
5.3 DOS and BEEM measurements of chemisorbed O$_2$ ..................... 136
CHAPTER 1
INTRODUCTION

Devices that either employ the electron spin alone or that also incorporate the charge degree of freedom as well move conventional electronics to the next level of technological development, with improvements in processing speed, circuit density, power demands, nonvolatility, and cycle lifetime [1]. Movement into completely new operation regimes such as quantum computing is possible as well. While many such devices are still at a nascent stage, an example of how quickly this promising new type of technology can be adapted is present in the giant magnetoresistance (GMR) effect. Just nine years after discovery, GMR hard disk read heads were incorporated into conventional drives and they have dominated the industry for the last eight years [2]. Tunneling magnetoresistance (TMR) [3] is another important spintronic effect that has just recently become commercially viable in a device known as the magnetic tunnel junction (MTJ) [4]. MRAM, a magnetic random access memory base upon MTJs is promised to be released in the first half of 2006, whereby information may be stored using nonvolatile magnetic domains. At the core of the device lies an insulating tunnel barrier layer, usually AlO$_x$ or (001) textured MgO, motivating efforts to understand and better control the oxide’s electronic structure.

In this thesis, I have used scanning tunneling spectroscopy (STS) to examine the density of states (DOS) at the surfaces of samples to be studied and ballistic electron emission microscopy (BEEM) to determine how these states couple through multilayers and interfaces. I will also discuss the electronic structure of tunnel barrier layers in the context of X-ray photoelectron spectroscopy, which is employed to understand the stoichiometry, to identify surface species, and to
understand interfaces between barrier layers and underlying electrodes.

Chapter 2 begins with a description of electron tunneling from metals through insulators or vacuum, a concept that is central to any discussion of STM and tunnel barriers. Two different spintronic devices employing ultra-thin oxide tunnel barrier layers are outlined: MTJs and Josephson junctions, as well as several applications and requirements for successful operation of these devices. Additional uses for oxide tunnel barrier layers will be addressed as well. The problem of spin injection into semiconductors, important for the successful development of spintronic devices allowing the manipulation of spin polarized currents will be addressed.

I will then move on in chapter 3 to give a description of STM measurements techniques utilized throughout this thesis and a brief review of two opposing theoretical treatments of BEEM. As both theories treat scattering at the interface from different standpoints, they can be brought together to facilitate interpretation and measurement of the scattering effects present at the interface between several different ferromagnets and GaAs.

Chapter 4 will cover some of the experimental details of the systems used to study these materials. Descriptions of techniques implemented to acquire images of surface electronic structure as well as modifications made to the various vacuum chambers will be discussed. Special attention will be paid to the care and feeding of the RHK BEEM system, in order to document many of the procedures encountered in its operation.

In Chapter 5, I will discuss the electronic properties of Aluminum Oxide (AlO$_x$) and the effects of several different treatment methods. While bulk, stoichiometric Al$_2$O$_3$ has a band gap of $\sim$8.8 eV, for the surfaces of amorphous AlO$_x$ films grown at room temperature the band gap is almost nonexistent. While this may be bene-
ficial for devices requiring ultrathin, transparent barriers, the band tails, localized states, and spatial inhomogeneities found in such amorphous AlO$_x$ layers can be very detrimental for high performance, low noise applications. Chemisorbed O$_2^-$ clusters have been identified at the surface strongly bound to oxygen vacancies in the AlO$_x$ [5]. Three treatment methods are utilized to improve the quality of the AlO$_x$, simply continuing the device fabrication through deposition of a top electrode, Electron Bombardment (EB), and Thermal Anneals. Measurements of the changes in the DOS when chemisorbed oxygen ions are moved into the oxide by either electron bombardment (EB) or by thermal annealing are discussed. Both treatments increase the oxide band gap, although EB which has a similar effect to the changes in the physical structure to the oxide as depositing a metallic overlayer with a high work function, has a different effect on the electronic structure of oxide states than anneals. EB treatment produces a smaller resultant barriers than anneals.

Chapter 6 discusses STS studies of half formed MgO tunnel junctions, where the (001) textured as-grown and annealed MgO barrier layers have been deposited either by reactive Mg sputtering or by e-gun evaporation. While bulk MgO has a band gap of $\sim 7$eV, once again, a much lower barrier height is observed in fits to IVs from fully formed devices ($\sim 0.5$eV). Measurements of the band structure as the full band gap degenerates in the transition from 30Å to 15Å films lends insight into how these fits can be explained. Initially sparsely populated distinctly resolvable defect states due to both oxygen and magnesium vacancies are present. These states gradually meld together as the films become thinner, forming band tails that extend to $\sim 500$ mV both above and below the Fermi level in the 15Å films. While a high temperature anneal ($\sim 375^\circ$ C) is an important processing step
to improve device properties and has been shown to reduce the extent of band tails, sparse local defect sites become chemically reactive, and over annealing (450° C) causes pinholes through the barrier layer for 15Å layers, similar to pinholes seen in unannealed 10Å layers.

Placing ferromagnetic materials in intimate with non magnetic metals, such as in a giant magnetoresistance hard drive read head, or a tunneling barrier (MTJ), has proven fruitful. One can then envision that utilizing ferromagnetic materials and semiconductors in tandem would produce novel characteristics, whereby the electron spin through ferromagnetism as well as the charge through doping level may contribute to the device characteristics. However, a central problem to such devices a method to create an imbalanced electron spin population in the semiconductor, whereafter it may be manipulated. Hence an understanding of the nature of the interface between ferromagnets and semiconductors is of considerable interest. To this end, In Chapter 7, I will discuss BEEM to measurements of scattering at the interface between GaAs and sputtered Fe, Co50Fe50, Ni81Fe19 (Py), and Molecular Beam Epitaxially (MBE) deposited Fe. The presence of three conduction band minima in GaAs at differing locations in both momentum space and energy facilitate determination of electron scattering at the semiconductor / metal interface. For the sputtered films, Py has the least amount of scattering and the highest hot electron transfer ratio, while MBE (001) oriented Fe has minimal scattering. I attribute this behavior both to the presence of a thin oxide layer at the interface between Fe and GaAs, and to interfacial alloying in the sputtered films.

Finally, Chapter 8 will conclude with a discussion of the most important results from my studies of oxide tunnel barrier layers and interfacial scattering in the
ferromagnet - GaAs system.
References for Chapter 1


While both aluminum and magnesium are widely abundant elements with excellent strength to weight ratios, aluminum has dominated the automotive marketplace despite the superior characteristics of Mg. The major difference between the two is the corrosion resistance. Both react readily with air, but the Al surface forms a protective cap \( \sim 15 \text{ Å} \) thick \([1]\), preventing further penetration of oxidation. When Mg oxidizes, however, cracks are formed due to the stress built from the higher density of Mg in MgO than in Mg, ie the MgO is under tensile strain. This allows the further exposure of Mg underlayers, and hence the oxidation proceeds to a much greater depth, compromising the quality of the Mg. The study of the oxidation of Mg has been undertaken for quite some time, although earlier studies of MgO concentrated on the corrosion resistance of Mg and Mg alloys under various conditions. Thus, such studies naturally considered only relatively thick films with an eye towards expanding potential uses of Mg into the automotive and aerospace industries as an improvement over Al based materials. Al has similarly been subjected to difficult environments in an effort to improve upon its corrosion resistance, and once again studies concentrated on rather thick AlO\(_x\) films. However, recent interest in ultra thin tunnel barrier layers has reinvigorated the studies of both of these barrier materials, although now the critical component has shifted to the understanding of the nature of the electronic structure of these thin barrier layers.

This interest has been launched through development of a number of devices and device structures that incorporate a tunnel barrier layer. While the primary motivation for the work in this thesis is the emergence of the magnetic tunnel
junction (MTJ) [2], tunnel barrier layers in Josephson Junctions, molecular gate
dielectrics, and interest in high K dielectrics to replace SiO$_2$ in conventional field
effect transistors all mandate in depth understanding of the electronic structure
of ultra-thin tunnel barrier layers. Up until quite recently, AlO$_x$ has been the
dominate material in such devices, largely due to the ease of deposition and the
relative insensitivity to processing parameters. However, contrary to early lack
luster MgO based tunnel junctions [3], the recent experimental demonstrations
of extremely high magnetoresistance in well oriented MgO films [4] [5] coupled
with the fact that these films are becoming simpler to grow in a technologically
feasible manner on amorphous electrodes [6] has moved MgO into the arena as the
dominant tunneling barrier for MTJs.

2.1 Tunneling Models

Tunneling of electrons through a potential barrier is one of the most readily ob-
servable predictions of quantum mechanics. Tunneling phenomenon are employed
in many aspects of physics, from the use of scanning tunneling microscope (STM)
to image surfaces on a atomic scale, to the development an understanding and
measurement of the spin polarized nature of ferromagnets, to the process by which
alpha radiation is emitted from a radioactive nucleus. As both the techniques
utilized in this thesis and the potential devices employ electron transport via tun-
neling, I would like to briefly discuss a few of the tunneling models used to treat
STM, BEEM, and magnetic tunnel junctions in particular.
2.1.1 Normal Metallic Systems

The simplest case to consider is that of a potential wall (vacuum) separating two normal metallic electrodes, as shown in figure 2.1. Derivation follows along the lines of [7]. In the simplified system of a nearly rectangular barrier, a separation of variables can be employed in the Schrödinger equation:

\[
-\frac{\hbar^2}{2m} \nabla^2 \Psi + \phi(x) = E \Psi, \tag{2.1}
\]

where \( \hbar \) is Planck’s constant, \( m \) is the effective mass of the electron, \( E \) is the total energy, and \( \phi \) is the barrier height. The result is that

\[
k_x = \sqrt{\frac{2m}{\hbar^2} (E - \phi - E_\parallel)}, \tag{2.2}
\]

where \( E_\parallel = \) is the energy associated with \( k_\parallel \), the momentum parallel to the interface. The transmission probability \( M \) that an incoming electron can be transmitted can be calculated from the WKB approximation [8], whereby

\[
M = e^{-2 \int k_x dx}. \tag{2.3}
\]
In our case, as a bias is applied across the initially square barrier, the barrier shifts to become trapezoidal in nature. Simmons [9] employed an approximation whereby

\[ M \sim e^{-\alpha s(E_f + \phi - E_x)^{1/2}}. \] (2.4)

Here \( s \) is the barrier width, \( \alpha \) is \( \sim 1.025 \text{ eV}^{-1/2} \text{ Å}^{-1} \), and \( E_f \) is the Fermi level. Tunneling requires empty states with density \( \rho_d \) in the destination electrode with probability \( 1 - (f(E + eV)) \) and full states with density \( \rho_e \) and probability \( (f(E)) \) in the emitting electrode, where

\[ f(E) = \frac{1}{(e^{(E-E_f)/kT} + 1)} \] (2.5)

is the Fermi function. Multiplication by the required densities of states and respective probabilities is required as well.

The full expression for tunneling current from the emitter electrode to the destination electrode is thus:

\[ I_{e\rightarrow d} = \int dEM (1 - (f(E + eV)) f(E) \rho_d(E + eV) \rho_e(E). \] (2.6)

The total current from the emitter to the destination then comes from subtracting the current that tunnels in both directions while the bias is fixed across the electrodes: \( I_{e\rightarrow d} - I_{d\rightarrow e} \). The result is the common starting point for many STM, BEEM and MTJ analysis (see for example [10]), hence we will start here as well for particular cases:

\[ I_{total} = \int dEM (f(E) - f(E + eV)) \rho_d(E + eV) \rho_e(E). \] (2.7)

Note that the barrier structure is neglected in this expression.

In 1963, Simmons [9] used the aforementioned WKB approach, and applied several approximations to the above formula in order to produce an analytical
expression for the tunnel current as a function of tunneling bias: the bias is assumed to be low, barriers are assumed to be thick ($\sim 10$ Å) and 1 eV high. In addition, and slightly disconcerting is the fact that the density of states of the two electrodes don’t enter into this picture at all, implicitly assuming that they vary slowly with energy. The result that Simmons derives is:

$$I = \frac{e}{2\pi h(\beta s)^2} \left\{ (\phi - \frac{eV}{2}) \exp[-A(\phi - \frac{eV}{2})^{1/2}] - (\phi + \frac{eV}{2}) \exp[-A(\phi + \frac{eV}{2})^{1/2}] \right\}, \quad (2.8)$$

where $\beta$ is a correction factor $\sim 1$, and $A = \frac{4\pi \beta s}{h} (2m_*)^{1/2}$, with $m_*$ the effective mass of the electron.

While this is an extremely useful starting point, this result has been feverishly applied to Magnetic Tunnel Junction IVs to determine an effective barrier height and width with little thought about the actual implications. One extremely important parameter is the effective mass of the tunneling electrons, $m_*$, which is often simply left as $m_e$, most probably resulting in inaccurate results. Also the assumptions may no longer be valid in the case of thin MgO barriers where the height is commonly fit to be around 0.5 eV, yet the bias is swept well beyond this value. In addition, any asymmetric voltage dependence which might arise either from work function differences in differing electrodes $^1$ or from the structural differences in otherwise identical electrodes stemming from growth of the bottom electrode on a metallic underlayer while the top electrode is grown upon an insulating layer is neglected. Some of these asymmetries may be addressed through a model developed by Brinkman Dynes and Rowell [12] allowing the introduction of a barrier asymmetry parameter.

$^1$For far reaching implications of the work function difference across the barrier upon the barrier physical and electronic structure in addition to the simple deviation from the squareness at $V=0$ see ref. [11]
2.1.2 Spin Polarized Tunneling

In addition to work function differences, another major factor can split the symmetry between the two metallic electrodes: Ferromagnetism. The exchange interaction splits the density of states of the ferromagnets such that one spin band (the majority band) is shifted to a lower energy with respect to the other (the minority band). Stoner’s original model treated this band shifting as happening in a rigid manner with no deformation in the shape of the bands as they are shifted with respect to one another, which turns out to be a reasonable first order approximation [13]. Since the Fermi level is present at a constant energy across both spin bands, the ferromagnet contains more majority spin electrons, resulting in a spin imbalance and a net polarization:

\[
P = \frac{\rho_\uparrow - \rho_\downarrow}{\rho_\uparrow + \rho_\downarrow},
\]

where \(\rho_{\uparrow(\downarrow)}\) is the density of states (DOS) at the Fermi level of the spin up (down) electrons. An example is shown for Fe in figure 2.2. Of course, for tunneling electrons, what is important is the number of spins at the Fermi level, and for some ferromagnets such as Ni, a negative spin polarization can occur [14]: there are more minority spins present at the Fermi level. However, experiments which measure the polarity of tunneling electrons [15] via techniques developed by Meservey and Tedrow [16] produce a positive polarization. This interesting discrepancy was first addressed by Stearns [17]. The Fermi level for most ferromagnetic materials is comprised of d type and s type bands, a cartoon of which is shown in figure 2.3. While the polarization at the Fermi level is determined mostly by the d bands, due to the much larger density of states they contribute, d bands are comprised of strongly localized wavefunctions which are unable to extend significantly into the
Figure 2.2: Fe DOS. Modified from [14].

Figure 2.3: Generic ferromagnetic "Nickel" DOS. Two primary bands contribute to the ferromagnetism, the delocalized s bands and the more strongly localized d bands. Electrons are more mobile in the s bands, and thus polarization of tunneling current may not correspond to bulk polarization of the electrodes.
tunneling barrier. Hence, the majority of the current is carried by the delocalized s bands which have a smaller effective mass and longer attenuation length in the barrier. These s bands can be polarized in a positive manner while the total polarization is negative, explaining the discrepancy between tunneling electrons polarization and the polarization at the Fermi level. For Fermi level transport (conduction) the larger density of states of the d electrons serve to provide different states into which the s conduction electrons may be scattered, resulting typically in current predominantly being carried by minority electrons [18]. In a MTJ, this type of behavior can influence incoherent tunneling electrons, whereby the available states to tunnel to may be of either d or s character.

2.2 Magnetic Tunnel Junctions

Tunneling between two magnetic electrodes separated by an insulating spacer layer was first studied by Julliere [19] in 1975. The tunneling current depends upon the relative magnetic orientation of the two ferromagnetic electrodes. He utilized an asymmetric system Fe/Ge/Co structure with a 100 Å oxidized germanium layer as the insulating layer. The analysis he applied is rather simple, looking only at differences between relative ferromagnetic alignments allows one to neglect all terms in equation 2.7 except those arising from the DOS of the two electrodes at the Fermi level. This is then analyzed in a parallel two channel spin model (See figure 2.4), whereby electrons are emitted from the left electrode and undergo no spin flip processes during the transport, and can only couple into the same spin channel from which they were emitted in the destination electrode. Therefore, in the case of parallel alignment, the conductance is proportional to a sum of the
Figure 2.4: Allowed tunneling processes for MTJs. The s and d band contributions to the density of states are evident.
products of the spin dependent density of states of the two electrodes:

\[ I_p \sim n_{e\uparrow} n_{d\uparrow} + n_{e\downarrow} n_{d\downarrow} \quad (2.10) \]

and for antiparallel alignment:

\[ I_{ap} \sim n_{e\uparrow} n_{d\downarrow} + n_{e\downarrow} n_{d\uparrow}, \quad (2.11) \]

where the subscript e or d implies DOS in the emitter or destination electrode.

Combining the above equations with the definition of the polarization, equation 2.9 allows one to express the change in tunneling magnetoresistance (TMR) - the optimistic TMR - as

\[ TMR = \frac{R_{ap} - R_p}{R_p} = 2 \frac{P_e P_d}{1 - P_e P_d}. \quad (2.12) \]

Although this expression is widely used for MTJs with amorphous insulating barriers, no attention is payed to the electronic structure of such a barrier layer. Despite the fact that this work was never successfully reproduced in amorphous semiconductors, interest in the TMR effect was launched through this experiment. Julliere’s model fails to reproduce many of the experimental observations, such as the bias dependence and the barrier material dependance, due at least in part to the fact that the details of the barrier are ignored.

A little later, after experiments had begun to demonstrate the inadequacy of this model, Slonczewski [20] applied a more in depth analysis in an attempt to explain several of these observations. He analyzes the case of an arbitrary angle (\( \theta \)) between the ferromagnetic electrodes, and uses two parabolic bands shifted with respect to one another by a value \( 2h_0 \). He works through the quantum mechanical problem for transmission through the (rectangular) barrier and considers wavefunction matching throughout the system. The important result that stems
from his calculations is that the conductance, $G$ is given by:

$$G = G_{fbf}(1 + P_e P_d \cos(\theta)), \quad (2.13)$$

where $G_{fbf}$ is an overall scale factor, $P_e(d)$ is an effective polarization given by:

$$P_e(d) = \left[\frac{(k_{\uparrow e(d)} - k_{\downarrow e(d)})}{(k_{\uparrow e(d)} + k_{\downarrow e(d)})}\right] \left(\frac{\kappa^2 - k_{\downarrow e(d)} k_{\downarrow e(d)}}{\kappa^2 + k_{\downarrow e(d)} k_{\downarrow e(d)}}\right) \quad (2.14)$$

Note that in the parabolic band approximation, the term in brackets is effectively the spin polarization, as the DOS is proportional to $\sqrt{E} \sim k$, so we have the spin polarization modified by a factor which is determined by $\kappa$, the vacuum decay constant, or the amount of barrier penetration by the wavefunctions. Substituting equation 2.14 into 2.13 and the expression for TMR, the first half of equation 2.12, where $\theta=0,\pi$ are taken as the P and AP orientations, we find that the Julliere formula is recovered (second half of equation 2.12), although now the polarizations are those given in equation 2.14. In effect some of the barrier parameters such as the height and width have been included in this analysis and the results through $\kappa$, but the details of the electronic structure of the barrier have been once again ignored. However, Slonczewksi’s treatment begins to show the importance of the transmission probability as $M$, from equation 2.7, is included in some sense through the inclusion of the second term in equation 2.14. The details of this transmission probability depend strongly upon the barrier properties, and may affect different spin types (as in the case of EuO, a magnetic tunneling barrier [21]) or different subbands of the ferromagnetic electrodes in different manners.

Subsequent theoretical studies explained the detailed shape of the TMR bias and temperature dependence in terms of magnons [22, 23], inclusion of more realistic band structure of the ferromagnetic electrodes [24, 25], disorder in the barrier [26], resonant tunneling via localized defect states within the barrier [27], and
interfacial states between the barrier and electrodes [28]. The feature that all of these more involved calculations hold in common is a method whereby the tunneling probability is taken into consideration, although the specific physical processes that govern its strength differ considerably. Those theories treating the presence of localized states and barrier disorder bring the importance of the barrier local electronic structure to the forefront, and extend the theoretical treatment to a more realistic system. However, few direct measurements of the electronic structure of the barrier layers have been performed, an issue that is addressed in later chapters of this thesis.

2.2.1 AlO$_x$ Based MTJs

AlO$_x$ is a very nice material for magnetic tunnel junctions because it can be deposited in a two step process, starting with a metallic Al which will wet underlying ferromagnetic electrodes uniformly and upon oxidation form a uniform barrier for thicknesses as little as 6 Å for evaporated films [29]. This combined with the much stronger tendency for Al to oxidize than the magnetic electrodes creates an oxidation barrier whereby the underlying electrodes are well protected from oxidation. As the DOS at the magnetic electrode - barrier interface is extremely important [30], any electrode oxidation will affect the TMR. Hence, for many years, the dominant barrier layer for magnetic tunnel junctions was AlO$_x$, and only in the last year has there been a substantial shift towards MgO.

The experiment that launched great interest in MTJs as practical devices was Moodera’s 1995 paper [2], showing a large (∼ 10 %) magnetoresistance at room temperature (see figure 2.5). Previously, attempts to duplicate Julliere’s results either required very low temperatures, or had extremely small TMR values at room
Figure 2.5: Demonstration of large TMR at room temperature. Antiparallel alignment results in a peak in the resistance. Sweeping to a large field causes both electrodes to align with the field and parallel to each other. Moodera’s experiment [2] catalyzed interest in MTJs, and as a result of this experiment a surge of experiments has generated a $\sim 60\%$ increase in the strength of the signal in AlO$_x$ based MTJs in the 10 years since this publication.

temperature. Thus, a device with a sizable TMR effect in ambient conditions, such as required by conventional electronics was a demonstrated as a possibility. Moodera utilized two dissimilar magnetic electrodes with different coercivities whereby it was possible to arrange for antiparallel alignment in magnetic fields intermediate to the magnetic layers’ coercive fields. As interest in MTJs has progressed, antiferromagnetic pinning layers such as FeMn or IrMn were incorporated in close proximity with the ferromagnetic underlayers, and various materials tricks were implemented to texture these antiferromagnetic layers in the appropriate orientation in order to create a strong pinning field. Special layers were also developed to produce as smooth a lower electrode as possible in order to minimize barrier roughness. Minimizing the barrier roughness is important both because it reduces "orange peel" coupling across the barrier which tends to lock the magnetic orientation of both electrodes in parallel alignment making independent switching events difficult, and because it produces local thinner regions where tunneling may preferentially take place, ie local tunneling "hot spots". Such hot spots can cause
a catastrophic failure of the barrier if the resistance is low enough and too much current passes through them.

Annealing treatments (in a magnetic field) are commonly used to improve and set the direction of the pinning by the antiferromagnetic layer. This usually has a profound effect on the TMR as well as improving the magnetics. The influence upon the magnetic switching is straightforward, but the improvement of the TMR can come from both changes in the barrier and electrode structures as well as the fact that direct antiparallel alignment may be simpler due to the electrode pinning. Annealing removes chemisorbed oxygen from the barrier surface in uncovered films [11], (see also Chapter 5) and reduces underlying electrode oxidation (Chapter 5), both of which will impact the electronic structure of the barrier. Hence, to understand the impact of annealing upon TMR, it is important to understand how annealing impacts the DOS of the barrier layer. This is discussed in detail in Chapter 5.

### 2.2.2 MgO Based MTJs

While number of different barrier layer materials have been studied (ZrO$_x$ [31], EuO [21], SrTiO$_3$ [32], AlN [33], HfO$_x$ [34], TaO$_x$ [35]), until very recently, no barrier layer has been able to produce a TMR ratio comparable to AlO$_x$ MTJs at room temperature in a reasonable resistance device and with the ease of fabrication available via conventional processes. EuO and EuSe barrier layers are interesting in themselves, as spin polarized electrons may be generated via an entirely different mechanism. These magnetic barriers provide different tunneling barrier heights for spin up and spin down electrons, and as current depends exponentially upon the barrier height, a small difference between the barrier seen by each spin type can
result in a strong polarization exiting the barrier, even for normal metal leads. However, as this desirable property of Eu barriers is quenched with temperature, and becomes nonexistent above ~ 150° K, such novel structures are probably useless for conventional electronics. Meanwhile, tunnel junctions comprised of AlO$_x$ barrier layers have now reached ~ 70% [36] at room temperature in MTJs with CoFeB electrodes for good thermal stability.

Initial tunnel junctions utilizing MgO barriers prepared in identical methods as what had worked well with the AlO$_x$: evaporation of Mg metal on the base electrode followed by plasma oxidation [37] showed lack luster TMRs, and were generally outperformed by the AlO$_x$ based MTJs. Therefore, interest in MgO as a tunnel barrier waned considerably until two theoretical treatments [38, 39] were published. The basic requirement for the Giant TMRs predicted these papers is that the MgO layer be coupled with either bcc Co or Fe, and whole stack be (001) oriented - basically grown in an epitaxial manner. This is a situation that post growth oxidation will not readily produce. Additionally, the fact that hcp Mg contracts upon the formation of the rock salt oxide structure may adversely influence the conformal nature with which the Mg metal covers the base electrode, diminishing the positive characteristics of the tunnel junction. Thus, it is not terribly surprising that techniques that had worked well with AlO$_x$ were not applicable to the deposition of MgO barrier layers, and that there was 9 year span during which AlO$_x$ based tunnel junctions dominated the systems probed and even worked their way into a few products.
Theoretical Treatment of MgO based tunnel junctions

Two groups, Butler at Oak Ridge, and Mathon at City University in London have independently employed first principles band structure calculations for a (001) oriented Fe/MgO/Fe trilayer utilizing the full band structure of the Fe electrodes. As in any tunneling structure, one would expect the tunneling current is dominated by the electrons with small transverse momentum; the strongest component of the tunneling electrons travel normal to the interface in the Γ-H (001) direction. The important results stemming from these studies come from the consideration of electron transport in the individual Fe subbands as they cross the MgO tunneling barrier. In the case of coherent electron tunneling (much more likely to occur in fully epitaxial tunnel junctions), the momentum of the electrons is conserved as they cross the insulating barrier. While the total polarization of the Fe electrodes is not extremely high (\(\sim 40\%\)), if one only considers the s-type bands present along the Γ-H direction at the Fermi level, Fe behaves like a half metal: while d and pd states are present at the Fermi level for both spin up and spin down, there are no s-type states present in the spin down bands (See figure 2.6).

The importance of considering the bands separately comes from analyzing the impact each band’s symmetry has upon its decay length in the MgO barrier. This comes about by matching the symmetry around \(k_\parallel = 0\) of the Fe bands as they couple into the bands in the tunneling barrier, through the 45° rotation that accompanies the MgO(100)//Fe(110) growth. In the vicinity of the band gap, the s states have by far the longest attenuation length, serving to preferentially promote the tunneling of those electrons over the d and pd type electrons. This is illustrated in figure 2.7.

We will look at conductance through the device in a parallel spin model, ana-
Figure 2.6: Fe band structure. $S (\Delta_1)$ states are present along the $\Gamma$-$H$ direction at the Fermi level only for the spin up band. The symmetry of the wave function determines its decay as it crosses the barrier, and the s state symmetry promotes a much longer decay length, and thus it has the dominant role in tunneling conductance. Modified from [14].
Figure 2.7: Tunneling DOS of Fe(001)/MgO(001)/Fe(001) system after [38]. The longer attenuation length of the $\Delta_1$ band coupled with its decay in anti aligned electrodes leads to much higher conductance in the parallel alignment of the magnetic electrodes than if they are antiparallel.
lyzing each channel separately. Two important issues come together in this picture. The first is that because of the longer attenuation length in the barrier of the s type electrons, the conductance is dominated by majority electrons if the electrodes are aligned parallel (top of figure 2.7). The second is that if the electrodes are aligned antiparallel, because of the coherent nature of the tunneling, electrons originating from the spin up band s state (fig. 2.7) are unable to find an s type state in the spin down band, and hence their wavefunction continues to be attenuated as it extends into the counter electrode. In spin down to spin up tunneling (lower right of fig. 2.7), the electron wavefunctions are so strongly attenuated in the barrier that little conductance is generated from this channel either. The end result is that the predicted TMR is huge in this system, a function of carefully considering each Fe band separately, and taking into consideration the individual transmissions through the barrier - basically carefully including the transmission coefficient (M factor) present in equation 2.7 in manner that was not taken into account in either the Julliere or Slonczewski models.

As we have seen, understanding tunnel barrier behavior thus requires careful consideration of band structures of the materials involved in each tunnel junction, especially so for the case of well ordered layers. In these calculations, the MgO barrier is taken to be ideal, and predictions for TMR values rising above 1200 % have been made. Experimentally, growing a perfect barrier layer and interfacial structure is quite difficult, and hence these theoretical predictions are probably a far cry from reality. Chapter 6 of this thesis will discuss the first direct measurements of the electronic structure of conventionally deposited MgO layers and how defects measured in the structure may explain the discrepancy between theoretical and experimental TMR values.
Experimental verification

Although these predictions for substantial improvement of device performance came out in early 2001, launching substantial efforts into MgO barriers, it took 3 years for promising results (88% TMR at R.T.) to be reported [40]. The same group followed this ~6 months later with a substantial improvement [5]. In these trilayer systems, MBE growth techniques were used, an attempt to create as perfect a system as possible. An important difference between [40] and [5] in the growth techniques was that the top electrode Fe in [5] was deposited at 200°C instead of room temperature. This large improvement in TMR due to one simple change in the deposition conditions is an indication of the importance of the electrode / insulator interfaces. I believe that this improvement is due to two major factors. Firstly, a layer of chemisorbed oxygen similar to that found on AlO$_x$ [11] is present on MgO layers. Annealing should help to remove this layer, reducing the amount of top electrode oxidation which may quench the TMR. Secondly, bringing the MgO to 200°C may help to improve its crystal structure. No post preparation anneal was performed, which may have had the same effect if done to those sample in [40].

A novel approach to fabricating MgO tunnel barriers was reported simultaneously [4]. In this paper, a technologically viable approach was utilized instead of careful MBE techniques, and surprisingly, with the appropriate underlayer texturing, worked quite well. The critical component here was to anneal the samples to a very high temperatures in terms of previous AlO$_x$ tunnel junctions (See figure 2.8). It is interesting to note that performance of the devices is in line with [40], until annealed. I believe that the same two effects are at play here: reduction of

$^2$See chapter 6
Figure 2.8: Impact of anneal temperature on tunnel junction performance (Modified from [4])

electrode oxidation; oxygen is sucked into the barrier, filling vacancies improving the stoichiometry and crystal structure. Incremental improvements have continued to push TMR values higher, but two pivotal changes in deposition parameters have moved MgO MTJs into a very important regime: Incorporation of CoFeB electrodes [4, 41, 42] and predeposition of a Mg layer [43].

Incorporation of CoFeB electrodes was important because in addition to improving device performance it both vastly simplified the fabrication process, and lent insight into the what the mechanism is behind the improvement of TMR with anneal temperature. CoFeB electrodes are amorphous, and MgO deposited on such an electrode tends to strongly orient in the necessary (001) crystalline structure [44]. This meant that all the careful work that Parkin’s group had performed in [4] in order to produce the proper underlayer texturing to seed the MgO growth was no longer necessary, enabling a MTJ stack to be deposited in a much more straightforward manner, which is very encouraging for scaling up to an industrial
process. Insight into the impact of annealing on the electrodes structure also became a little clearer as a result of [42] and [44]. While the in the as-deposited state, electrodes were amorphous and MgO was not - yielding devices still gave marginal performance. However, upon annealing giant TMR develops, and TEM [42] and RHEED [44] analysis shows that the crystalline MgO has served as a template to induce crystalline structure in the CoFeB electrode. Thus the electrode structure is essential to experimental observation of performance MTJs.

Predepositing a thin layer of Mg [43] enables high TMR with a very low resistance area product, such as is desired for applications as a magnetic sensor (hard disk read head). This Mg layer probably serves as an oxidation barrier layer for the base electrode during the deposition of the barrier. In electron beam evaporated films from an MgO source, oxygen is liberated (see chapter 6) and becomes the dominant background gas, probably leading to some electrode oxidation. It is likely that RF sputtered films deposited from a MgO target also behave in a similar manner, liberating some oxygen. While not the dominant background gas, its presence is still sufficient for some electrode oxidation. This thin Mg layer therefore serves as a getter for the O and its crystalline orientation is encouraged during the anneal. Therefore, the barrier does not have to be as thick before it is able to suck up the residual oxygen in the ferromagnetic electrodes.

In all of these studies where a high TMR was successfully produced, an important factor is noted: MgO was deposited from the beginning, not through a process where the whole barrier was deposited as metallic layer which was later oxidized. The later results in an amorphous barrier which cannot be annealed into a crystalline form at temperatures which will not destroy other essential layers due to increased atomic mobility and interlayer diffusion. Another point of interest is
that when these MgO barriers are fit using Simmons models, the barrier height that falls out is quite low, $\sim 0.4$ eV or so. This is well below what one might expect from fixing the Fermi level at mid gap, as MgO should have a gap of $\sim 7$ eV or so. This behavior is described in detail in Chapter 6.

### 2.2.3 Devices

There are several parameters one needs to optimize to produce a useful device. TMR is, of course, the obvious one. A higher TMR is always desirable, as this will help the signal to noise ratio in any circumstance, however improving the TMR without regard to any other device parameter involves making the tunnel barrier quite thick. For MgO, the reasons for improvement in TMR with barrier thickness stems from the electron tunneling distribution becoming more and more forward focused [38], and hence one only has to consider the $k_\parallel = 0$ component, giving the strongest effect from the half metallic nature of the Fe $\Delta_1$ bands [39]. In addition in $\text{AlO}_x$ and MgO based tunnel barriers, the thicker the device, local tunneling hot spots with a reduced TMR (pseudo pin holes or metallic shorts) in the barrier are less likely, and the barrier becomes better ordered with lower likelihood that localized states in the tunnel barrier will adversely interact with tunneling electrons (Chapter 6). However, as the tunnel barrier becomes thicker, the resistance area (RA) product will increase exponentially for an ideal barrier, and super-exponentially if the electronic structure becomes more bulk-like as the thickness increases. The device resistance is important because eventually one would like to integrate the tunnel junctions with some sort of conventional electronics. The two primary applications take place in different RA product regimes (See figure 2.9), but each requires a overall tunnel barrier thickness of 15 Å (MRAM - section 2.2.3) or $\sim$
10 Å (Magnetic sensors - section 2.2.3) or less. Additionally two other parameters are of interest. In any real circuit, a finite bias must be applied across the junction in order to read out a reasonable signal. MTJs show a bias dependence whereby the TMR is quenched as the bias across the junction is increased (See figure 2.10). The parameter of merit here is known as $V_{1/2}$, the voltage whereby TMR drops by a factor of two. $V_{1/2}$ tends to decrease as thickness decreases as well, so engineering working devices involves weighing several tradeoffs. Finally, as only layer in the devices is designed to switch while the other stays fixed, this switching or
free layer should be relatively soft. This worked reasonably well with Permalloy (Py=Ni$_{80}$Fe$_{20}$) and AlO$_x$ barrier layers, however with MgO, as crystalline Fe or CoFe electrodes are commonly used, the crystalline anisotropy can adversely influence the switching characteristics of the free electrode. I have heard recent reports that Py has been incorporated with MgO resulting in TMR values of $\sim 100\%$ in the right RA product regime for MRAM. The electrodes exhibit good magnetic characteristics, so this problem may have been ameliorated.

**Read heads and field sensors**

The first application that I would like to address for magnetic tunnel junctions is that of a magnetic field sensor, specifically employed as a hard disk read head. This is in some sense a simpler application to deal with than a memory array as the operating parameters do not need to be as tightly controlled across millions of MTJ. While identical units are highly desirable, it is possible for devices to be tested and either discarded, or the reference voltage for determining what a ”1” or ”0” is can be adjusted in the packaging phase to null out any offsets the individual read characteristics.

Hard disk magnetoresistive thin film read sensors have gone through two major technologies since inception. Previous incarnations of read heads involved an inductive design, where basically a current was excited in a loop of wire as a change in magnetic flux threaded the loop. Initial thin film MR read heads employed anisotropic magneto resistance (AMR), discovered by Lord Kelvin in 1857. Due to the spin orbit interaction [45], a current flowing through a magnetic material will undergo a resistance change of a few percent depending upon whether it flows parallel or perpendicular to the direction of the local magnetization. Sensors are
thus oriented with the crystalline anisotropy (easy axis) in a particular direction. The presence of a nearby local domain on the hard disk can (with the help of adjacent soft magnetic layers) reorient the moment within the magnetic strip, leading to a change of resistance of a few percent.

This was a substantial improvement over the inductive shared read / write head design, but as Windows 95 was developed and the advent of Microsoft and related bloatware, it became important for disk drives to have a larger storage capacity. In 1988 the Giant MagnetoResistance (GMR) effect was independently discovered by Albert Fert and Peter Grunberg in magnetic multilayers, whence a substantial resistance change upwards of 50% is possible in multilayer current in plane (CIP) geometries. These read heads were implemented within ten years in IBM disk drives. However, CIP sensors are somewhat spatially extensive limiting bit density on the platter to about 100 Gb/in$^2$ (what a great unit!) [46], and current perpendicular to the plane (CPP) spin valves with a resistance change of $\sim 10\%$ were implemented. The CPP GMR effect is similar to that of MTJs, except that instead of tunneling across a barrier layer, electrons conduct through a normal metal spacer layer. Appealing to a parallel spin channel model, one can see that a higher current should conduct when the ferromagnets on either side of the normal metal are aligned parallel and there is a good match in the density of states of the spin up and down subbands on either side of the normal metal, as opposed to when they are anti parallel and a poor match exists. This goes along the lines of optical polarizer / detector experiments, expect that this angular dependence for GMR goes roughly as $\cos(\theta)$ instead of $\cos^2(\theta)$. Of course the usual caveats about whether s or d type electrons are caring the current (mostly s) applies. However, the presence of a large number d states for s electrons to scatter into during the
conduction process helps to explain why the GMR effect is lower than the TMR effect [18]. In the CIP geometry, the GMR effect can be explained by the scattering at normal magnet / ferromagnetic interfaces and electron channelling within the lower resistance normal metals [47, 48].

Programmers have continued to enjoy the freedom of sloppy code writing, and as digital cameras, MP3s, the I-pod and digital movies came out, the consumer’s thirst for more and more storage space continues to be unsatiated. TMR based read head sensors are currently being heavily investigated to fill this gap, as they have demonstrated a substantial improvement in magnetoresistance signal over CPP GMR based sensors. However, in a magnetic sensor, in addition trying to raise the signal as much as possible, one of the primary concerns is how to minimize the background noise. A primary noise source related to the barrier properties is Johnson noise. Johnson noise is addressed in a little more detail in Chapter 4, but the important features are that it scales with the square root of the device resistance and is flat with respect to frequency (white noise). Therefore, lowering the resistance of the read head is of primary concern. This was not much of an issue with the previous low resistance sensors based upon metallic multilayer stacks, but once an insulating layer is incorporated it becomes a pivotal issue. This is the reason that current read head destined MTJs are developed with a goal of less than 1 Ω·µm².

**MRAM**

Current memory types employed in conventional electronics are a compromise of several different operating parameters: speed, nonvolatility, density, power consumption, and lifetime. Different types of memory are optimized with respect to
Table 2.1: Comparison of current memory types

<table>
<thead>
<tr>
<th>*</th>
<th>Speed</th>
<th>Nonvolatile</th>
<th>Dense</th>
<th>Refresh</th>
<th>Low Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRAM</td>
<td>Moderate - Fast</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>FLASH</td>
<td>Slow</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>SRAM</td>
<td>Fast</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>DRAM</td>
<td>Moderate</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

Some, but not all of these parameters, for example, DRAM which is fast and dense is plagued with charge continually bleeding off of storage capacitors, and hence is neither low power or non volatile. Flash is extremely slow and has limited write cycles. This limitation stems from the manner in which flash is written: a gate is taken to a very high bias, and Fowler - Nordheim tunneling allows some electrons to tunnel onto the floating gate as a high current density is run across the channel. This is a slow process, and has tendency to generate of oxygen vacancies in the tunnel barrier after $\sim 50,000$ cycles. Once these vacancies become decorated with a hole, a defect state arises within the barrier and, it becomes easy for stored charge to bleed off the gate. Data is no longer nonvolatile.

A chart showing current leading memory types is presented in table 2.1. Although MRAM’s current primary strength is as a replacement for battery backed SRAM in servers, it may eventually be able to replace many of these memory if it can be made dense enough in a large array size. Another regime where it may quickly become a dominant player in the market is in mobile devices where on the fly changes can be made in memory architecture: previously one had to design and plan which amounts of which memory were required: a certain amount of SRAM for processor caches, certain amount of DRAM for conventional memory, and a
certain amount of flash for longer term data storage. With a single MRAM cell the partitioning between these various tasks can been reallocated as circumstances warrant.

Although a major problem was addressed through "Savtchenko" or toggle switching [49], several other large concerns are still present that may affect the MRAM scalability. Toggle switching has eliminated what was probably the biggest barrier to large memory arrays. Switching of a free layer (the MTJ magnetic electrode not adjacent to an antiferromagnetic pinning layer) was accomplished via strong currents applied to two crossed Co cladded Copper write lines (see figure 2.11). The magnetic field from just one line had to be insufficient to switch a bit, but the summation of fields from both lines had to be sufficient to switch all of the bits. This requires that coercive field of each bit be very uniform - slight differences in the magnetic properties of individual bits may cause some to switch when only the field from one line is applied - the "half-select" problem. Utilizing a nearly balanced synthetic antiferromagnet layer (two magnetic layers separated by a Ru spacer), enables carefully timed pulses along the bit and word lines to reliably switch only the addressed bit (see ref. [49]).

With this clever design, the scaling problems stem from the tunneling barriers themselves. In order to determine which state ("1" or "0") a given bit is in, the resistance is measured and compared with a standard value midway between the parallel and antiparallel resistance values. As there are going to be deviations from device to device, this midpoint is determined with respect histograms of the resistance distributions (See figure 2.12). While some of the resistance distribution can be from something as simple as differences in device areas and can be cleaned up with better patterning techniques, a large part may be intrinsic to the barrier
Figure 2.11: Individual MRAM bit and arrays.
Figure 2.12: MRAM resistance distributions. Reference voltage lies midway between both values. In order to ensure that all bits in each state are read in the correct manner, the peaks must be separated by $\sim 14 \sigma$. 
layer. Hence understanding the details of the barrier layer’s electronic structure and improvements that may be enacted upon it are crucial (See chapter 5).

While current generations of devices utilize an AlO$_x$ tunnel barrier with a smaller intrinsic $\sigma$ than MgO $^3$ layers, the higher TMR values still allow faster access times. $^4$ Identifying and understanding intrinsic defects which may be responsible for these resistance spreads in MgO barrier layers is paramount to increasing the array size and density of MRAM bits. Similar to the discrete doping problem in next generation transistors, as the cell size shrinks, the resistance difference between a bit that has one additional defect within its area may be sufficient to change its resistance values in a manner which will upset read distributions.

Both MgO and AlO$_x$ undergo different wear out mechanisms with time that adversely influence their long term reliability. The primary concern for AlO$_x$ is a time dependent resistance drift $^5$ [51], perhaps due to the stress induced hot spot formation. Attempts to understand and model this behavior will be discussed in chapter 5. In MgO, differing deposition methods may help to alleviate this problem (chapter 6).

### 2.3 Other Uses for Thin Insulating Oxide Layers

While MTJs are a primary motivation for the tunnel barrier layer studies$^6$, ultra thin barriers are contained within a myriad of devices, and have many other useful implementations. I will briefly outline a few of these other devices in the following section.

---

$^3$0.83 % cf 1.5 %

$^4$17 ns for MgO vs 25 ns for AlO$_x$ based MTJs [50]

$^5$Resistance always decreases with cycle number

$^6$In no small part because they show the greatest promise as a technologically useful device
2.3.1 Josephson Junctions

A Josephson junction (JJ) first theorized by Noble Laureate Brian Josephson consists of a "weak link" between two superconducting electrodes. This weak link is typically formed by an insulating tunnel barrier space layer. A typical device is comprised of a Nb/Al/AlO$_x$/Nb stack, where the Nb will drive the adjacent Al superconducting if measurements are to taken above the Al transition temperature. This structure allows convenient adjustment of one of the essential (JJ) parameters, the barrier transmissivity (which we will see effects the critical current), through an oxygen dose.

The intimate proximity of the two superconducting electrodes is sufficient to allow Cooper Pairs to tunnel across the barrier layer either with or without photon emission. The later results in the DC Josephson effect, a supercurrent can flow in the absence of applied voltage up to $J_c$, the critical current. This DC current is dependent on the phase ($\phi$) between the two superconducting electrodes: $J = J_c \sin(\phi)$. The emission of a photon gives rise to the AC Josephson effect whereby an AC supercurrent of frequency $\nu = \frac{d\phi}{dt} = 2eV/\hbar$ (1 $\mu$V $\rightarrow$ $\sim$0.5 GHz). Magnetic fields and currents in the films reduce $J_c$, and at high frequency, the capacitance across the junction will also reduce $J_c$ [52].

It is readily seen that a JJ is an excellent source of high frequency oscillations, and they are currently being considered as the bases of two types of very fast computers. A conventional computer with very high operation frequency is the more straight forward of the two, and if a large bias can be sustained across the junction, implying the need for both a large critical current and low junction

---

7 and paranormal activity researcher
8 JJs may be used for a processor [53] or for memory [54]
capacitance, this may be conceivable. While making the tunneling barrier thinner will increase the capacitance in a linear fashion \((C \sim A/d)\), \(J_c\) is exponentially dependent upon the barrier thickness \([55]\). There clearly is much to be gained from making the barrier as thin and highly transparent as possible, while attempting to maintain as perfect defect free structure as possible, warranting investigations of ultra thin barrier layers. \(\text{AlO}_x\) has long been employed as mentioned above, but \(\text{MgO}\) may as well have strong possibilities if it can be coupled with a lattice matched superconductor. A promising candidate in this respect is \(\text{Mo}\). \(\text{MgO}\) may have advantages over \(\text{AlO}_x\) in the noise characteristics, although this is still a question under some debate. However, the relatively simple crystal structure (rock salt) should lend itself to higher stability against atomic fluctuations around defect sites, which are common in disordered \(\text{AlO}_x\) barriers. This would lead to reduced \(1/f\) noise characteristics which is crucial for the second type of fast computer: a quantum computer.

A quantum computer derives its speed not from the frequency of calculations, but from the efficiency. Instead of operating on bits in predetermined states: 0’s or 1’s, quantum bits, qubits can exist in a quantum superposition of states, with a measurement collapsing the wavefunction, and yielding a 1 or a 0 with certain probability. While this might seem rather unpredictable, and quite useless, it has profound implications if applied to particular problems. Initially little interest was placed upon the construction of such a beast, especially with the extreme difficulty in isolating the qubits from their environments and yet being able to allow them to interact on a limited basis in order to perform calculations. However, with the discovery of Shor algorithm \([56]\)- a quantum algorithm that factors large numbers with the computation time a mere polynomial of the length of the number to be
factored \(^9\), considerable interest was piqued. Later several other useful algorithms were developed, such as an efficient search on an unsorted data set [57]. However, the current basis of nearly all cryptography stems from multiplication of very large prime numbers, the reverse of which is quite difficult. Many people down at the NSA, and other such agencies concerned with reading each other’s mail became incredibly interested in having one of the things all to themselves, and the prospect of decrypting information more than offsets any problems with keeping the computer at liquid Helium temperatures - a show stopper for conventional electronics. Quantum computing is inherently unconventional. In fact Shor’s algorithm was implemented on a seven qubit quantum Nuclear Magnetic Resonance based computer at IBM in 2001, successfully tackling the difficult problem of factoring 15 into 3 and 5.

While impressive, this NMR implementation suffers severe scalability limits, and it turns out that JJs are one very promising implementation that may be scaled up to a size where typical size numbers can be tackled [58]. While there are several different qubit implementations involving JJs, the simplest is the charge based qubit (See figure 2.13), whereby charge can be stored on the ”box” which is capacitively coupled to the gate potential and coupled to the second superconducting electrode through the insulating barrier. The gate voltage can be adjusted to allow electrons to tunnel onto and off of the box. While the number of electrons is generally dominated by this charging energy, in the voltage regime midway between that required for an integer number of electrons on the box, Josephson tunneling between the two superconducting electrodes can serve to mix the \(n\) and then \(n+1\) levels, resulting in a superposition of \(n\) and \(n+1\) electrons on the box, and

\(^9\)conventional computers take an amount of time that is exponential in the length of the input number
Figure 2.13: Charge based JJ qubit.

hence a qubit. While this is a simple implementation, it turns out to be difficult to accomplish the desired operations, and hence more involved JJ qubits employing magnetic flux, either as the qubit or to tune the Josephson coupling have been envisioned and fabricated.

One crucial problem for all qubits is the decoherence time, that is the time it takes for interaction with the environment to wash out the quantum superposition and effectively force the qubit to make up its mind between a 1 or a 0. In the case of JJs, dynamic fluctuations and instabilities within the barrier can reduce the decoherence time, so methods to remove such noise sources by stabilizing atoms within the barrier are highly desirable (Chapter 5).

### 2.3.2 Gate Dielectrics

Alternative gate dielectrics are being employed in a number of situations. I will briefly highlight two uses. Desires to understand molecular electronic structure
as such devices are increasingly finding their way into thin film displays, possibly enabling flexible / wearable computing has emphasized the need for ultrathin insulating layers to cleanly probe their DOS. NaCl has been employed with excellent results [59], and AlO$_x$ is commonly used to as well. This allows one to probe the structure of a molecular system without induced the dipoles a molecule / metal interface. Of course any real system needs to have such metallic contact, but one would like to see if the molecule is behaving in isolation as theory would predict. In addition, a gate can serve as a third contact spaced off by an insulating layer, and hence modulate transport through the molecular system.

Another application for gated contacts is in a standard field effect transistor, the workhorse of the electronics industry. As transistors are getting smaller, the gate insulator and channel lengths are becoming thinner and smaller. A transistor is no longer able to be "on" or "off" as direct tunneling through the gate oxide becomes a substantial problem. From equation 2.8, we see that tunneling current changes as an exponential function of the barrier width (s), and an exponential of the square root of the barrier height. Therefore, if it is possible to find a system which gives the same capacitance at a thicker barrier width then SiO$_2$, even at the expense of a lower barrier height, this direct tunneling component can be suppressed and transistor scaling may continue for a few more generations. The solution is to employ what are known as high K dielectrics. As the capacitance of a parallel plate capacitor $\sim \frac{K\epsilon_0 A}{d}$, where $A$ is the plate area, $d$ is the spacing and $K$ is the dielectric constant, any increase in $K$ will allow $d$ to increase by the same amount to preserve a given capacitance, increasing the barrier width. Both MgO and AlO$_x$ have $K$'s of about 9, while SiO$_2$ is about 3. If their electronic structure can be optimized in the ultra thin regime, either may eventually replace SiO$_2$ in
the conventional transistor. Also, MgO has a reasonable lattice match with GaAs, a semiconductor which has been lacking a good insulator, so there is potential for MgO / GaAs structure field effect transistors.

2.4 Spin Injection into Semiconductors

All of the devices successfully utilizing the electron spin degree of freedom discussed above involve electron transport either tunneling through insulating barriers or transporting through non magnetic and magnetic electrodes. One whole class of materials has been left out, the ”bad” metals and ”bad” insulators - semiconductors. Semiconductors form the basis of the computer age, and so the thought if utilizing electron spin within Si or GaAs based semiconducting devices is tantalizing as new knobs will be available to adjust devices responses. Dilute magnetic semiconductors (DMS) as a source of spins in semiconductors have long been researched but several problems are inherent with these systems: Mn, a common magnetic dopant is a donor, and in fact nearly all successful magnetic semiconductors are p type, where as one would like to be able to freely dope the system n and p type, in order to construct transistors, diodes, and the like. Additionally, all such semiconductors have relatively low Curie points, become nonmagnetic, and generally crappy semiconductors above around 100° K or so. There are predictions that Mn doped GaN and ZnO may achieve the elusive room temperature requirement, however [60]. Co doped TiO$_2$ has also been pursued but clustering of Co (and Mn in GaN and ZnO) thus far has precluded a distinct homogenous room temperature DMS.

Focus for producing spins in semiconductors has turned to injecting spins into a conventional nonmagnetic semiconductor. Optical methods utilizing circularly po-
larized light work reasonably well, and measurements have demonstrated a "long" spin lifetime within the semiconductor of more than 100 ns [61], more than necessary for several calculations. Implementing a pump-probe laser system in a solid state device is somewhat challenging and hence many efforts have turned to electrical spin injection. The simplest implementation electrical spin injection is to place a ferromagnet into intimate contact with a semiconductor and to inject spin polarized current from the ferromagnet into the semiconductor in this manner. There is a substantial problem with this implementation however: the conductivity mismatch between the metal and the semiconductor which limits the spin injection to \(\sim 0.1\%\) [62]. This can be understood in a simple manner from the fact that since there is a much lower available density of states for each spin channel in the semiconductor both "channels" are easily filled from the much large number available states in the ferromagnet. Rasba [63] theorized an elegant solution, utilizing a tunnel barrier, which would force a high resistance at the interface, and hence dramatically improve the efficiency of spin injection.

This approach has been employed utilizing both a conventional tunnel barrier layer such as AlO\(_x\) and MgO, where MgO has been employed with great success [64] and utilizing the enemy: heavily doping the semiconductor at the interface to strengthen the Schottky barrier that naturally forms at metal semiconductor interfaces [65, 66]. Therefore, understanding the nanoscale electrical transport at such interfaces is of crucial importance to improving spin injection efficiencies. Electron scattering and momentum redistribution at such interfaces may be detrimental to successful spin injection. This will be covered in Chapter 7.
References for Chapter 2


Invented in the 1982 by Binnig and Rohrer [1], Scanning Tunneling Microscopy (STM) is a very well known and well understood technique at present with many excellent sources for further information. I recommend [2, 3] for in depth reviews. However, several of the methods utilized for data acquisition in this thesis are derived from lesser used variations on the standard techniques, and hence will be described herein.

3.1 STM Techniques

In general STM images are comprised of a convolution of the sample topography and the Density of States (DOS) of both the sample and the tip. However, as there is roughly an order of magnitude decrease in tunneling current for each additional Å in tip - sample separation [2], generally the density of states effects are only important for extremely flat surfaces. As the desire in these studies is to measure electronic structure in as-deposited films, the extensive preparation techniques required to achieve atomically flat films are not employed. Therefore, in the somewhat rougher thin films deposited in these studies, the overwhelmingly dominant contribution to the STM images is the sample topography and such images will hence forth be regarded as pure topographic in nature.
3.1.1 Measuring Local Work Function

Scanning Tunneling Microscopy derives its resolution both from precise control of the STM tip placement using piezoelectric elements and from the exponential dependence of the tunneling current upon the gap width. Equation 2.7 can be reduced [1] to

\[ I_t \propto e^{-2\kappa s}, \]  

(3.1)

where \( \kappa \) is the vacuum decay constant given by \( \kappa = \frac{4\pi m^{1/2}}{h} \phi^{1/2} \). Here \( m \) is the mass of the electrons in the barrier, and for vacuum tunneling, using the free electron mass gives \( \kappa = 1.025 \phi^{1/2} \). Where \( \phi \) is the effective height of the barrier in eV which is given from the application of the WKB approximation as the average of the work functions of the two electrodes (sample and tip). This allows one to determine the local work function at the sample surface, and hence detect the local dipoles present. The work function can be extracted via either spectroscopy or a lock-in imaging method. In the case of spectroscopy, it is a simple manner to adjust the sample - tip spacing and collect a measurement of the exponential tunnel current dependence on the gap width. If one wishes to acquire a spatial map of the local work function, however the process is slightly more involved.

While scanning in constant tunnel current mode, a lock-in amplifier may be connected to apply a small (\( \sim 0.2 - 0.4 \, \text{Å} \)) oscillation to the \( z \) piezo. This oscillation must be above the frequency with which the feedback loop can operate, so as not to be compensated for in the control electronics, but simultaneously below the STM filter setting for lock-in detection. Now, rearranging equation 3.1,

\[ \phi = \left[ \left( \frac{1}{1.025} \right) \frac{\partial (\ln I_t)}{\partial s} \right]^{1/2} = \left[ \frac{\Delta I_t}{1.025 I_t \Delta s} \right]^{1/2}. \]  

(3.2)

\( \Delta s \) is known through the magnitude of the lock-in oscillation signal, \( I_t \) is the
tunnel current set point, and $\Delta I_t$ is the measured lock-in output signal. Lock-in data may thus be acquired simultaneously with topographic information. See fig. 3.3 for an example of imaging of local workfunction along with several other imaging techniques.

### 3.1.2 Measuring Local Density of States

The local DOS (LDOS) can be similarly determined from a differential technique, either by current - voltage spectroscopy, or via imaging at a specified bias and measuring differences in the LDOS as a function of tip position. The expression for tunneling current is given (equation 2.7) as:

$$I_t = \int dE M(f(E) - f(E + eV)) \rho_d(E + eV) \rho_e(E).$$

(3.3)

Here the tip is the emitter and the sample is the destination electrode, hence $\rho_e \Leftrightarrow \rho_t$ and $\rho_d \Leftrightarrow \rho_s$. Simplifying by taking the Fermi function to be a step distribution ($kT \sim 0.25 \text{ eV} < eV_t \sim 1-2 \text{ eV}$), and the Fermi level to be 0, taking the derivative with respect to $V$ yields:

$$\frac{dI_t}{dV} \propto M \rho_s(eV) \rho_t(0) + \int dE M \frac{\rho_t(E)}{dV} \rho_s(E + eV) +$$

$$+ \int dE dM \frac{\rho_t(E)}{dV} \rho_s(E + eV).$$

(3.4)

Assuming relatively constant tip DOS and the tunneling matrix (M) to be constant in energy as compared to the sample DOS, $\frac{d\rho_t}{dV} \propto \rho_s(eV)$, so $\frac{dI_t}{dV}$ gives a measurement that is roughly proportional to the density of states at the sample surface. Spectroscopically, this measurement can be taken in two fashions. The easiest manner is to take a number I vs V curves at fixed tip - sample separation (STM feedback is turned off), and then average a group of them up and take
numerical derivatives. In a perfect system, this would be all that was required, but as there is always a small amount of drift present (inability to maintain the tip at exactly the same place over the sample during data acquisition), as well as a finite amount of noise present, errors creep into such measurements. Also a smearing out of any time dependent features may also be due to the sample changing as it is being measured - especially important when studying thin insulating samples. An electron that is tunnel injected into the surface of the film must eventually make it to the STM preamp through a relaxation process that involves defect levels distributed throughout the insulator. While injection of 100 pA only requires relaxation of $\sim 1$ electron per 10 nanoseconds, if the insulator has been treated or is thick enough, this process can be compromised. 5 C/cm$^2$ (requiring $\sim 10$ ms @ 100 pA tunnel current) has been shown to be sufficient to cause thin SiO$_2$ based capacitors to breakdown [4], and hence it is not surprising to see that the oxide may change electrical properties while it is being measured. Hence a method to measure individual $\frac{dI}{dV}$ curves is highly desirable. The presence of even a small amount of noise precludes numerical calculation on individual traces as small noise induced oscillations in IVs can result in horrendous amplitude oscillation in calculated DOS.

The solution is to acquire $\frac{dI}{dV}$ spectra in real time simultaneously with the IV data via a lock-in measurement. The lock-in provides a small (10 to 50 mV) oscillation which is added to the tip bias as the bias is swept across the IV range of interest. The lock-in detects the component of the tunnel current that is oscillating at the same frequency, and hence provides an output that is proportional to $\frac{dI}{dV}$ (See fig. 3.1). This procedure can also be applied while imaging in constant current mode to create a map of the DOS across the sample surface. This is a very powerful method for correlating surface electronic structure and topographic information as
Figure 3.1: Topographic and DOS images, as well as conventional IV and direct $\frac{dI}{dV}$ measurements. The small wiggle in the tip bias (horizontal arrows) creates an oscillating component in the tunneling current (vertical arrows). Different regions in the sample DOS image hence yield different spectroscopic results.
well as pinpointing regions of interest for detailed spectroscopic study.

3.2 Ballistic Electron Emission Microscopy

While STM provides a method for measuring electronic structure at film surfaces, BEEM provides a means to measure structure and transport through such films. BEEM was developed as a three terminal extension of STM in 1988 [5] allowing the observation of ballistic electron transport through films and subsurface features. Initially utilized as a tool to probe Schottky barrier structure on a nanometer scale, BEEM has matured into a general tool for understanding the nature of ballistic transport and electronic structure of a variety of systems. The basic setup for a BEEM experiment is given in figure 3.2. The sample of interest is grown upon a semiconducting substrate, whereby a Schottky barrier is formed at the interface. This barrier serves as a filter for ballistic electrons. Electrons are tunnel injected from the STM tip with an energy, $eV_t$, where $V_t$ is the tip bias. If $V_t$ is greater than the Schottky barrier height, $V_b$, the electrons transport through the film without scattering inelastically, and the momentum matches well at the interface, they will maintain enough energy to pass over the Schottky barrier and couple into the conduction band of the semiconductor. As the dominant scattering at this energy level is electron - electron scattering, scattered electrons will lose approximately half of their kinetic energy [6]. In the 1-2 V energy range typically used for BEEM experiments, this will reduce their energy to below that required to pass over Schottky barrier, and thus the vast majority of collected BEEM electrons are ballistic in nature.

This process takes place as the STM tip is scanned across the surface, producing a spatial map of ballistic transport through the sample. If combined with
Figure 3.2: Experimental and energy diagram for BEEM. Electrons are tunnel injected into the film of interest from the STM tip. If the electron passes transports through the film without scattering inelastically, and possess correct energy and momentum, it may surmount the Schottky barrier formed at the interface between the semiconductor and the metal, and couple into the conduction band of the semiconductor. Such electrons are collected as BEEM current by the op amp connected an ohmic contact on the back of the semiconductor. No BEEM current can be collected until the injection bias is above the Schottky barrier height.
the techniques described above, a host of information can be obtained about the sample. An example of a simultaneously acquired STM topograph, BEEM image and DOS map on a 135 Å Au film is shown in figure 3.3. A workfunction map is shown as well. It is not possible to acquire workfunction maps simultaneously with DOS maps, so there is a slight amount of sample drift as the microscope was reconfigured for this measurement. Images are acquired at -1.2V. The DOS image is rather flat with several regions of higher DOS at -1.2 V of ∼2-3 nm in diameter. While most appear as similar bright regions in the BEEM image, there is one notable exception in the upper right corner where the impurity does match well with the band structure of the underlying Au. This indicates that it may be of a different type or perhaps poorly adhered to the Au surface as compared to the other impurities. While contrast in the work function image mostly stems from step edges, with the workfunction reduced as expected at step edges [7], the afore-mentioned impurity also images distinctly in the workfunction image, indicating the strong presence of dipoles, as compared with similar regions from the DOS map. It is thus bound to the Au surface in a different manner than its neighbors, leading to poor ballistic transmissivity.

BEEM is generally modelled as a three stage process: tunneling from the tip, transport through the film, and passing over the Schottky barrier. Hence, BEEM contrast does not have to stem only from surface features, although this is the contrast mechanism which will produce the highest spatial resolution in the BEEM images - electrons will diverge slightly as they traverse the film. As ballistic transport through the film is required, contrast can indicate the presence of a buried barrier [8], magnetic contrast [9], as well as many other scattering centers. The final obstacle is the Schottky barrier, and hence BEEM contrast can also be due
Figure 3.3: BEEM, STM, DOS, and local workfunction images of 135 Å Au film. Note that some features which appear identical in DOS images are differentiated in either the BEEM or the workfunction images (arrows). This is an indication of the utility of combining several different imaging and spectrographic techniques to correctly identify otherwise similar features.
to spatial inhomogeneities in the Schottky barrier. There are many models which
treat each of these three steps in varying degrees of detail. I would like to pay
special attention to the simplest two models that treat the final step, transport
over the Schottky barrier in a careful manner, as such interfacial scattering will be
addressed in Chapter 7.

3.2.1 Bell Kaiser Model of BEEM Transport

As BEEM was initially developed by Bell and Kaiser [5] at the Jet Propulsion
Laboratory, the Bell - Kaiser (BK) model, further described in [3] was the first
attempt to understand the technique. The fundamental assumption is that no
scattering takes place at the metal - semiconductor interface, as one might expect
in a perfect epitaxial system. Hence, total energy and transverse momentum ($k_t$)
are conserved. Modelling the Schottky barrier as a step potential of height $eV_b$
(Figure 3.4), if we separate the energy of the electron into a component normal to
the interface ($E_x = \frac{\hbar^2 k_x^2}{2m}$) and a component transverse to the interface ($E_t$), and
label the base Fermi level as $E_f$, $eV$ below the Fermi level of the tip (for a negative
injection bias) the condition on $E_x$ for collection is

$$E_x \geq E_f + eV_b.$$  \hfill (3.5)

Simply put, the energy of the electron must be greater than the Schottky barrier.

Similarly, conservation of energy as the electron crosses into the semiconductor
implies $E_{semi} = eV - eV_b$, and requiring that $k_t$ is conserved as well gives

$$E_{semi} |_{k_x=0} = eV - eV_b = \frac{\hbar^2 k_t^2}{2m^*} = E_t \left( \frac{m}{m^*} \right).$$ \hfill (3.6)

We evaluate $E_{semi}$ at $k_x = 0$ to determine the maximum possible transverse mo-
The total energy in the base, $E_t + E_x$ is given by:

$$E_t + E_x = E_f + eV$$  \hspace{1cm} (3.7)

Eliminating $eV$ between equations 3.6 and 3.7 yields:

$$E_t \leq \left( \frac{m^*}{m - m^*} \right) (E_x - E_f - eV_b).$$  \hspace{1cm} (3.8)

Now, utilizing a simplified expression for tunneling current (sample and tip density of states are taken to be constant [5]) equation 2.7 becomes

$$I_t = \int dEM (f(E) - f(E + eV)).$$  \hspace{1cm} (3.9)

Utilizing the Simmons WKB approximation for $M$, equation 2.4,

$$M \sim e^{-\alpha s(E_{f(tip)} + \phi - E_x)^{1/2}}.$$  \hspace{1cm} (3.10)

Here we note that as electrons are tunneling from the Fermi level of the tip $E_{f(tip)} = E_f + eV$ is used. Hence the expressions for the limits on $E_x$ and $E_t$ must also be adapted:

$$E_x^{\text{min}} \geq E_{f(tip)} - eV + eV_b$$  \hspace{1cm} (3.11)
\[ E_{\text{t}}^{\text{max}} \leq \left( \frac{m^*}{m - m^*} \right) (E_x - E_{f(tip)} + eV - eV_b). \]  
(3.12)

Substituting equation 3.10 into 3.9, and separating the energy into \( E_x \) and \( E_t \) yields:

\[ I_t = \int_0^\infty dE_x e^{-\alpha s(E_{f(tip)} + \phi - E_x)^{1/2}} \int_0^\infty dE_t(f(E) - f(E + eV)). \]  
(3.13)

The BEEM current then comes from those electrons initially injected with the appropriate momentum, \( E_{x}^{\text{min}} \leq E_x \leq \infty \), and \( 0 \leq E_t \leq E_{t}^{\text{max}} \), or:

\[ I_c = R \int_{E_{x}^{\text{min}}}^\infty dE_x e^{-\alpha s(E_{f(tip)} + \phi - E_x)^{1/2}} \int_0^{E_{t}^{\text{max}}} dE_t(f(E) - f(E + eV)), \]  
(3.14)

where \( R \) is incorporated to measure electron attenuation in the metal film. It is convenient to normalize 3.14 by 3.13. It is useful to note that the \( f(E + eV) \) term represents the probability a state is occupied at a voltage \( V \) above the energy of the tunneling electrons. For tip biases above the Schottky barrier, where BEEM current will be collected, this is well above the Fermi level of the sample, and hence the occupation probability is very small. Performing the first integral over \( E_t \) yields an expression for \( I_c(I_t) \) that can be calculated for each value of \( V \) and used to fit BEEM \( I_c(V_t) \) curves:

\[ \frac{I_c(I_t)}{I_t} = \frac{R \int_{E_{x}^{\text{min}}}^\infty dE_x M(E_x) \left| E_{t}^{\text{max}} + kTln \left( \frac{e^{\frac{E_x-E_{f}}{kT}}+1}{e^{\frac{E_x-E_{f}+E_{t}^{\text{max}}}{kT}}+1} \right) \right|}{\int_0^\infty dE_x M(E_x) kTln \left( e^{\frac{E_{f}-E_x}{kT}} + 1 \right)}. \]  
(3.15)

This is the expression for the BEEM current that is collected by a zone centered conduction band minimum (CBM). The voltage dependance is contained in \( E_{t}^{\text{max}} \) and \( E_{x}^{\text{min}} \). If however, the CBM is not at the \( \Gamma \) point, the expressions for \( E_{t}^{\text{max}} \) and \( E_{x}^{\text{min}} \) (no longer 0) become considerably more complex. They can be found by allowing a nonzero vector of the band minimum, \( k_0 \) in the equation 3.6:

\[ E_{\text{semi}} = \frac{\hbar^2 |k_t - k_0|^2}{2m^*}. \]  
(3.16)
Equation 3.16 and the expression for $E_t$ from equation 3.6 can then be substituted into equation 3.7, and the result solved for $E_t$ [10]:

$$E_t^{\text{min,max}} = E_0 \left[ \frac{2m \cos^2(\theta)}{m - m^*} \left( 1 \pm \sqrt{1 - \frac{m - m^*}{m \cos^2(\theta)} + \frac{m^* \xi}{m \cos^2(\theta) E_0}} - 1 \right) + \frac{m^* \xi}{m - m^*} \right]$$

(3.17)

Here, $\xi = E_x - E_{f(tip)} + e(V - V_b)$, $E_0 = \frac{\hbar^2 |k_0|^2}{2(m - m^*)}$, $\theta$ is the angle between $k_t$ and $k_0$ and $k_{0t}$ is the projection of $k_0$ onto the interfacial plane. This is a simplification of the actual situation to make the problem more tractable. What is mathematically going on here is that the discrete locations of the CBM in k space (see figure 3.5) are being transformed and an effective mass is being used to turn the CBM into an annulus in k space. Ideally, one should rewrite the integrals in terms of $k_x$ and $k_t$ and properly describe the CBM in that picture. However, even when utilizing the simpler integrals in energy space, the requirement for division of the two 1 dimensional integrals at each voltage value (equation 3.15) is somewhat time consuming and produces singularity problems in some cases as it is. Turning to the integrals in k space produces rather nasty time consuming calculations, difficult to use for curve fitting.

The electron tunneling distribution is strongly forward focused, as electrons which cross the vacuum gap with some transverse momentum have to cross a wider barrier than those with minimal $k_t$, and the tunneling probability is an inverse exponential function of barrier width. This implies that if electrons do not undergo momentum scattering, very little contribution will be collected at the off center CBM (See figure 3.6).
Figure 3.5: Conduction band minima for GaAs (100). The Γ point has the lowest Schottky barrier height $\sim 0.9$ eV, followed by L at $\sim 1.2$ eV and finally X at $\sim 1.4$ eV. While X and Γ project onto the zone center ($k_t=0$), there is no zone center projection for the L valley.
Figure 3.6: Projection of electron beam upon GaAs CBM. For forward focused electrons (a), for energies within $\sim 1$ eV of the $\Gamma$ CBM Schottky barrier, the Gamma valley is the strongly dominant collector. L contributes almost negligibly to the BEEM collector current if incident electrons undergo no scattering. (b) for an incident beam of electrons that is isotropically scattered, all CBM contribute to BEEM collector current. The rate at which they increase with bias is related to the effective mass in each CBM and the number of channels (symmetry) contributing to each CBM.
3.2.2 Ludeke Bauer Model of BEEM Transport

The Ludeke Bauer (LB) Model [6] for follows the opposite premise as BK: the underlying assumption is that electrons propagate through the film in the same manner as above, but upon reaching the metal-semiconductor interface, they scatter isotropically and redistribute their momentum states completely. This model obviously applies to systems with a strong scattering at the interface. Once again, coupling into the semiconductor consists of matching those momentum states of the newly scattered electrons (the projection of the Fermi sphere in the metal upon the interface) with the CBM in the semiconductor. Thus a threshold for BEEM is present from every CBM with a barrier height contained within the voltage that is swept out in the IV. All scattering at the interface is elastic, and all effects from the attenuation in the metal film, impurity scattering, and other inelastic electron scattering are accounted for in another overall scale factor.

Tunneling from the tip is modelled in a slightly different manner from BK theory. The essential difference is that planar tunneling theory is expanded with the adsorption of a single atom on the plane representing the tip [11]. As this atom forms the narrowest portion of the tunneling barrier, the vast majority of the tunnel current will flow through it. This is in all likelihood a realistic model as one expects the very end of the tip to deviate from a plane, and contain a small protrusion through which the majority of the tunnel current flows. The tip distribution function: \( f_T(\varepsilon) \) that is produced in this model is a sharply peaked (at the Fermi energy of the tip) exponential function at \( T = 0 \). This is expected, as while the tip is occupied up to its Fermi level, all electrons with energies greater than the sample Fermi level (tunneling to unoccupied states in the sample) can tunnel, and electrons with higher energies are more likely to tunnel (they see a
lower barrier). In reality the tunneling distribution is thermally smeared, which has the basic result that a few electrons are available to tunnel above the Fermi level of the tip, and the function utilized [6] is:

\[ f_T(\varepsilon) = \frac{b e^{b \varepsilon}}{1 + e^{b \varepsilon}}, \]  

(3.18)

where the value of \( b = \frac{|\ln(0.5)|}{E_{1/2}} \) comes from the requirement that the tip distribution be normalized. The shape of the BEEM IV is weakly dependent on \( E_{1/2} \), the full width at half maximum of the tip distribution function [6, 12], which is given by 0.28 at room temperature for standard tunneling conditions [6].

What remains now is to find the matching between momentum states in the semiconductor and the metal. Electrons in the metal base will be injected with an energy \( E_f + eV + \varepsilon \), where \( E_f \) is the Fermi level of the base, \( V \) is the tip bias, and \( \varepsilon \) allows us to account for all tunneling electrons which will be injected into the base at various energies. Treating the base as a free electron metal, the projection of the Fermi sphere on the interface thus has radius \( \frac{\sqrt{2m(E_f + eV + \varepsilon)}}{\hbar} \), and area \( \frac{(2\pi m(E_f + eV + \varepsilon))}{\hbar^2} \). Here some small adjustment may be made away from the free electron approximation through the adjustment of \( m_e \) in order to include d band effects, for example. If an electron surmounts the barrier and crosses into one of the CBM of the semiconductor, it will have energy \( eV - eV_b + \varepsilon \). If we represent the ellipse in phase space that will be projected on the interface by a circle of equal area utilizing the density of states effective mass, the area is given by \( \frac{2\pi m_s(eV - eV_b + \varepsilon)}{\hbar^2} \). The fraction of the scattered electrons that can propagate into the semiconductor is thus given by:

\[ \frac{\eta m_s(eV - eV_b + \varepsilon)}{2 m(E_f + eV + \varepsilon)}, \]  

(3.19)

Where \( \eta \) the is the degeneracy number each CBM. Only half of these correspond to
the direction away from the interface, towards the semiconductor, hence the factor of 2. The complete expression for the BEEM current is thus given by accounting for the impinging electron energy distribution \( f_T(\varepsilon) \), and integrating over all electrons that can contribute to the BEEM current \( e(-V + V_b) \leq \varepsilon \leq \infty \). This yields the following expression:

\[
\frac{I_c}{I_t} = R \frac{\eta m_s}{2 m} \int_{e(-V+V_b)}^{\infty} d\varepsilon \frac{b e^{-b \varepsilon}}{1 + e^{\frac{b \varepsilon}{kT}}} \frac{(eV - eV_b + \varepsilon)}{(E_f + eV + \varepsilon)} \tag{3.20}
\]

Practically, however, due to the Fermi distribution present \( f_T(\varepsilon) \) in the upper limit only needs to be slightly above the Fermi level of the tip \( (E_f(tip) = 0 \) in this description, and \( E_f \) in eqn. 3.20 is the sample Fermi level). While the appropriate effective mass is clear for the spherical \( \Gamma \) valley in GaAs \( (0.068 \ m_e) \) [13], it is not quite so obvious for the L valley. McNabb [14], outlines a procedure for determining which effective mass to use for the L valley and derives an effective mass of 0.125. This value along with a degeneracy of 4 will be used for the L valley contributions in the LB model. For the X valley contributions, there are two types of projections on the interface, one at the \( \Gamma \) point, with \( m_t = 0.23 \), and also the ellipses, with \( m_t = 1.3 \) and \( m_t = 0.23 \). The total area of the projections of these ellipses dictates that an effective mass of 0.3 with a degeneracy of 4 should be used for the outer lobes, and an effective mass of 0.23 with a degeneracy of 2 for the lobes at the \( \Gamma \) point. The total \( \frac{m_t}{2} \) value for the X valley in the LB model is hence 0.83. For the BK model, the \( \Gamma \) point will dominate the contribution, and hence one only needs to worry about that location: \( m_{BKx} = 0.23 \). The total BEEM current is then the sum of the contributions from each of the valleys. One overall scale factor is utilized to account for attenuation of ballistic electrons while traversing the base.
3.2.3 Modelling Interfacial Scattering

It is interesting to note that for zone centered CBM for the voltages typically used in BEEM, both the BK and the LB models should give nearly identical energy dependence for a single zone centered CBM [15]. To see this result, check the contribution of the Ε valley in the bottom graph in figure 3.7 (R values have been scaled to the same transmittance value at 1.6 V for the Ε valleys). This stems from the fact that while the impinging electron distribution is already strongly columnated for reasonable voltages, the CBM fall entirely within the momentum distribution contained by transporting electrons. There is however still a slight difference that stems from how the tunneling distribution is treated: planar tunneling vs the single adsorbed atom.

While modelling only the Ε valley produces nearly identical \( I_c(V_t) \), from the different spectral shapes of the total collector current \( (I_c(V_t)_\Gamma + I_c(V_t)_L + I_c(V_t)_X) \) in the BK and LB models it is clear that the interfacial scattering assumptions have a dramatic impact upon the IV’s produced. However, the expectation that 100% of electrons scatter at the interface not held for all films. This has been demonstrated for the Au- GaAS and Au-Si systems by Smith [16, 17]. Hence momentum scattering at the interface can be used as a measure of interfacial disorder. Here, thesis, this will be accomplished by fitting to a simple weighted sum of the two models : \( [(1 - SP)(BK) + SP(LB)] \), where the relative contributions of each CBM is fixed by the model. SP thus represents a scattering parameter that is 0 when none of the incident electrons are scattered, and 1 when 100% scattering is required from the fit. It is now possible to utilize the model described above to understand how sample treatment and growth methods, as well as the interfaces formed by different bases effect momentum redistribution at the metal
Figure 3.7: BK and LB calculations for BEEM current for the $\Gamma$ valley and L valley contributions to $I_c$ for a Au / GaAs system and the resulting total collector currents. There is a dramatically different spectral shape for the total current in the LB model, which stems from the strong L valley contribution due to the large L valley effective mass.
- semiconductor interface. This will be treated in Chapter 7.
References for Chapter 3


CHAPTER 4

EXPERIMENTAL PROCEDURES

In the last chapter, we have seen several theoretical treatments of both STM and BEEM, and in this chapter I would like to address the experimental system utilized for the acquisition of the data presented in this thesis. In the process, I will describe several important maintenance procedures that are not covered in the documentation, as well as a few changes that have been implemented. As two thirds of the studies presented in in this thesis take place on oxide surfaces that have been treated given a controlled oxygen, heat, or electron bombardment exposure, an Ultra High Vacuum (UHV) vacuum environment is essential. Sample study with the STM typically takes one or two days and hence samples must be relatively immune to interactions with residual gasses on this time scale. Typical base pressures during studies are approximately $4 \times 10^{-10}$ Torr, with an oxygen partial pressure below one twentieth of that, resulting in less than 2 monolayers of oxygen striking the surface per day. As the sticking coefficient for oxygen on annealed aluminum oxide films is quite low (.016) [1], and as this is $\sim 10^{-7}$ times the dose giving to aluminum oxide samples one does not expect any substantial change in the sample surface to take place during the course of the experiments. While the initial sticking coefficient for oxygen on Mg metal is $\sim .25$ [2], this will drop off dramatically after the first three to four monolayers of oxide are formed [3]. Therefore, as little as a factor of ten or so increase in the pressure of the scan chamber could start to create aging problems, perhaps most prominently in the annealed AlO$_x$ samples. Upon my arrival to the group, the UHV system consisted of the X-ray Photoelectron Spectroscopy system (XPS), Old BEEM and a single sample preparation chamber connected as shown in Figure 4.1(a). Shortly
thereafter a new BEEM system was purchased, and for the reasons stated above, it was imperative that integration of the newly purchased STM with the old sample preparation chamber needed to take place in an all UHV environment.

Due to the constraints of the vacuum transfer system through the shared load lock, the spatial requirements of the electronics racks for XPS, and the lack of regular use that XPS was enjoying (especially for any samples that were fabricated \textit{in situ}), we decided that the most prudent solution was to avoid the complicated (and probably failure prone) trolley system that we had devised to enable interconnection of all the systems via a single shared load lock. XPS was parked against one wall and the lab took on the layout as shown in Figure 4.1(b) and (c).

In the off chance that it became necessary to study a sample grown in one of the sample preparation chambers \textit{in situ} using XPS, we set up a vacuum transfer station. It was designed to be a general use pumping station as well and is frequently put into use to pump out cryostat and transfer line jackets as well as other routine around the lab uses. The vacuum transfer cart consists of a Pfeiffer turbo cube, a small chamber with a gate valve, a transfer arm for moving samples between the two load locks and the attached chamber, and a quick flange attachment for roughing out cryostats. A sample can be made in one or both of the preparation chambers, transferred into the cart, wheeled across the room and transferred into the XPS system while maintaining UHV conditions. In practice, both ends require brief bakes and cooling to arrive at optimal pressures. (0.75 day per LL) This yields a transfer that takes place at $\sim 1 \times 10^{-9}$ Torr for the majority of the process (10 hours), and a five minute exposure to $1 \times 10^{-7}$ in the XPS load lock. The end result is that samples taken through the process are
Figure 4.1: Layout of D7, past and present. Meshing the new BEEM and sample preparation system with the old equipment required substantial reorientation of the XPS system.
exposed to almost 100 Langmuir\textsuperscript{1} of background gasses during the transfer, a far cry from UHV. This adjusts the lower limit on the range of dosages that can be studied, and eliminates the possibility of studying sample aging effects, such as in reference [4]. However, neither of these concerns is a terrible loss, as due to the age of the XPS system, reasonable spectra take at least 12 hours to acquire. In addition, the fact that sample treatment methods such as annealing the samples before the vacuum transfer result in consistent, measurable changes shows that the threshold where sample aging effects on these treated samples is not reached in the transfer process.

However, what is unfortunate is the fact that growing and transferring a sample ties the STM and preparation chambers up for about a day during which no data can be taken. In order to minimize the amount of time the both STMs are unusable, special XPS sample transfer pucks were machined as shown in figure 4.6 in the lower left position. The wobble stick in prep II (described in section 4.4.5) is used to place individual chips with distinct sample structures in each of the four positions after film deposition is complete. The sample transfer cart is outfitted with a fork and puck system like that present in both sample preparation chambers, and hence the puck can be placed on this transfer fork, and wheeled across the room under UHV for entry into the XPS system.

\begin{section}{Old BEEM}

Although the majority came from the RHK BEEM system, much of the data provided in this thesis was taken in Old BEEM, a system described in detail in [5] and [6]. While a workhorse in its youth, as Old BEEM aged, several of the

\textsuperscript{1}0.000001 Torr-sec
interior parts became susceptible to wear, and a few changes to Old BEEM have been implemented. Perhaps the most significant was the installation of a new piezo tube scanner. The shorting out of the high voltage wires supplying scan waveforms inside old scan tube turned out to be a premonition of things to come. Although it was unknown at the time of installation, the Kapton coated magnet wire that had been used throughout the wiring of new been was prone to aging problems, which manifested themselves at a later time as intermittent shorts. This process is accelerated through the stresses due to wires flexing from raising and lowering the two spring system the important parts of Old BEEM hang from [5], as well from decomposition due to thermal cycling in the $\sim 100^\circ$ C bake out process required to achieve UHV.

However as no good UHV compatible replacements exist, the solution may be to update the entire wiring harness as these wires begin to fail. It was just such an intermittent short between the power and ground wires which caused either the BEEM or STM op amp to burn out three times, over a period of approximately 6 months, and eventually once the root cause was discovered, led to a replacement of many of the power and signal wires within the system. As Burr Brown\textsuperscript{2} had changed their package design for the OPA-627 low noise operational amplifier, whereby the TO-99\textsuperscript{3} package is connected to V-, and hence can no longer be grounded as required in the implementation of Old BEEM, another op amp with similar noise characteristics was required.

After a lengthy search revealing a paradigm shift in power wiring across nearly all vendors, a single op amp was found that fit the design requirements. This was the Analog Devices AD-549. However, its use is limited to applications with a

\textsuperscript{2}now owned by TI

\textsuperscript{3}metal can
very low input capacitance (i.e. a short unshielded input wire), for which it suits Old BEEM very well. This limitation stems from the relatively large input voltage noise, six times the OPA627’s $15 \frac{nV}{\sqrt{Hz}}$ at 10 Hz. However, as input voltage noise manifests itself in a multiplicative manner with the input capacitance, and the 549 has $\frac{1}{8}$ th the intrinsic input capacitance of the 627, in applications with very short input wires, it will have better noise characteristics than the 627.

This concept can be understood from an analysis of the operation of the current to voltage preamplifier. The Old BEEM preamplifiers are wired in a simple inverting configuration, as shown in Figure 4.2 (a). 4.2 (b) shows the addition of a small input voltage noise, and the input capacitance as well to aid in an analysis following that of Ref [7]. As in a typical noninverting opamp

$$V_{out} = V_{in}(1 + \frac{R_{out}}{R_{in}}),$$  \hspace{1cm} (4.1)

or in this case:

$$V_{out} = V_{noise}(1 + \frac{Z_{out}}{Z_{in}}) = V_{noise}(1 + 2\pi f R_{fb} C_{in}).$$  \hspace{1cm} (4.2)

This explains the differences in the noise spectra between the two 627 and the 549. While the 627 had a flat signal response at $4 \frac{nV}{\sqrt{Hz}}$ (Johnson noise from the 1 GΩ feedback resistor) up to about 1 kHz after which this input voltage noise \ capacitance based noise appears in the frequency spectrum, the 549 is flat for one more kHz, demonstrating the small differences between these two op amps in this configuration. This extra bandwidth is unimportant as inherent capacitances in the feedback resistor coupled with the lower gain bandwidth product in the 549 limit BEEM frequency response to well below 1 kHz.

A few other changes that may be implemented in the near future are to integrate a lock-in amplifier in a similar method as is described in the case of New BEEM
Figure 4.2: Inverting current to voltage preamplifier. Typical implementation (a). Input capacitance ($C_{in}$) and voltage noise ($V_n$) included (b)
in section 4.5.4. This will require accessing the tip bias and designing a low noise sum circuit to add in the lock-in oscillation. If imaging of the local work function is desired, design of a more difficult step up and high voltage sum circuit will be required.

The 14 bit ADC in the Nanoscope III scan controller limits the tunnel current resolution to steps of .6pA, so if very low tunnel currents $\sim 1$ pA are desired, the gain on the tunnel current must be increased. The relatively simple integration of a second stage gain on the tunnel current should be available through implementation of the second channel of the current frequency devices filter box. If electrical drift (mainly due to the offset null box) can be minimized, a factor of 100 second stage gain should result in a step size of 6fA, and a Johnson noise floor of $10 \frac{fA}{\sqrt{Hz}}$, giving 200 fA of Johnson noise in a typical 500 Hz bandwidth, enabling scanning with around 1 pA of tunnel current.

4.2 Prep I

The old sample preparation chamber has been a rather fluid piece of equipment, with its capabilities adapting to accommodate experimental requirements. I designed and installed a vacuum annealing furnace in the 4.5” flange opposite one of the transfer arms, where a nonfunctioning mass spectrometer had been mounted. A picture if the oven is shown in figure 4.3.

The oven uses large currents to resistively heat the wound tungsten filaments, and hence draws power from the large step down transform used to drive the thermal boats as well. John undertook the arduous task of machining the molybdenum end rings while I wound the tungsten coils and machined the more friendly parts. The coils are attached to the moly rings using moly washers and stainless steel
Figure 4.3: Vacuum annealing oven. A thermocouple extends within the oven and contacts the sample for temperature measurement while the sample is annealed. Maximum temperature is $\sim 700^\circ$ C.
screws and nuts, so the whole unit should be capable of at least of 1100° C, above the melting point of the copper gasket vacuum seals. It is current limited in the present setup. While originally implemented to understand the effects of annealing on the electronic structure of AlO_x, a 500° anneal in the furnace has become a staple of sample preparation for GaAs based samples to flash off the layer of oxide left at the surface after the previous sample preparation steps outlined in section 4.6.

4.3 Load Lock

The new load lock was originally designed to allow transfer into either of three chambers mounted at 90° from each other. To accomplish this goal the transfer mechanism consists of two forks for holding pucks mounted to a rotary feed through hanging off of a flexible coupling, basically an inexpensive wobble stick. It works surprisingly well, and has enabled vacuum transfers to XPS to be integrated in a seamless manner.

4.4 Prep II

While a short list of the capabilities and attachments for our larger sample preparation chamber is covered in Ref. [8], I will go into a little further detail on a few of the features, paying special attention to the various changes that have been undertaken in the system. Figure 4.4 shows a picture of Prep II with the appropriate parts labelled.
Figure 4.4: Prep II. Evaporation flange, sputter guns, turbo and ion pumps, wobble stick flange, and transfer arms and height adjustment apparatus are clearly shown.
4.4.1 Sample Transfer

The sample transfer mechanism that takes pucks into New BEEM requires a slight relative vertical movement of the two forks situated at 90° from one another. This is accomplished via the dovetail frame that can move the entire long arm and ion pump assembly vertically about 1/2". It is important that sample growth and calibration take place at a standard height position as indicated by the stainless steel ruler. The requirement for a 46 inch rotary linear transfer arm allowing samples to be rotated to face the sputter guns for sputter deposition required the use of a magnetically coupled transfer arm. The long thermionics transfer arm that I settled upon to accomplish this task did not live up to expectations. After approximately two years of use, the magnets began to decouple sporadically, and required maintenance to remove gall marks along the shaft and lubrication with graphite powder at six month intervals. In the time that has elapsed since our purchase, Thermionics came to the conclusion that the design for these longer arms was insufficient, and reengineered the system. The arm they later sold us as a replacement with a whopping $250 discount seems to function reasonably well, although with an occasional sticking that is somewhat worrisome - it may begin to need the maintenance as well.

4.4.2 Evaporation Flange

Aycan designed and implemented the evaporation flange that hangs below the chamber on the right side. It contains three electron beam deposition sources (eguns), and was designed with the thought of integrating several Knudsen cells (K-cells) as well in the future. However, as I began to use this evaporation flange regularly, an important system change rendering potential future integration K-
cells a bit more involved then originally thought was required. An insert and shield to provide cooling around the eguns and K cells as well as shielding adjacent K-cell and egun sources from one another had to be removed due to excessive shadowing effects. Two of the eguns were not uniformly coating samples during evaporation due to shadowing from this shield. A new implementation of this shield would have to be fabricated in order to properly install the K-cells. A liquid nitrogen shroud surrounding the eguns is filled during evaporation to maintain chamber base pressure at approximately $2 \times 10^{-9}$ during evaporation of Fe, and $\sim 1 \times 10^{-8}$ during evaporation of the MgO. Failure to use the shroud results in an increase in the base pressure during evaporation of about a factor of 5 - 10 due to extensive out gassing from the egun that is used without the close proximity of a "cryo-pump". The much higher base pressure during deposition of MgO is due to the disassociation of MgO and the liberation of O and O$_2$ gas, as verified with our residual gas analyzer.

### 4.4.3 Atom Source

The nitrogen atom source from Oxford Applied Materials that sits above and to the left of the large evaporation flange may be reconfigured as an ion source as well for nitridation of materials relevant to Josephson junctions such as NbN and AlN. Changing plasma tube from Boron Nitride to Alumina, and a reconfiguration of the optics will allow for plasma oxidation as well, the MgO preparation method that Freescale Semiconductor finds the most promising for MgO based MTJs.
4.4.4 Sputter System

The aperture plate of the atom source is protected from two AJA 2" Sputter guns directly opposite it by a shutter. Unfortunately, the installation of these two sputter guns extended the system pump down time considerably. While atmosphere to UHV had been achievable in less than 24 hours after a brief vent before the installation of the sputter guns, now it requires at least four days of baking. This is due primarily to the increase in surface area coupled with low conductivity associated with the Ar and O gas lines for the sputter guns. While the guns were originally installed with the intention of DC Magnetron sputtering, recently John has successfully added the capability to Rf sputter from insulating targets as well. During sputtering, a teflon blind is rolled down to protect the sample and tip staging area from excessive deposition of the source material. A capacitance manometer and throttle valve located directly below the turbo pump control the pressure during sputtering while two mass flow controllers to the right of the chamber control the Argon-Oxygen sputter gas mixture. Typical operating parameters are 1 - 3 mTorr pressure and 8 sccm of Ar (+.5 sccm of O$_2$ for reactive MgO deposition).

4.4.5 Sample and Tip Staging System

Without a doubt, the most important function of Prep II is that of a sample staging system. Samples are taken out of the shadow mask system used in for deposition and loaded onto specialized pucks for scanning in the RHK system. Sample sizes are identical to those used in Old BEEM so that samples can be cross checked between the two microscopes in an all UHV environment should problematic behavior arise - very useful for troubleshooting sick microscopes. However, the ability to handle bare samples and to load them onto the RHK scan pucks as well as the
Figure 4.5: Wobble stick jaws and RHK scan puck. Jaws are designed to facilitate *in situ* loading and unloading of bare samples onto scan pucks as well as moving the pucks themselves. Handling of bare tips is required as well for *in situ* tip cleaning and preparation.

Requirement for manipulating bare tips and pucks with single wobble stick located in the sample staging area was nontrivial. I designed and machined a special pair wobble stick jaws in order to accomplish all of three of these tasks. They are shown in figure 4.5, along with a RHK scan puck.

Samples can be gripped with the tabs that protrude beneath the jaws where they begin to curve together to place the samples under the spring clips on the scan puck. The cutout in the center of the jaws provides a view of the sample and spring clips during this process. The tabs can protrude along the sides the raised, gold-coated section of the sapphire washer in the RHK pucks and also facilitate sample removal. This washer was custom machined by PFC Semiceramic for a very reasonable cost. The Au backside contact for BEEM pick up was deposited in the CHA evaporator by ion milling the surface for 20 minutes, depositing a 5
nm Ti binding layer, and then 200 nm of Au through a custom machined shadow mask for the correct pattern. These pads have held up well so far, but may have to be refreshed in the future as the Au wears off.

The jaws are thin enough that they mate nicely within the .1” grooves cut in the pucks where forks typically engage, and the curvature at the end prevents the puck from slipping off the end under the jaw closing pressure. Handling of bare tips is accomplished at the very end, where the two segments meet. Tip preparation procedure will be outlined with the help of Figure 4.6, the tip and sample staging system.

Tips are prepared ex situ via a controlled etching of .01” tungsten wire in a 4 Molar KOH solution, as outlined in Ref. [5], and transferred into the chamber on a specialized tip puck that assists with tip manipulation as well. This prevents the RHK tip change pucks from ever having to leave the vacuum system, as gasses absorb to the teflon posts and extensive outgassing results upon their reintroduction to the sample preparation chamber. The general procedure for tip preparation is similar to a procedure outlined in Ref. [6], although specific details vary slightly. Tips are gripped above the rim in the collet, and are placed in a receptacle that can be brought to ±2000 V for tip treatment. This high voltage unit (white macor disk with metal center) is then rotated under the filament that hangs below the center puck storage post. The tip is is then brought to +2000V, and current is run through the filament until around 1.5-1.7 mA of emission current is measured (about 8 A) for about 2.5 minutes. This method of electron bombardment serves to heat up the very end of the tip and remove the tungsten oxide that has formed on the freshly etched surface during the brief atmospheric exposure. Above 800° C, the stable form of WO₃ decomposes into W and WO₂, which is volatile and
Figure 4.6: Sample staging area. A special puck to transfer in and assist with tip loading is on the upper left post. A RHK tip change puck is in the middle, and to the right a puck for sample growth and transfer into the chamber. On the lower shelf in the left spot is a puck for transferring multiple samples to XPS using the transfer cart. On the right is the system for unpacking samples from the shadow mask holders. To its right is a multiple use electrical feedthrough that can be plugged into appropriately equipped pucks using the wobble stick. It has been used for a faraday cup to measure electron flux, and could be used for substrate heating during deposition as well. The middle post is an unoccupied puck station. The lower macor dish holds the tip annealing station, and the source filament hangs beneath the vacant puck storage station. A sliding tray for sample storage is on the far left.
sublimes off the tip surface [7]. Clean W metal is left behind. The voltage polarity is then switched, and by measuring the voltage at which a current of 12 µA is field emitted, the the sharpness of the tip can be gauged. Typically, I aim for -1200 to -1300V. If the tip doesn’t fall within these requirements, further sharpening can be accomplished by introducing Ar gas into the chamber up to a pressure of $1 \times 10^{-5}$ mTorr. This Ar is ionized by the field emission of electrons from the tip [9]. Positive Ar ions then impinge upon the tip sputtering off material and sharpening it further. A dull tip can be sharpened in this process with about a 50% success rate. I have found that Ar sputtering works substantially better than Ne sputtering in Prep II.

Prepared tips can then be loaded into the RHK tip change pucks, using the auxiliary tip transfer puck to regrip them below the collet flange. This is accomplished by loading the tip into one of the slots cut in the top of the transfer puck from above, and then grabbing the part that protrudes into the space cut away in the upper groove. Tips need to be regripped with the sample loading protrusions on the jaws facing down. The tip can then be carefully loaded into the RHK tip change puck, making sure that the locking wire and the slot it engages with are aligned with one another. Thereafter the tip change procedure proceeds as outlined in the RHK VT400 manual. A special puck has been modified to remove tips that have rotated around during the movement of the RHK tip change puck and cannot be pulled out of the scan head using a conventional tip change puck.

4.5 New BEEM

Located behind Prep II, we come to the piece of equipment responsible for the majority of the data in this thesis, the RHK VT400 BEEM system. Unfortunately,
Figure 4.7: New BEEM. The continuous flow cryostat protrudes from the right side of the chamber. Rotary feedthroughs from the top and bottom move scan head and sample stage with respect to one another. The camera on the upper right is used to accurately position the tip over the sample.
its design was as new to RHK as it was to us. They had never designed a system
which integrated an eddy current damped spring suspension system and variable

temperature capability. Since BEEM is a relatively infrequently used experimen-
tal technique, while RHK was a company that built commercial AFM and STM
systems, BEEM was also completely new to them. However, this gap in their
knowledge was filled by working closely with them as the system was designed.
The meshing of the cryostat with the spring suspension system was less then ideal,
and as a result the ultimate measured sample temperature is 125° K, \( \sim 75 \) above
what was advertised. This will be further addressed in section 4.5.2. A few inter-
esting bits of trivia about the system concern the broken tap lodged in the sample
stage, and the loose bolt that found its way into the BEEM feedthrough, short-
ing two internal grounds together, and resulting in excessive noise in the BEEM
channel.

4.5.1 VT400 Mechanical

The VT400 is based upon a beetle\(^4\) scan head design. The scan head rests via three
piezoelectric legs on the scan puck which has three accompanying ramps for coarse

approach. It may be lowered from the top of the system and then decoupled from
the lowering mechanism as it comes into contact with the scan puck. A shorter
scan tube protrudes from the center of the scan head directly over the sample,
where the STM tip locks in place. (see figure 4.8.)

In order to produce coarse motion, the three piezoelectric legs are provided
with a saw tooth type voltage waveform with a slow rise time and a very quick
fall. In this manner the leg deforms slowly maintaining contact with the surface as

\(^4\)also known as a Johnny Walker
Figure 4.8: Beetle scan head design. Coarse motion is provided via the stick-slip motion of the three piezoelectric legs. However, the axis are not necessarily orthogonal; approaching the tip results in some lateral motion as well.
the initial slope is applied. When the voltage quickly returns to its lowest value, the leg quickly returns to the unflexed state, momentarily losing contact with the surface, and hence over many such events the scan head "walks" along the surface. The waveforms presented to the three legs can be coordinated to move each leg simultaneously in the x or y direction for x or y translation with respect to the sample, or in a spiraling fashion, either up or down the ramps for coarse approach to bring the tip within tunneling range. One thing that is very nice with this design, is that alignment between the x and y scan axis on the inner piezo scan tube and coarse motion is very simple. The coarse positioning is taken care of in a predetermined fashion with the signals that are sent to the legs and everything is rigidly epoxied in place. Once a calibration is done between the relative alignments, if needed, the wave forms sent to the coarse positioning can be adjusted so that a step in the "+X" direction corresponds to the same direction for the tube scanner.

This three legs upon which the scan head rests occlude optical access to very little of the sample. This open design makes for relatively easy integration of photon counting or collection and polarization analysis experiments. It also opens up a large line of sight whereby the end of the tip can be image with relative ease in order to monitor the approach and make sure that one is landing the tip over the desired area. The draw back in this aspect is that as the approach is done via rotation of the scan head, the legs will move through different positions where they block optical access to different viewports. As each tip will have a different length, tunneling will be established with a different rotation of the scan head relative to each viewport, and imaging equipment may have to be moved to a different angle to achieve a clear line of sight.

The microscope was shipped with a black and white CCD camera with a long
focal length lens allowing magnification of approximately 100 X at a distance of about 1.5 feet. This greatly simplifies imaging tip sample approach and enhances the ease with which one can land on the device area of a sample - a 100 µm × 100 µm window etched in field oxide as described in section 4.6. I have found that the clearest images of the device window can be obtained by placing an incandescent light source on the viewport opposite the camera. With careful adjustment of the intensity and camera aperture, the window will appear in stark contrast, and can easily be located.

Additionally, the beetle design whereby the scan head is lowered down from above onto the RHK scan pucks makes the system much easier to work on. Unlike Old BEEM where the entire scan head / sample holding unit is a relatively substantial weight hanging at the end of a shaking dual spring unit, disassembly is is quite straight forward. The top flange, which the scanning apparatus, tip bias, and related electronic and mechanical system can be removed for maintenance. The bottom flange can be easily dropped as well (care must be taken to disconnect the spring suspension and the copper braid for cooling at the cryostat first), and sample stage unit can be lowered and the eddy current damping, lower feedthroughs, sample heater filament, and associated wiring can be serviced. Alignment between the two sections is a rather time consuming process, but if one is careful realignment does not need to be performed as long as the stage is adjusted, for example to change the heater filament.

If done carefully, the procedure to change the heater filament results in minimal disturbance of the alignment between the scan head and sample stage. The procedure is as follows. Remove the top flange and store it out of the way. Before dropping the bottom flange, one must first carefully disconnect the copper cooling
Figure 4.9: RHK bottom flange.
braid at the cryostat end by first removing the the two flat head screws securing the radiation shield. This is actually quite difficult, and I find that a clean stubby flat screw driver with the end ground thinner so as to fit in the screw slots is the only tool that will work well. These screws are extremely short, so care must be taken not to lose them as they come loose. The shield pops off, and then four allen head screws holding a copper block attached to the end of the braid may be loosened. There is an indium coated sapphire plate that sits between this block and the copper block at the end of the cryostat. Sometimes it sticks to the copper block on the braid, so care must be taken not avoid its falling and breaking. It is important as it maintains electrical discontinuity between the chamber and the sample stage for noise reasons. Cooling performance is not adversely affected its presence. The springs can be disconnected and removed. The bottom flange is now free and can be removed to a bench top. The outer stage (aluminum hockey puck sized piece) can be removed by loosening three screws holding bars that secure with viton ropes (another stage in the vibration isolation) attached to the bottom of the sample stage. It is then lifted over and away from the gold plated cooled sample stage. Access should now be clear to the macor filament enclosure. It may be helpful to disconnect the filament current supply wires at the bottom flange to free up a little movement with the macor piece. There is a single screw that affixes the filament inside of the macor tube with a clamping mechanism. Before removing the filament note the height within the macor cylinder in order to reproduce this spacing with the new filament. The filament can then be taken out and replaced. It is a good idea upon reassembly to carefully check the mechanism that pulls the filament back into the stage as when it is raised completely so as to avoid problems with it interfering with sample loading later.
Upon reassembly, the ingenuity of the spring suspension and damping design becomes apparent. The spacing between the copper fins and magnets for the eddy current damping system is adjusted via four external linear feedthroughs. This is important as the springs will relax slightly during bake out following any major repair. A nonisolated electrical feedthrough on the bottom flange provides a means to check that copper fins are not shorted to the magnets introducing ground loop into the system and short circuiting the vibration isolation system. One thing to keep in mind is that the isolation works best if the fins are evenly spaced around the magnets, so one must be careful not to finish adjustments with the stage hanging too shallow in the magnets. I like adjust everything as close as possible upon reassembly while the system is vented, and then do final touches after the bake has been completed.

However, for all the above advantages that are present in the beetle design, there are several large disadvantages that have manifested themselves over time. The primary problem for usage in the current system stems from the fact the many chambers are brought together in intimate contact, and hence vibrations run unhindered up and down the length of the system. This may not seem a large problem; after all we have the spring suspension to take care of such concerns. Yet the spring suspension is designed to absorb only minor vibrations and most motion (for example from the turbo pumps or building swaying) only takes place on the scale of microns. Large bumps and jars (and even many smaller ones) couple into the chamber quite easily. The result is that if anyone is trying to (gently) move samples around in the chamber, at the very least, large scan line artifacts appear in the images. If something binds and then unsticks in a violent manner, and a bit of a shock wave propagates through the chambers, and a tip crash can
occur. An accidental bump is sufficient to mimic the slip-stick coarse motion and translate the tip with respect to the sample; several times, the scan head became completely dislodged from the scan puck and came to rest on two legs and the tip - not very good for tip robustness. The bottom line is that with the current setup everyone has to tip toe around the lab so as not to upset the dragon. The more rigid construction of the sample-scan unit in Old BEEM does not require such care.

Another problem that frequently crops up with this design is that it greatly complicates tip approach if one is trying to engage upon a specific area on a sample, such as the case with nearly all of our BEEM samples (see section 4.6). In this case, the rotation of the scan head is always accompanied by substantial translational movement as well, and one has to watch the system very carefully and make periodical lateral adjustments as the tip is engaged to make sure the region of interest stays beneath tip. I think this effect stems from inequalities in the tensions of the wires carrying the high voltage signals for the piezoelectric elements that join to the scan head. This brings us to the last major problem with this design: the multitude of wires. The independent wiring of four piezoelectric elements requires 20 connections, which can be reduced to 16 wires travelling to the scan head by recognizing redundancies in this particular scan head arrangement. However, as the tip is approached, each of these 16 wires flexes, and raising and lowering the scan head onto and off of the scan pucks additionally flexes these wires considerably. The end result is that several times during the first year, a wire popped loose and had to be resoldered, requiring a vent. This is a straightforward, if tedious, procedure. After the third incident, I removed and resoldered all the wires with a slightly longer length then had been previously been present.
None of the high voltage wires have become unsoldered since. It is important to use the California Fine Wire .003” Cu wire with heavy polyimide (H-ML) coating and Eutec 157 soldering compound for any reparations. This polyimide is UHV compatible, and has held up to the bake and flex cycles quite well so far. The wire must be very thin to minimize vibrational coupling from the chamber into the scan head.

This same wire is used to carry the tip bias, and likewise somewhat prone to stress cracks in the solder joints, especially deep within the scan head. This problem manifests itself through a flaky connection tip connection and difficulty in establishing tunneling upon approach. The repair is rather simple, although time consuming and sensitive. The top flange with the scan head assembly is placed on a stand with the scan head facing downwards, in the same orientation as if it were mounted on the chamber. The head is partially lowered so as to expose the plug and socket where tip bias changes from a thicker wire enclosed in a stainless steel tube to the .003” wire. This plug is disconnected, the scan head is lowered, and all the high voltage piezo wires can be disconnected at their tie down points. Then the scan head can be removed from the assembly, and a teflon shield that covers the union between the thin .003” tip bias wire and a thicker piece that runs down the inside of the scan piezo tube can be removed. Then one just needs to cut a new length of wire and solder it in place. However, the other end of the thicker wire is also soldered to the tip collet receptacle, so extreme care must be taken to avoid overheating this joint. All repairs should be done with clean tools, and without the use of solder flux. In order to remove surface oxides and so achieve better wetting of metallic surfaces with the solder, the solder flux contains HCl as well as several fluoride compounds, the combination of which has
be shown successful to etch PZT thin films [10]. Hence I avoid solder flux as much as possible in the proximity of the scan tubes.

4.5.2 Cooling

New BEEM was purchased with the intention of not only doubling the capabilities of the system, but also enabling movement into a new region of parameter space. The system is capable of (limited) variable temperature through the introduction of a Cryo Industries UHV continuous flow cryostat. A copper block sits inside the vacuum flange, through which piping runs. This piping is brazed to a channel that is cut in the copper block, and the cryogenic liquid continuously flows through the block, cooling it. An indium coated thin piece of sapphire separates this block from another block which is indium bonded to a copper braid connected to the sample stage. This insures that the sample stage is electrically isolated from the chamber ground, important for noise considerations. The sample stage is spaced off from the room temperature section of the microscope with a rather thin piece of stainless steel that has many holes cut in it in order to reduce its thermal conductivity. The isolation is not great, but reasonable.

Cooling a sample is of interest because it changes the basic assumptions about which types of samples can be studied via BEEM. Many of the samples studied give a very low BEEM current, especially buried AlO$_x$ samples [8], which produce on the order of 50 fA of BEEM current per nA of injected tunnel current at a 2V bias. As we saw in chapter 3, BEEM samples consist of a Schottky diode that serves as a filter that only allows ballistic electrons to surmount the Schottky barrier and be collected as BEEM current. This extremely low current collection implies samples need to be of very high resistance to avoid any low level current leakage across
the diodes that may wash out any detected current. Another argument for high sample resistance concerns the fact that electrons traversing the Schottky barrier may decide to travel back through the sample diode instead of traversing the 1GΩ BEEM feedback resistor if the sample resistance is lower than the feedback resistor value [8]. Johnson noise contributed by the diode should also be smaller than that given by the feedback resistor, implying once again that sample resistance needs to be at the least greater than the BEEM feedback resistor. From thermionic emission, in the limit of no voltage applied across the diode the current density across a Schottky barrier is given by [11]:

\[
J = \frac{qA^* T}{k} e^{-\frac{qV_b}{kT}},
\]

implying that the resistance across the barrier is given by:

\[
R = \frac{k}{qA^* T} e^{\frac{qV_b}{kT}}
\]

where \(A^*\) is the effective Richardson constant, about 110 A/cm\(^2\)/K\(^2\) for electrons and about 30 A/cm\(^2\)/K\(^2\) for holes. \(q\) is the electron charge, \(V_b\) is the barrier height, \(T\) is the temperature, and \(k\) is Boltzmann’s constant. The sample area can be patterned, as described in [5], [8], and section 4.6, but this only gives reduction in noise that is linear with respect to the sample area decrease. Also, in both microscopes, \(\sim 50 \mu m\) is the smallest dimension over which the tip can reliably be positioned. The true gain here comes from the temperature, which is contained in the form of an exponential comparison with the barrier height. This has be addressed to demonstrate which alternative barriers become useful for metal Si systems [8], although several readily form silicides, resulting in a lower than

\(\text{in reality there is always a few } \mu \text{V due to differences between the op amps on either side of the diode}\)
predicted barrier height. Another possibility which may become of great interest is to use a variation known as hole BEEM, or BHEM, whereby the tip is kept at a positive bias, holes are injected in the sample to be studied, and a p type substrate is used. Thereby ballistic transport of holes is measured. Although this may initially appear to be of dubious value, recent interest in probing molecular energy levels on a nanometer length scale is a strong motivation. Most molecules are hole carriers, and thus probing the energy levels present is much more straightforward using BHEM.

While Schottky originally derived a simple equation relating the barrier height to the work function of the metal:

\[ \phi_b = \phi_m - \chi, \quad (4.5) \]

with \( \phi_m \), the metal work function and \( \chi \), the semiconductor electron affinity, a much smaller dependence of the barrier height on metal work function is measured experimentally. This is commonly attributed to either interfacial states introducing a dipole at the interface or metal induced gap states [12] which pin the Fermi level of the metal at some point in the band gap - usually substantially closer to the valence band. This is strengthened by the fact that the sum of the barrier heights for barriers formed on both n and p -type semiconductors is usually quite close to the value of the band gap. The end result is that a very rough "rule of thumb" describes such contacts to first order:

\[ V_b = \frac{2}{3} E_g, \quad (4.6) \]

with \( E_g \) the band gap of the semiconductor, and \( V_b \) referring to the barrier height for a n-type substrate, although in reality there is still a bit of dependence on the work function, with higher work function materials tending to form higher barriers.
on n-type substrates, at the expense of the barrier height when formed on a p-type substrate. Therefore, the barriers tend to be much lower (approximately half the value) on p-type substrates as opposed to on n-type substrates. If the temperature can therefore by dropped to approximately half that of room temperature (\(\sim 150^\circ K\) is achievable in new BEEM with liquid nitrogen), a metal which forms a sufficiently high Schottky barrier on a n-type substrate at room temperature should also form one that is sufficiently high to eliminate noise issues on a p-type substrate at low temperature. In reality, there is also a bit of an improvement from switching to p-type substrates as the Richardson constant is also about \(\frac{1}{4}\) of its value for holes as compared with the value for electrons. The most promising p-type Schottky system that can easily be created in our chambers is probably Al-GaAs, which has a barrier height of \(\sim 0.63\) eV [11], and should have a high enough sample resistance at \(\sim 230^\circ K\).

Before building and testing the VT400 system, RHK aggressively quoted its capabilities as being able to achieve temperatures as low as \(\sim 50^\circ K\). The problem was that they had not yet integrated the spring suspension system with the cryostat, which places considerable constraints upon the quality of the thermal contact between the sample and the cooling block. It turned out that in our systems the sample thermocouple never reads below \(\sim 150^\circ K\) for cooling with liquid nitrogen, and we get to a whopping \(\sim 125^\circ K\) by switching to He. It took a long time for RHK to finally admit that they hadn’t tested the system with liquid He before delivery, and that the temperatures that they quoted us were valid, but only when taken at the sample stage with liquid nitrogen, and not at the actual sample. Comparing the thermal conductivities of the thin stainless steel post that spaces off the sample stage and working through the copper braid that takes heat
out to the cryostat, working through the sapphire plate that spaces the two copper blocks, provides a stable temperature of about 115 K for the sample stage if cooled with liquid nitrogen and about 50 K or so if cooled with He. This is in a simple model utilizing heat transfer given by $q = -k \nabla T$. Modelling the system as a 1-dimensional rod, integrating, and assuming a steady state solution becomes this becomes:

$$\dot{Q} = \frac{kA}{L}(T_1 - T_2),$$

(4.7)

with $\dot{Q}$, the rate of heat transfer, $k$, the thermal conductivity, $A$ the cross sectional area through which conduction is taking place, $L$ the length of the wire, and $T_1$ and $T_2$ the temperatures at both ends.

This is verified experimentally, and therefore the sample stage will come to the quoted temperatures, but the sample is measured to be a far cry away. Part of the reason behind this discrepancy is probably the presence of the sapphire washer that sits underneath the sample to provide electrical isolation for the backside for BEEM contact, but provide good thermal conductivity. Sapphire actually has higher thermal conductivity than copper over the temperature range that we are interested in (see [13]). However, heat flux into the sample comes from two sources, radiative from the rest of the chamber, contributing about about 0.03 Watts assuming both the chamber and the sample puck follow black body emission, in accordance to the Stefan-Boltzmann law:

$$P = \sigma A(T_1^4 - T_2^4),$$

(4.8)

with $\sigma$ the Stefan - Boltzmann constant $\sim 5.67 \times 10^{-8}$, $A$ the area of the object, and $T$ the temperatures of the object and the surrounding area. There is, of course, very little convection, so the other source of heat into the puck are the four wires
for STM, BEEM, and the two thermocouple pick up wires. These guys provide approximately .2 watts in, dominating the radiation contribution, so little is to be gained by enclosing the sample puck in a radiation shield. However, heat from these sources gives a strongly nonuniform introduction of heat into the sample, primarily directly at the thermocouple. This thermocouple is poor contact, with the sapphire plate on the sample puck, which leads me to believe that it tends to read higher significantly higher then the actual sapphire temperature, which should be considerably closer to the temperature of the sample stage. The best way to accurately measure the sample temperature would probably be to try to use some type of temperature programmed desorption experiment with the Residual Gas Analyzer, or to watch in STM images for surface adsorption or liberation of a background gas on a particular sample surface as an indication of sample temperature. I think we will find that the system gets at least a little cooler than indicated. Another possibility is miscalibration of the thermocouple on the sample puck. However, it has been verified to be accurate at $77^\circ$ K.

### 4.5.3 Heating

While it should be possible to heat samples in excess of $1000^\circ$ C using electron beam heating with the filament that resides under the sample as a source of electrons, two problems arise: one would have to coat the back of the sapphire plate in the sample puck with a metal that could be contacted independently electrically and floated at a high bias. The other is that at high temperatures, the thermal conductivity of sapphire drops off very quickly, and if care were not taken it might be possible to melt off the metallic coating on the backside of the plate. However, sample heating is more readily and reproducible attained in the vacuum oven, although that has
an upper limit of around 700° C.

If one is interested in heating the sample while scanning, this can only be accomplished using radiative heating, where the sapphire plate limits attainable temperatures to \( \sim 200° \) C. Long term heating is not terribly useful for BEEM as \( \sim 200° \) for 1 hour will degrade the Schottky barrier in Au/Si systems. GaAs based diodes may be more resistant. However, the process of heating in this manner causes the filament to glow, a source of photons which create photo current, quickly drowning out an measurable BEEM signal. I built a simple step up electronics box which boosts the current provided from the Lakeshore temperature controller’s feedback circuit, so any temperature up to \( \sim 200° \) can be maintained while scanning with the STM.

**4.5.4 Electronics**

The SPM 1000 electronics box that came with the system is very flexible, allowing for additional imaging and spectroscopy capabilities to be integrated with the system in a relatively straightforward manner. This unit serves to interface the computer data acquisition software with the various electronic subcomponents in the microscope. The SPM 1000 generates all the high voltage scan signals as well as buffering and digitizing the preamp input signals for computer collection. There is a plethora of BNC plugs present in the back, for easy access and to allow summing of auxiliary signals to the tip bias and other parameters during scan acquisition.

Filtering of the input signals from the preamps is done in second stage gain box, which only addresses the BEEM channel. It has a single buffered RC low pass filter along with additional 10 or 100 × gain on the BEEM channel, providing a 6dB per octave drop off the STM channel passes straight through. A 6dB per
octave set with the 3dB point at 50 Hz is not a sharp enough slope for effective filtering of 60 Hz noise components, one of the dominant frequencies present in the BEEM channel. Acquisition time to capture enough data for effective averaging for sensitive signals is impacted by the efficacy of the filtering. For sample surfaces which are sensitive to tunnel injection and can only be studied for a short time period, such as AlO$_x$, this adversely impacts the signal to noise ratio (SNR). For stable sample surfaces, it extends the time required for data acquisition. In order to ameliorate these problems, two Frequency Devices active 8 pole low pass Bessel filters were added in line with both STM and BEEM channels. The Bessel filters were picked because they have a very small phase shift, and the best impulse response, with minimal ringing of the circuit.

One of the strongest reductions in the SNR for tunneling spectroscopy measurements came from the implementation of a method to directly measure the derivative of the tunnel current with respect to the tip bias, giving an approximate measurement of the local density of states (DOS) at the sample surface$^6$. The control electronics provides a nice way to apply small amplitude signals to the tunneling gap as well. As addressed in chapter 3, this provides a measurement of the local work function, and hence insight into the presence of dipoles at the sample surface. While this ultimately turned out not to be useful MgO, it may be of great value in scanning exposed organic molecules, lending insight into their bonding to any underlying surface, as well as perhaps the local arrangement. Both of these techniques require the integration of a lock-in amplifier, and the controlled sweep of the tunnel gap$^7$ require the ability to change which DAC is connected to each channel, as well as where the lock-in oscillation signal is routed.

$^6$This is described in the previous chapter
$^7$for acquisition of IS curves, where S is the tunneling gap
Figure 4.10: Floating preamp design. Tip bias is connected to the noninverting input. Oscillating this input hence results in a large oscillation of the measured tunnel current.

To this end a switch box was built which allows one of the DACs to be either responsible for either coarse positioning with the beetle, or for modulating the sample-tip distance. Lock-in oscillation can couple into either the tunnel gap or the tip bias, and the lock-in can detect the frequency matched output from either the STM or the BEEM channel. Carefully setting the oscillation frequency and the STM piezo response time should allow similar detection in BEEM signals, where it may be possible to directly measure direct BEEM derivative IVs, useful for determining the bias dependance of conduction channels within samples under study.

Introduction of the tip bias oscillation required a change in the implementation of the STM preamplifier. In the original configuration of the system, the STM preamp was designed to float at the tip bias, a relatively noisy design, and the sample surface was held at ground. However, in addition to this noise issue, the noninverting input of the preamp was tied to the tip bias (See figure 4.10).

The result is that any oscillation applied to the tip bias causes a preamp response. To avoid this situation, connections to the sample were changed so that it would be possible to directly contact the backside with the BEEM preamplifier.
This required the design and implementation of an external noninverting amplifier. I elected to build one around the OPA627 as it would require the use of a relatively long input wire, and hence for reasons addressed in section 4.1, minimal input voltage noise was the crucial design consideration. Building *ex situ* in a grounded box allows the incorporation of a circuit board, and hence an op amp where the TO-99 can does not need to be held at sample ground. The design is shown in fig. 4.11.

It consists of a 1st stage gain with a $10^8$ feedback resistor in an inverting current to voltage amplifier configuration (100mV / nA), followed by an adjustable second stage gain (Burr Brown INA 110) which inverts the signal once again, to produce an amplifier that responds in the to an adjustment of gap width in the manner that the
control electronics unit expects. This preamplifier box is attached to the sample ground, and its reference ground is tied to that of the BEEM preamp. In this manner, BEEM images, DOS maps (as described in chapter 3), and topographic structure may all be obtained simultaneously. The draw back is that the BEEM current is a little cleaner if the sample is at true ground instead of the virtual ground offered by the op amps in this configuration (about a factor of 2 for a $2 \, \Omega$ sample), so for low BEEM current images, one has to choose which parameter needs to be optimized, the STM or BEEM channel.

4.6 Sample Preparation

As outlined in section 4.5.2, the Johnson resistance noise at room temperature is determined through both the materials choice and the sample area size. The procedure for reducing the area is to deposit an insulating oxide layer ($\text{SiO}_2$) on the substrate and to etch a window in the sample using photolithography. A small metal trace is then deposited upon the sample to reduce capacitive coupling across the diode, as covered in Ref [6]. For details on Si processing see Ref [5]. The GaAs process described in Ref. [8] has been modified slightly in light of the vacuum annealing oven, and I will cover those modifications here. In an attempt to create a self contained description, I will start from the beginning of the GaAs process. Typically many wafer blanks can be prepared about once per year and stored for latter use.

4.6.1 Oxide Deposition

The first step is to deposit $\text{SiO}_2$ in the IPE PECVD machine in Duffield hall. Unfortunately, something has changed with this tool in the move to Duffield, and
Table 4.1: Deposit SiO\textsubscript{2} in IPE PECVD.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Dip wafers in Ammonium Hydroxide: DI Water 1:10 solution for 30 Sec. Quench and rinse in DI water. N\textsubscript{2} Blow Dry.</td>
</tr>
<tr>
<td>(2)</td>
<td>Wipe down and clean IPE system platen. Run CF\textsubscript{4} clean for 10 min. Season chamber 2 min (run SiO\textsubscript{2} process with no wafers).</td>
</tr>
<tr>
<td>(3)</td>
<td>Vent and carefully load wafers, as GaAs is prone to fracturing if heated too quickly. Four wafers can be done at once. Center them on platen.</td>
</tr>
<tr>
<td>(4)</td>
<td>Deposit 500 nm SiO\textsubscript{2}: 44 Watts Rf power @ 275\textdegree C 6 sccm SiH\textsubscript{4}, 54 sccm N\textsubscript{2}O 54 sccm, 450 mTorr pressure</td>
</tr>
</tbody>
</table>

the oxide films it produces are no longer as good quality as the had been when the tool was located in Knight lab. This manifests itself in the final step: samples that are annealed in the vacuum oven introduce problems with the oxide film, and a large area, low quality short develops, producing very low quality diodes with low resistances upon subsequent deposition of the metallic overlayers. Films that are not annealed do not have this problem. It may be possible to circumvent this problem by using the GSI PECVD, a much more reliable tool, but last time I checked, only Si substrates were allowed. I list the parameters that seem to work the best for deposition of the SiO\textsubscript{2} in the current setup in Table 4.1.

Etching the surface oxide in Ammonium Hydroxide and then quenching in water helps clean the wafer surface and creates a uniform surface oxide to promote the adhesion of the SiO\textsubscript{2}. The IPE is frequently left in an unknown (and unclean) state, so careful preparation maximizes reproducibility of the deposited films. When loading the wafers, I typically hold it with the tweezers on the platen.
Table 4.2: Spin photoresist

<table>
<thead>
<tr>
<th></th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Acetone and Isopropanol (IPA) spray clean wafer while spinning</td>
</tr>
<tr>
<td></td>
<td>Do not let Acetone dry on wafer. Dry IPA with N\textsubscript{2} while spinning</td>
</tr>
<tr>
<td>(2)</td>
<td>Apply (\sim 1) mL P-20 adhesion layer with dropper</td>
</tr>
<tr>
<td></td>
<td>immediately spin at 3000 rpm, 60 sec.</td>
</tr>
<tr>
<td>(3)</td>
<td>Apply (\sim 1) mL Shipley 1813 resist</td>
</tr>
<tr>
<td></td>
<td>immediately spin at 3000 rpm, 60 sec.</td>
</tr>
<tr>
<td>(4)</td>
<td>Hard bake on hotplate 115\textdegree, 60 sec.</td>
</tr>
</tbody>
</table>

Table 4.3: Expose photoresist - HTG 3HR contact aligner

<table>
<thead>
<tr>
<th></th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Align sample to mask with machined plexiglass holders.</td>
</tr>
<tr>
<td></td>
<td>The wafer fits into slight groove and mask fits over top.</td>
</tr>
<tr>
<td>(2)</td>
<td>Expose for (\sim 12) sec.</td>
</tr>
<tr>
<td></td>
<td>Exposure length depends on lamp intensity.</td>
</tr>
</tbody>
</table>

for about 10 sec. so that not all of the wafer comes in contact with the 275\textdegree surface at once. Sometimes the wafers will shatter if simply placed on the hot platen. After deposition, I measure the thickness using the Leitz MVSP to get a calibration for how long the oxide will need to be etched, as the thickness will vary from run to run even though identical deposition parameters are used.

4.6.2 Oxide Patterning

Silicon dioxide patterning is done in BOE 1:6 \((\text{HF}:\text{NH}_4\text{F}:\text{H}_2\text{O})\), using a 1.3 \(\mu\text{m}\) photoresist mask. Typical etch times are on the order of five minutes. Details are given in tables 4.2, 4.3, 4.4, and 4.6. The first BOE etch patterns the windows
### Table 4.4: Develop photoresist

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Develop in 300 MIF, ~120 sec, slight agitation</td>
</tr>
<tr>
<td>2</td>
<td>Quench and rinse in water</td>
</tr>
<tr>
<td>3</td>
<td>N₂ blow dry</td>
</tr>
<tr>
<td>4</td>
<td>Inspect with microscope for sharp lines</td>
</tr>
</tbody>
</table>

### Table 4.5: Etch SiO₂

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
</table>
| 1 | Buffered oxide etch 6:1, ~5 minutes. (Depends on oxide thickness)  
    | Check each 2 minutes for completion.                          |
| 2 | Quench and rinse in water                                       |
| 3 | N₂ blow dry                                                    |
| 4 | Strip resist in heated resist strip bath, 10 minutes per bath  |
| 5 | Buffered oxide etch 6:1, ~15 sec.                             |
| 6 | Quench and rinse in water                                       |
| 7 | N₂ blow dry                                                    |
Table 4.6: Prepare ohmic contact

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Dip wafers in Ammonium Hydroxide: DI Water 1:5 Solution for 1:30 Sec. Quench in IPA. N₂ blow dry.</td>
</tr>
<tr>
<td>(2)</td>
<td>Load 2 wafers into CHA, backsides exposed. A special chuck is used to hold 2” wafers. Wafers are rotated in situ to allow evaporation on 2 wafers per pumpdown</td>
</tr>
<tr>
<td>(3)</td>
<td>Deposit 75 nm Au via thermal evaporation per wafer ~5 Å per second. A pressure of 1 ×10⁻⁶ is sufficient.</td>
</tr>
<tr>
<td>(4)</td>
<td>Place on room temperature hot plate, Au side down</td>
</tr>
<tr>
<td>(5)</td>
<td>Ramp hot plate to 350° C, hold at 350° C for 1/2 hr. Ramp back to room temperature.</td>
</tr>
</tbody>
</table>

and guidelines for the wafer saw. The final ~15 sec etch rounds the edges of the SiO₂ windows to help metal continuity for the STM pickup the metal trace as it rounds the edge.

### 4.6.3 Ohmic Contact Preparation

Ohmic contacts are prepared by depositing a Au film in the CHA evaporator on the backside of the GaAs wafers and heating on a hotplate to promote interdiffusion of the Au at the interface.

### 4.6.4 Die Preparation

Sample wafers are cut into dice using the KS 7000 wafer saw. This procedure is addressed in table 4.7 At the end of this procedure, a number of blank chips are prepared which can be stored indefinitely, requiring only a brief clean before
Table 4.7: Prepare sample dice

<table>
<thead>
<tr>
<th>(1)</th>
<th>Spin photoresist to protect oxide from scratches while loading into chuck</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2)</td>
<td>Cut along lines patterned in oxide</td>
</tr>
<tr>
<td>(3)</td>
<td>Load chips into basket and strip photoresist, heated resist strip bath</td>
</tr>
<tr>
<td>(4)</td>
<td>Rinse in water. N₂ Blow Dry.</td>
</tr>
</tbody>
</table>

depositing the sample stack of interest.

4.6.5 Film Growth

Immediately before growing films, samples go through a 1 minute IPA ultrasound step, and another Ammonium Hydroxide : Water 1:5 bath to remove oxide that has built up during the storage period. Samples are quenched in IPA. The introduction of the vacuum oven in the chamber has provided another means to further remove the final layer of oxide present at the sample surface. This final clean step profoundly influences the orientation of subsequent films. In the case of Fe on GaAs, a completely untextured film is grown on the oxide surface, without the oven anneal, but a nearly epitaxial film is grown on the bare GaAs surface, because of the excellent lattice match between Fe and GaAs.

4.7 X-ray Diffraction Measurements

X-ray diffraction is a powerful method to determine the crystallographic structure, orientation, and phases present within a material of study. The standard geometry (see figure 4.12) is designed so that incident x-rays impinge upon the the surface normal at an angle, and a detector is set at twice that angle with respect to the
incident x-rays. The basic equation describing this diffraction process is known as the Bragg Law [14]:

$$\lambda = 2d \sin \theta,$$

(4.9)

where $\lambda$ is the x-ray wavelength, $d$ is the crystal plane spacing, and $\theta$ is the angle of the incident x-rays with respect to the sample. X-rays diffracted from the lattice planes interfere coherently when this condition is met, resulting in the addition of their amplitudes, and hence an overall increase in the intensity which is proportional to the square of the amplitude. The situation for which the Bragg law is satisfied in a perfect crystal takes place at discrete points in real space, and is actually rather rare. Hence, a detector may be moved around, or the crystal rotated in order to find the diffraction spots. Another method is to create a powder of the crystal which will then be randomly oriented in all directions. Diffraction from such a randomly oriented sample will result in a cone, or a ring when projected onto a two dimensional surface (see figure 4.12 b).

Measurements of the sample orientation were obtained in the X-ray Diffraction Facility of the Cornell Center for Materials Research using a Bruker General Area Detector Diffraction System (GADDS) tool. This tool employs a two dimensional detector that gives a simultaneous measurement of $2\theta$ and $\chi$, yielding a section of a Debye-Scherrer ring [14]. This geometry is shown in figure 4.12.

The two dimensional detector is set centered about $2\theta$, off center of the incident beam. Therefore, data from a randomly oriented sample will consist of arcs. Measurement of $2\theta$ values proceeds along the center of the detector, from right to left. Proceeding upward along an arc produces a change in $\chi$, which is indicative of the planes which are parallel to the sample surface, or the surface normal orientation of the film. Examples of data collected with this system are provided in fig 4.13.
Figure 4.12: X-ray diffraction geometry, (modified from [14]) (a) shows a top view of the instrument, (b) shows diffraction rings indicating $2\theta$ and $\chi$ in a randomly oriented film.
Figure 4.13: XRD data of evaporated Fe grown on GaAs oxide (a) and cleaned GaAs(b). (c) shows data from a sputtered CoFe film. The Fe grown on GaAs is randomly oriented. CoFe has some texturing, with 110 planes oriented 45 degrees out of plane. The Fe grown on bare GaAs is extremely well textured. Distinguishing the Fe 200 peak from the GaAs 400 substrate peak is somewhat difficult.
It is clear from the uniform arc in 4.13 (a) that the film is randomly oriented with no texturing. The arc comes from the diffraction signal given by the 110 planes at $2\theta \sim 44^\circ$, the strongest intensity diffraction peak for Fe. Data from this film appears very much like that from a standard powder sample, with a random microcrystalline orientation. While the presence of arcs in the sputtered CoFe data 4.13 (c) demonstrate a large degree of disorder, the fact that there are two higher intensity regions located at $\chi = \pm 45^\circ$ is an indication that there significantly more texturing than in the evaporated Fe. The Fe that has been grown at $\sim 150^\circ$ C on bare GaAs 4.13 (b) is very nearly epitaxially deposited. There are two observable peaks normal to the film surface. The higher intensity peak that is present at $2\theta = 66^\circ$ is the 400 GaAs substrate peak, while the peak at $2\theta = 65^\circ$ is the 200 Fe peak (the atomic structure factor forbids 100 reflections in the bcc and zinc blend basis sets [14]). The shifting of the intensity of the 200 peak relative to the 110 peak (not visible in this sample) alone is indication that the film is textured in the $<001>$ orientation, and the fact that the diffraction spot is so intense and strongly peaked along $\chi = 0$ shows that this film is nearly epitaxially ordered. These strongly textured Fe films serve as the base layer upon which I deposit $<001>$ oriented MgO.

4.8 XPS

A detailed discussion of the XPS system and analysis is given in Ref. [15], so I will only give a brief overview of the basic principles in the context of AlO$_x$ here. In XPS, an x-ray (photon) impinges upon an atom contained within the sample. Its energy is absorbed, leading to the emission of a core electron. This process is shown in figure 4.14. XPS is governed by the photoelectric effect:
Figure 4.14: X-ray photoelectron spectroscopy. X-rays impinge upon the sample ejecting an electron from core levels within the atom. Electrons from the top few nanometers escape and are analyzed by the spectrometer, whence their binding energies may be determined.

\[ BE = h\nu - (KE + \phi) \]  \hspace{1cm} (4.10)

where \( h\nu \) is the energy of the incoming X-rays, \( BE \) is the binding energy of the emitted electron, \( KE \) is the kinetic energy of the emitted electron, and \( \phi \) is the workfunction of the sample. In practice, the source consists of x-rays of a known energy (in our machine, a monochromator selects out the Al K\(_{alpha}\) x-ray lines at 1486.3 and 1486.7 eV). Setting the Fermi level of the spectrometer equal to that of the sample via an electrical connection and calibrating to a sample with known binding energies (a gold film) eliminates the problem of accounting for their respective work functions [15]. Thus becomes possible to measure the original binding energy via the calibrated kinetic energy. Confining studies to metals or thin insulating films (as is the case in the studies performed here) prevents samples from charging as electrons continue to be expelled from the sample. In the case
of very thin insulating films, electrons can move through defects in the insulator and fill the vacancies generated in the emission process from the Fermi level of metal underlayers. This is the opposite process that allows the STM preamp to collect tunnel injected electrons. As the attenuation lengths are very short for these photoelectrons (∼2nm) while x-rays penetrate and generate electrons throughout the sample, only those electrons generated within a few nm of the surface will make it out for collection. In this manner, XPS is a surface sensitive technique.

Figure 4.15 shows a survey scan from an AlO$_x$ sample. Oxygen and Aluminum lines are present along with a little carbon. As carbon monoxide is one of the primary gasses left in UHV environments, samples tend to accumulate a little bit of this adventitious carbon at ∼ 284 eV [16]. Performing high resolution scans of individual lines allows one to resolve component peaks within both the O and Al regions (figure 4.16). The aluminum high resolution scans exhibit the presence of both aluminum metal and aluminum in AlO$_x$. Due to the short attenuation length of the photoelectrons, electrons emitted from the underlying aluminum film will be attenuated as they traverse the oxide overlayer. Thus the ratio of the intensities of the two peaks is used to calculate the thickness of the AlO$_x$ film if the attenuation lengths of the electrons originating from the two layers and the Scofield numbers (roughly a scattering cross section for incident x-rays to create photoelectrons) are taken into account. [15]. Once the presence of chemisorbed oxygen has been identified (See Chapter 5), the oxygen spectrum can be used to calculate the stoichiometry of the AlO$_x$ layer. This calculation utilizes the relative intensities of the Aluminium AlO$_x$ at 76 eV peak and the Oxygen AlO$_x$ peak at 532 eV, along with the electron attenuation lengths and the Scofield numbers.
Figure 4.15: XPS survey scan of a 1.5nm AlO$_x$ film. Oxygen and Aluminum XPS lines are present, along with trace Carbon contamination.
Figure 4.16: XPS high resolution scans of Al and O regions. Both regions can be resolved into two individual constituent peaks. Aluminium peaks are identifiable as Al\(^0\) (metal) and Al\(^{3+}\) (AlO\(_x\)) at \(\sim 73\) eV and \(\sim 76\) eV. Oxygen peaks are at \(\sim 532\) eV (AlO\(_x\)) and \(\sim 534\) eV (chemisorbed O\(^-\)).
References for Chapter 4


5.1 Introduction

The prevalence of aluminum oxide layers formed by room temperature oxidation as the barrier in Josephson junctions (JJ) [1] and magnetic tunnel junctions (MTJs) [2] continues to motivate efforts to better understand and control its electronic structure. While bulk, stoichiometric Al$_2$O$_3$ has a band gap of $\sim 8.8$ eV, [3] for amorphous AlO$_x$ films grown at $\sim 20^\circ$ C it is a much smaller. This is beneficial as thin, transparent barriers provide the high critical current densities (JJs) and low specific impedance levels (MTJs) required by many applications, but band tails, localized states, and spatial inhomogeneities that may also be found in amorphous AlO$_x$ [4–6] can be very detrimental for high performance, low noise applications. Such localized or defect states in the barrier can cause electrons to tunnel in a strongly incoherent manner via states present in the barrier, potentially reducing the spin polarization of tunneling current [7, 8]. Reducing the presence of these localized states and removing or reducing band tails should produce devices with better operating characteristics. One commonly utilized approach to increase tunneling magnetoresistance is to anneal the samples in a magnetic field once the growth is complete. While this substantially improves the magnetic switching behavior, structural and electronic changes within the tunnel barrier layer cannot be ignored. Sousa and co-workers attribute barrier changes to oxygen to moving into the barrier and to becoming more uniformly distributed throughout the barrier layer, which would reduce the band tails and homogenize the distribution of density of states (DOS).
Several attempts at measuring AlO$_x$ layers have utilized conducting atomic force microscopy (CAFM). These studies which have shown inhomogeneous current distributions at the nanoscale, attributed to either a variation in local barrier heights [9] or in barrier thickness [10]. However, CAFM is not able to measure the local DOS at the surface, and the physical contact of the scanning cantilever - at a potential voltage differing from that of the base electrode - with the surface of the barrier layer will cause a substantial distortion of its electronic properties. In addition, a serious challenge for such surface spectroscopy studies of the electronic properties of AlO$_x$ is that the surface is invariably covered, even in ultra-high vacuum (UHV), with chemisorbed oxygen bound by positively charged oxygen vacancies in the oxide, with the degree of coverage depending on oxide thickness. [6, 11]

In this chapter, I will expand upon previously published results [12], starting out with a discussion of the electrical and structural properties of both Al and AlO$_x$ in the as-grown state, and then discuss how these properties are modified as the oxide undergoes different treatment methods. The effects of deposition of a top electrode, exposing the surface to a low energy flood gun electron bombardment (FGEB), and \textit{in situ} annealing will be addressed. Scanning tunneling microscopy will be utilized to examine the density of states (DOS) of the AlO$_x$ surface, and to determine how these states change when chemisorbed oxygen ions are moved into the oxide via one of the aforementioned treatment methods. Ballistic electron emission microscopy (BEEM) gives a measurement of how such states ballistically couple through the oxide layer. BEEM and Scanning tunneling spectroscopy (STS) measurements taken together allow a complete picture of the electronic properties of the oxide surface, and remove many of the ambiguities inherent in CAFM measurements.
In addition, X-ray photoelectron spectroscopy (XPS) is utilized to determine the physical structure of these ultra-thin oxide barrier layers. The combination of these three measurement techniques is powerful in developing a full picture of the oxide and an understanding of how the physical and electronic structure evolve in tandem as these oxide layers undergo the various treatment procedures.

While partial deposition of a Co top electrode leaves clusters adhered to exposed areas of AlO\textsubscript{x}, completing the deposition of the top electrode forces chemisorbed O clusters into the barrier layer, improving its stoichiometry, similar to the physical changes enacted via FGEB. Both FGEB and thermal anneal treatments greatly reduce low energy band tail states and narrow the DOS distribution over an oxide area. However FGEB causes different changes in the DOS than annealing. The former, if sufficiently energetic, results in locally well defined conduction band onsets at \( \sim 1 \) V, while the latter results in a progressively higher local conduction band onset, exceeding 2.3 V for 500\(^\circ\) and 600\(^\circ\) C anneals.

### 5.2 Sample Fabrication

I fabricated the samples for this study via thin film thermal evaporation and post-growth processing in UHV. For most samples, I deposited 12 nm of Au on hydrogen terminated (111) Si to form a high quality Schottky barrier (SB) to serve as the BEEM detector. (111) Si has been shown to give a higher BEEM signal than (001) Si [13], and hence was chosen as the substrate. This was followed by a 1.2 nm buffer layer of Cu, 1.2 nm Co, and finally 1 nm Al. Samples were then transferred into the load lock for a 10 torr-sec exposure to oxygen\(^1\) (99.9985 %).

\(^1\)This dose is much greater than that required to form a uniformly transmissive sample if a top electrode is deposited [14].
purity). X-ray photoemission (XPS) measurements show that this exposure forms a \( \sim 1 \) nm AlO\(_x\) layer [15]. Some samples were then transferred back into the sample preparation chamber to be annealed for 3 minutes in the UHV vacuum oven while others were vacuum transferred to the XPS system for exposure to FGEB. FGEB treated samples were subjected to either 10 eV or 20 eV electrons at a current density of about 10 \( \mu \)A/cm\(^2\) for 2 hours. Upon completion of processing, samples were either transferred to an adjacent UHV chamber for \textit{in situ} STM and BEEM measurements or vacuum transferred to the XPS system for measurement. Samples that were annealed at \( T_a \geq 500^\circ \) C had the Au/Cu/Co underlayers replaced with a single Co 20 nm layer. No BEEM measurements were taken on those samples.

### 5.3 The Metallic Aluminum Surface

The understanding of the impact of such treatment methods begins with a detailed knowledge of the properties of untreated films. I will start by building up the system from a metallic Al top layer and contrast the spectroscopy with that acquired from an oxidized sample before moving on to discuss changes enacted through treatment of oxide surfaces. It is instructive to consider an Al (111) textured surface as well as the randomly oriented Al surface that typically results from deposition of Al on Co or another ferromagnetic electrode such as in a tunnel junction. Figure 5.1 shows topographic and BEEM images for an Al (111) (a) and (b) and a randomly oriented Al surface (c) and (d). Al is known to grow (111) oriented on thin well ordered Cu films [16]. This is strongly supported by the flat terraces imaged in the STM image of fig. 5.1 (a). However, when grown on Co, the Al is not so well ordered and many different crystalline faces are exposed, resulting in a gradual rounded appearance of the Al surface with a roughness about
Figure 5.1: STM and BEEM images of Al(111) and randomly oriented Al. STM topographic images (a,c) and BEEM current images (b,d) for a Si (111)/Au(3nm)/Cu(1.2nm)/Al(111)(20nm) (a) and (b) and a Si/Au(1nm)/Cu(1.2nm)/Co(1.2nm)/Al(1nm) (c) and (d) taken at a tip bias of -1.5V. Black to white is 1.5 nm for (a) and 3.0 nm for (c), and 6pA/nA for both BEEM images. Note the presence of fewer adsorbed species denoted by the black spots in the BEEM images for the less reactive (111) surface.
twice that of the (111) oriented surface, as shown in fig. 5.1 (b). The important features to note are the presence of adsorbates which image as black spots in both of these films. These adsorbates are formed from reactions with the low level of background gasses present in the system. The less reactive (111) oriented film [17] exhibits a much lower density of adsorbates and they are primarily bound at step edges where a different crystalline plane is exposed. In the case of the untextured Al, the adsorbate density is much higher due to the higher reactivity of the surface. It becomes important to utilize the dark spots in the BEEM images to steer around the adsorbates present on the surface in order to measure the local electronic structure of the underlaying surface.

5.4 As-Grown AlO$_x$

Aluminum oxide that has been exposed to a significant oxygen dose exhibits a much higher density of these clusters than the numbers that result from the low levels of background gas exposure. Cluster density increases with oxygen dose and aluminum thickness, to the point where an exposure to atmosphere for 1 hour on a 20 Å Al film will result in nearly complete coverage [18]. For the studies contained here samples will be confined to 10 Å of Al and a 10 Torr sec does, which results in a typical partial coverage as shown in figure 5.2. These clusters have been identified as chemisorbed O$_2^-$ through the combination of spectroscopic measurements, a careful consideration of the possible gaseous sources, density variation with oxygen dose and Al thickness, EELS measurements and X-ray near edge absorption measurements [6]. The presence of an oxygen species bound to the surface of the aluminum oxide leads to concerns that during subsequent deposition of the top ferromagnetic electrode, considerable oxidation may occur. As the details
Figure 5.2: STM (a) and BEEM (b) images of a 10 Å Al film exposed to 10 Torr-sec of oxygen. While this is only a few percent of the optimum dose for a MTJ, the ubiquitous presence of chemisorbed $\text{O}_2^-$ clusters (dark spots in BEEM image) at the surface creates questions as to how they will interact with top electrodes upon completion of the stack.
of the interfacial structure has been shown to be crucial for proper device performance [19, 20], the presence of any ferromagnetic oxide could dramatically quench the TMR in a MTJ. In a JJ, a weakly bound species at the interface between the superconducting electrode may either oxidize the electrode, or move between metastable states, creating a source of 1/f noise and decoherence. Therefore, identification, characterization, and techniques for elimination of these chemisorbed \( \text{O}_2^- \) clusters may prove to be essential to furthering device performance.

STS and BEEM measurements [6] on both an 8 Å Al film that has been dosed with a 300 \( \mu \text{Torr-sec} \) oxygen dose and on one of the chemisorbed \( \text{O}_2^- \) clusters are shown in figure 5.3. While the \( \text{AlO}_x \) background has available states that extend very close to the Fermi level (0 V), this is not the case for the \( \text{O}_2^- \) clusters, where there are no available states for the STM tip to tunnel inject into until the bias is greater than \( \sim 1.5 \) V for this particular cluster. BEEM \( I_c(V_t) \)s taken on the oxide background show the typical Schottky turn on expected from an all metallic system. This is an indication that in this very thin oxide layer (300 \( \mu \text{Torr-sec} \) dose) electrons tunnel injected into this incompletely oxidized surface may couple through the oxide layer into the underlying metallic electrode in a ballistic manner. The result is BEEM \( I_c(V_t) \)s that are similar in shape and magnitude to spectra taken over a metallic Al surface. However, electrons tunnel injected into the clusters at higher bias clearly do not couple ballistically into the underlying metal layers, as demonstrated by the strong attenuation of the BEEM current at high bias (dashed BEEM \( I_c(V_t) \)).

This BEEM signature of the \( \text{O}_2^- \) clusters is extremely useful in identifying their presence upon the surface of films which have undergone treatment. It has been shown that the exact region where available states open up will vary from cluster
Figure 5.3: DOS and BEEM measurements of chemisorbed O$_2^-$ and AlO$_x$ background for a 300 µ Torr-sec 8 Å Al film. Upper plot is DOS, lower are BEEM spectra. The dashed lines are measurements taken over the cluster, while the solid lines are measurements taken over the AlO$_x$. The O$_2^-$ clusters show no states up to $\sim$ 1.5 V, while the AlO$_x$ shows DOS extending to at least 0.5 V. Measurements shown later with better signal will show that tails extend almost to the Fermi level (0 V)
Figure 5.4: DOS diagram for cluster and underlying AlO$_x$. An electron injected at a tip bias less than $\sim 1.4$ V is injected directly into the underlying electrode. When a $\sim 1.4$ V bias is exceeded, states become available in the cluster, and hence an injected electron relaxes out in an inelastic process due to the poor match with the DOS of the cluster and underlying electrode. Hence, these higher energy electrons are not collected as BEEM current.

to cluster, and thus so will the precise location of the peak in the BEEM spectra. The exact details of the DOS threshold depends on the size of cluster, Al film thickness, and various other factors but has not been studied in explicit detail [18]. However, it is always present in the 1-2 V range. These measurements allow us to construct a model of the energy structures of both the chemisorbed O$_2^-$ clusters adhered to the surface of the film, and the underlaying oxide in the as-deposited form (fig 5.4).

Utilizing the combination of BEEM and STS, one can distinguish between where the STM is tunneling to the chemisorbed oxygen that is stabilized into
nanoscale clusters, and where the STM is tunneling to the bare oxide surface. If the STM tip is located over a cluster and held at a low injection bias where there are no available states to tunnel to in the cluster, tunnel injection will take place directly into the available states in the oxide, and hence the initial behavior of the BEEM $I_c(V_t)$ is nearly identical with that obtained from measuring the oxide background. However, as the tip bias becomes sufficiently high that direct injection may take place into cluster states the electrons will longer have a ballistic path available to them, and instead exist to the underlying metal in an inelastic process, resulting in the strong reduction of the BEEM signal. However, for the thicker 10 Torr-sec AlO$_x$ films utilized here, when the STM is located over an uncovered region of the aluminum oxide, due to a low density of states on the oxide, the STM tip must approach close enough to establish feedback that there is substantial tunnel current directly through the oxide layer to the base electrode. Thus, a fraction of the tunnel-injected electrons travel ballistically to and across the underlying SB if they have the requisite energy and momentum values. The result for untreated, oxidized samples is BEEM spectra that are the same in form but reduced in amplitude from those obtained from unoxidized samples (see figure 5.5).

The measurements on the films were obtained using BEEM to determine locations where tunneling is to the uncovered surface. Figure 5.5 shows typical results of the differential logarithmic conductivity, $d\ln(I_t)/d\ln(V_t)$, proportional to the local DOS of the surface, together with the BEEM spectrum, $I_c(V_t)$. The tip was held steady during measurement, with $\sim$ 1 nm lateral drift, and 20 $I_t(V_t)$ scans were averaged at each location. The Al metal DOS measurements exhibit the clear presence of states all the way to the Fermi level, $E_f(V_t =0)$, maintaining finite con-
Figure 5.5: DOS and BEEM measurements for metallic (solid lines) and 10 Torr-sec dosed (dashed lines) Al films. The DOS of the metal and oxide appear similar, with a parabolic energy dependence. However, one crucial difference is seen. The DOS for the metal does not reach 0 at the Fermi level, indicating finite conductance. For the AlO$_x$, however the DOS does go to zero at \( \sim 150 \) mV above \( E_f \), indicating the beginnings of a band gap. While BEEM \( I_c(V_t) \)'s taken on the oxide are reduced in amplitude from those acquired over the metal (inset of b) when scaled, it is evident that the energetic dependence is identical.
ductance at $E_f$, as one would expect. The uncovered, as-formed $\text{AlO}_x$ surface is somewhat surprising in that it yields DOS curves with a nearly parabolic dependence on bias with states extending to within 150 mV of the Fermi level. While the details of the local DOS varied across the uncovered oxide, at no location was the DOS onset higher than 200 mV. These DOS curves have a much more metallic character than expected from barrier layer, indicating the presence of strong disorder distributed throughout the uncovered $\text{AlO}_x$.

XPS studies lend insight into the origin of this disorder. As outlined in the last chapter, utilizing XPS, one can calculate the stoichiometry of as grown $\text{AlO}_x$ oxide films. The result for these 10 Torr-sec 10 Å Al films is an oxygen to aluminum ratio of $\sim 1$ [15]. The film is highly oxygen deficient, resulting in a plethora of oxygen vacancies distributed throughout. An oxygen vacancy in close proximity to a metallic electrode will tend to become positively charged. This is because electrons will tend to tunnel to the Fermi level of the metal underneath located at a lower energy level than that of the oxygen vacancy states. In addition, oxygen that lands on the surface of the aluminum oxide may also pick up electrons from these vacancy sites due to the strong electronegativity of oxygen. Hence a method by which the individual $\text{O}_2^-$ molecules tend to cluster up and become bound to the surface becomes clear. As the oxide grows, oxygen vacancy sites become distributed throughout the growing layer. Adsorbed oxygen gas molecules may acquire a negative charge and become localized over an oxygen vacancy (figure 5.6). As a result of this oxide passivation, a slight modification needs to be made to the well known Mott - Cabrera model for oxide growth [21]. In this model, oxide growth goes through several stages. The initial stage is the adsorption of oxygen molecules on the surface of an unoxidized aluminum layer. The oxygen reacts to form a
Figure 5.6: Model for AlO$_x$ from STS, BEEM, and XPS measurements. Chemisorbed O$_2^-$ clusters are bound through a weak electrostatic attraction to positively charged oxygen vacancies. If the dose becomes high enough a surface passivation layer may form, providing an mechanism for oxide growth limitation.
thin layer of aluminum oxide. In the next phase, oxygen molecules adsorb to the aluminum oxide surface. Electrons tunnel out of the aluminum metal underneath into the oxygen molecules due to the much higher electron affinity of oxygen. This then sets up an electric field which draws Al cations along grain boundaries to the oxide surface where it reacts with the oxygen. The rate limiting step is the electron tunneling through the oxide.

If, however one takes into account the presence of the chemisorbed $O_2^-$ species coupled with the high oxygen vacancy concentration distributed throughout the film, a different mechanism may dominate the continued oxide growth. $O_2^-$-vacancy pairs will form a stable system, where electrons are screened from tunneling out of the Al film to the surface oxygen molecules. There is then no field set up to draw out Al cations, and if the surface becomes sufficiently saturated with $O_2^-$ clusters, additional impinging oxygen may not find an uncovered spot to bind to. Indeed, AlO$_x$ films which have been exposed to atmosphere show nearly complete surface coverage [18]. This system of chemisorbed $O_2^-$ paired with vacancies is not a desirable situation for devices where one would like to utilize a perfect structureless insulator. Therefore, methods to remove the surface oxygen clusters and improve the oxide stoichiometry are of considerable interest.

On caveat though: as XPS is sensitive to the chemical nature of the various oxygen species, while BEEM / STM has a minimum size resolution, it is possible to detect this chemisorbed oxygen species using XPS on, for example, very thin Al films where it may not be evident from BEEM / STM images of the oxide surface. This is because the chemisorbed oxygen may either form clusters which are too small to resolve or too mobile to image via STM / BEEM if not locally stabilized.
5.5 Top Electrode Deposition

Perhaps the simplest and most appropriate treatment method is to continue growing the device. Deposition of a top electrode will impact the structure of the AlO$_x$, and will be studied first. Figure 5.7 shows a BEEM image for a 10 Å of Al film exposed to $\sim$7 Torr-sec of oxygen and then overcoated with $\sim$3 Å of Co.

This thickness of Co is sufficient to nearly completely cover the oxide surface with at least a monolayer of Co, leaving only a few percent of uncovered AlO$_x$. The black background covering most of the image indicates the presence of a Co layer. Electrons which are tunnel injected into this top metallic layer are no longer transmitted ballistically through to the BEEM collector, an indication that overcoated AlO$_x$ is strongly scattering ballistic electrons [18]. In the middle of the image, we see a bright patch of uncovered AlO$_x$ peaking through the Co overlayer. Also noticeable around the edges is the presence of several $\sim$5 nm dark regions, the characteristic size of both Co grains and O$_2^-$ clusters. However, BEEM $I_c(V_t)$s are able to sort out the difference between the two. The characteristic shape seen in fig. 5.3 is present in the BEEM $I_c(V_t)$s taken over the indicated O$_2^-$ clusters. Therefore, the partial deposition of a top electrode is insufficient to remove these clusters from the surface of exposed AlO$_x$. However, this does not answer any questions about what may have happened to O$_2^-$ clusters beneath the top electrode. It is difficult to tell from BEEM data whether they reacted with it, were driven into the oxide, or formed a layer at the interface.

In order to understand what is happening underneath the top electrode, we turn to XPS. The identification of the peak positions in the oxygen spectra due to chemisorbed O$_2^-$ and AlO$_x$ has been covered in Chapter 4. Chemisorbed O$_2^-$ forms a peak at $\sim$534 eV, while AlO$_x$ forms a peak in the XPS scans at $\sim$ 532 eV.
Figure 5.7: BEEM image of a partially covered AlO$_x$ surface. Scans are at a tip bias -2V, color scale is 7 pA black to white. $\sim$ 3 Å of Co have been deposited on an oxidized aluminum surface. The Co shows up as the black background in the BEEM image. The windows of AlO$_x$ poking through still exhibits the presence of chemisorbed O$_2^-$ clusters on its surface, as demonstrated by the $\sim$5 nm size dark spots within the window and the accompanying BEEM signature.
Figure 5.8: XPS scan of oxygen 1s region of an Al film dosed with 1 Torr-sec oxygen with (a) and without (b) a 10 Å Co overlayer. While the chemisorbed O$_2^-$ peak is clearly present in the uncoated sample, it is driven into the AlO$_x$ layer upon deposition of the Co [15].

Figure 5.8 (b) shows the oxygen 1s region of an Al film that has been dosed with 1 Torr-sec oxygen.

There is the obvious presence of the chemisorbed species. Upon deposition of 10 Å of Co, the chemisorbed layer is removed via reaction with either the Co or the Al layers. Calculations of the thickness and stoichiometry of the AlO$_x$ layer yield significant increases in both cases [15], indicating that the chemisorbed species is reacting with the Al layer. The small presence of the CoO$_x$ peak may be incidental to the vacuum transfer process. Therefore, overcoating the chemisorbed oxygen covered AlO$_x$ surface with a top electrode with a high work function serves to drive the chemisorbed oxygen into the AlO$_x$, filling oxygen vacancies. It has been shown
that the extent of this interaction depends on the workfunction difference across the oxide layer [15]. Depositing a top electrode with a higher work function than that of Al sets up a potential difference across across the AlO$_x$. This field points towards the electrode of highest work function, and in the case of a Co overlayer, will cause the negatively charged oxygen species to move into the AlO$_x$, creating a more stoichiometric form. Therefore, measurements of the density of states of the strongly disordered uncovered oxide as shown in figure 5.5 are not indicative of the electronic structure of that insulator when covered by a top electrode.

### 5.6 Flood Gun Electron Bombardment

Determining the electronic structure of the buried oxide utilizing STS is a challenging prospect. However, exposing films to FGEB has a similar effect in the physical structure to deposition of a top electrode with a high work function, and provides a method whereby such AlO$_x$ films may be left uncovered while the electronic structure may be probed. Figure 5.9 shows this behavior. FGEB drives the chemisorbed O$_2^-$ clusters into the oxide, causes the AlO$_x$ to grow thicker, and improves the oxide stoichiometry to a O/Al ratio of about 1.2 [15]. The higher the flood gun bias, the stronger the effect. This is consistent with the workfunction model described earlier. The presence of negative charge at the surface of the oxide sets up an electric field in the same direction as depositing an electrode with a higher work function, drawing chemisorbed oxygen into the film. In addition, the presence of electrons on the surface may serve to create and additional charge on the O$_2^-$ clusters, sufficient to dissociate them into a more reactive species. Increased AlO$_x$ growth rate due to the dissociation of incident oxygen molecules into more reactive oxygen ions via 50 eV FGEB has been demonstrated [22], so dissociation of the adsorbed oxygen
Figure 5.9: XPS scan of oxygen region of AlO$_x$ (a) and (c) films exposed to 10 (b) and 20 (d) V FGEB. The chemisorbed O$_2^-$ is removed in this process, with the strongest effect enacted via exposure to the highest energy electron beam. 20 V FGEB exposure nearly completely reacts in the chemisorbed layer.
Figure 5.10: Model for FGB induced AlO$_x$ growth and densification. The extra electric charge from the incident beam of electrons causes surface oxygen molecules to dissociate, and react into oxygen vacancies, producing thicker, better quality oxide.

is quite possible. This behavior is shown in the model in figure 5.10. FGB films are stable if kept in UHV, but the reintroduction of oxygen is sufficient to remove oxygen from the barrier and drop the stoichiometry back to where it was in the as-grown case, an O/Al ratio of $\sim$1.0. This lack of stability is exacerbated during STS studies as one of the problems for systematically surveying oxide surfaces is that prolonged measurement over one particular region may locally degrade the oxide via hot electron effects. The primary effect of such prolonged and/or high current STM measurement over a small region of the surface is to partially reduce the oxide, generating positively charged oxygen vacancies, which can locally stabi-
lize a nanocluster of chemisorbed \( O_2^- \) on the surface. However, BEEM is effective in detecting this degradation if the surface is scanned at high enough bias that the tunneling is to unoccupied states cluster states, but the result is a significant limitation of the ability to measure the oxide surface. The requirement for frequent verification that a cluster has not formed under the STM tip shortens the length of time that any one region may be studied. This oxygen instability in uncovered \( AlO_x \) is addressed in more detail in section 5.8.

To determine the effect of filling oxide vacancies on the electronic structure of \( AlO_x \) layers, samples were subjected to FGEB and then examined by STS and BEEM. Samples were subjected to either 10 V or 20 V FGEB at a current density of \( \sim 20 \mu A/cm^2 \) for 2 hours. The 10 V sample was dosed again (300 torr-sec), and bombarded a second time, which XPS has shown further stabilizes oxygen in the \( AlO_x \) barrier [11].

As illustrated in figure 5.11, FGEB exerted a substantial effect on the electronic properties of the oxide. After the 10 V treatment, STS measurements on the uncovered oxide surface showed no detectable oxide states from 0 (\( E_f \)) to \( \sim 0.5 \) V, with a roughly parabolic energy dependence above 0.5 V. The details of the DOS varied slightly with location, but at no point was the onset either lower than 0.35 V or higher than 0.65 V. However, due to the inability of the STS measurements to completely survey the oxide surface and to the limited sensitivity of the measurement, a small density of remnant low energy states in the oxide may still be present. STS measurements made with both positive and negative tip bias showed that the local DOS is roughly symmetric about \( V = 0 \), indicating that the Fermi level is pinned near the center of the oxide band-gap for these \( AlO_x \) layers. For the 20 V FGEB the region of zero DOS increased further to approximately 1.1
Figure 5.11: Differential logarithmic conductivity, $d \ln(I_t)/d \ln(V_t)$, acquired from STS for thermally oxidized aluminum samples with different flood gun electron bombardment (FGEB) voltages. As the bombardment voltage increases, more chemisorbed $O_2^-$ clusters are driven into oxygen vacancies in the aluminum oxide resulting in a better defined conduction band edge.
V, above which the DOS increased rapidly, as shown in Fig. 2(a). At no point did a DOS measurement on a fresh region of the oxide show an onset lower than 0.8 V, or higher than 1.2 V.

The low energy oxide states are strongly correlated with the vacancy concentration in the oxide - as these positively charged sites are progressively filled with oxygen ions the band gap grows. What is somewhat surprising is that the band gap is relatively uniform from spot to spot as examined by STS, both for the 10 V FGEB sample, which only partially removed the chemisorbed oxygen, and for the 20 V FGEB sample. This indicates that a relatively uniform driving force is responsible for the formation of the vacancies in the oxide as it grows, and that the electric field established across the oxide by the FGEB is rather uniformly effective in filling these vacancies. The small variations in the DOS from measurements taken across the film may be an indication of small fluctuations in the levels of local vacancy concentration.

5.7 Annealing

Thermal annealing of AlO$_x$ layers had quantitatively different effects. XPS shows that the chemisorbed oxygen and metallic aluminum signals decreased while the oxidic aluminum signal increased with increasing anneal temperature $T_a$, but some chemisorbed oxygen still remained after a 3 minute anneal at 500°C, indicating that while the oxide grows thicker, it still had positive charged vacancies at that point (see figure 5.12). One notable result from the XPS measurements is that very high temperature anneals are required to enact substantial changes in the physical structure of the tunnel barrier layers. These temperatures may not be attainable for MTJs, as Mn diffusion from the antiferromagnetic pinning layers can become
Figure 5.12: XPS measurements of annealed AlO$_x$ layers. While similar effects to FGEB are enacted, annealing to 500° C is insufficient to completely remove the chemisorbed oxygen. The predominant effect is an increase in the thickness of the AlO$_x$ layers, while the stoichiometry increases only slightly.
a substantial problem as low as 350° C [23]. Indeed, a 170° C 1/2 hour anneal has been shown via STEM to be sufficient to move a small, but detectable amount Fe into an AlO$_x$ layer [24]. The enduring presence of oxygen vacancies in thermally treated films is verified through calculation of the thickness and stoichiometry of annealed samples. The primary effect of the high temperature anneals is to increase the thickness of the oxide layer. A small stoichiometry increase is measured as well. The untreated film is calculated to be $\sim 11$ Å thick, with a stoichiometry of 1.0, while the 300° C anneal produces an $\sim 11.5$ Å and the 500° C anneal produces a $\sim 13$ Å barrier layer. The measured O/Al ratio increases to $\sim 1.1$ for the 500° C, a marginal increase. It would appear that the chemisorbed oxygen is not confined to reacting into surface oxide layers as is the case for FGEB treatment. FGEB may produce a thin layer of close to perfect stoichiometric oxide at the surface (which shows up as a lower than 1.5 O/Al ratio during XPS measurements as XPS averages over a layer that is not confined to the outermost surface) [15]. However, during the anneal some of the chemisorbed oxygen layer may be removed to vacuum, while some is clearly driven in to the AlO$_x$ to form a thicker oxide layer, suggesting that anneals imparts sufficient energy to either diffuse aluminum from the bottom of the oxide layer through to the surface where it reacts with the O$_2^-$, or to move the O$_2^-$ in the other direction.

Typical results from STS measurements on uncovered regions of the oxide surface after 3 minute anneals at different $T_a$ are shown in figure 5.13. The effect of increasing $T_a$ was to progressively increase the DOS threshold, from $\sim 1.2$ V for $T_a = 300$° C, to $\sim 1.8$ V for $T_a = 375$° C. For $T_a = 500$° and 600° C, while the main DOS threshold moved up to $\sim 2.25$ V, in both cases there was generally a lower DOS band-tail that extended approximately 0.5 V below this main thresh-
Figure 5.13: Differential logarithmic conductivity, $d \ln(I_t)/d \ln(V_t)$, acquired from STS for thermally oxidized aluminum samples with different anneal temperatures. As the anneal temperature increases, the measured band edge moves further away from the Fermi level. However, substantial band tails are still present for samples annealed at the highest temperatures.
old, indicating the presence of some residual defect states or disorder in the oxide, even at these relatively high anneal temperatures.

While STS provides insight into the DOS of the oxide surface, an understanding of the states that extend through it can be garnered from BEEM (figure 5.14). From STS measurements, the presence of localized states on the oxide surface has been substantially reduced through anneals, leaving mostly extended states through which ballistic transport through the oxide can take place. Further insight into the electronic structure of both the $300^\circ C$ and the $375^\circ C$ sample is gained through examination of normalized BEEM $I_c(V_t)$, where, in addition to the SB threshold at $\sim 0.8 \, V$, a second threshold is observed, weakly at $\sim 1.1 \, V$, and more strongly $\sim 1.7 \, V$, for $T_a = 300^\circ$ and $375^\circ$ C, respectively. This data suggests the onset of extended states that allow ballistic transport through the oxide layer above that energy.

BEEM $I_c(V_t)$ spectra are taken with the STM operating in a constant current mode, so even at low tunnel biases where DOS measurements give very few available states, a 100 pA current is injected into the oxide surface. The weak threshold extending from the SB to the region where DOS begins to open up, is an indication that electrons injected in this bias range are strongly scattered at the surface. The small BEEM current level below the second threshold may be attributed to direct tunneling through the oxide. The second, more pronounced threshold for current collection occurs approximately at the same bias voltage states are measured in the via STS. Hence, annealing has removed the presence of localized states in the barrier: only once the DOS at the surface becomes nonzero is appreciable BEEM current, a measurement of the extended states of the oxide, collected. Through thermal treatments, localized states in the barrier are removed.
Figure 5.14: BEEM measurements of transport through annealed oxide layers. Data are normalized to their signal level at two volts to accentuate the thresholds which occur at approximately the same energy as a threshold for DOS is measured via STS. ($\sim 1.2$ V for $T_a = 300^\circ$ C, and $\sim 1.7$ V $T_a = 375^\circ$ C.)
Indeed, valence band XPS and transmission electron microscopy studies of ~4 nm, AlO\textsubscript{x} layers have found a transition from an amorphous form for a 100\degree C growth temperature to largely γ-alumina for 400\degree C growth. [25] The large increase in the oxide band gap observed when T\textsubscript{a} is increased to 375\degree C and above is in accordance with those studies if we attribute the DOS difference between the 20 V FGEB sample and the high temperature annealed samples as arising from the former being amorphous and the latter largely crystalline. There is also a pronounced increase in the stability of the annealed oxide layers; these oxides are much slower to develop chemisorbed clusters while being studied by STM.

In order to more fully understand the effect that treatments have upon the homogeneity of the AlO\textsubscript{x} surface, a 50 nm X 50 nm area was scanned with current image tunneling spectroscopy (CITS). For CITS acquisition, during acquisition of the topographic image, scanning is stopped, and a STS I\textsubscript{t}(V\textsubscript{t}) curve is taken at each of 1024 equally spaced points. After acquisition of each I\textsubscript{t}(V\textsubscript{t}) curve, scanning is resumed until the next point is encountered. This results in a spatial map of tunneling current verses voltage across the sample surface, from which DOS can be calculated. Figure 5.15 shows a histograms of the DOS values measured across the surface at a sample bias of 1.5 V.

This gives a measurement of the homogeneity of each sample surface, depending upon the treatment method it has undergone. It is clear that the various treatments have dramatically transformed the sample surfaces. The degree to which this transformation takes place is exhibited by the spread of the calculated DOS values. While the sample treated with oxidation only, (a), has the most dramatic spread in the DOS values with long tails in the distribution, DOS values cluster more tightly around the mean as the treatment intensity increases from 10 V
Figure 5.15: DOS values across the surface for differently treated films. (a) is the oxidation only, (b) the 10 eV FGEB, (c) a 500° C anneal, and (d) a 600° C anneal. Lines are gaussian fits to the data. The untreated film shows a much wider distribution of DOS values, indicating a larger inhomogeneity of electronic structure across the sample surface. The 600° C annealed films shows the tightest distribution. Also note that the peak in the DOS values moves to a lower value as treatment intensity increases.
FGEB (b) to the 500° C anneal (c), and finally to the 600° C anneal (d). The peak in the histogram in (a) is also at a considerably higher value than that for the treated samples. At the highest anneal temperature, the full width at half maximum decreases by a factor of 5 from that measured for the untreated sample. In addition, the mean value shifts from 2 (untreated) to .4 (600° C anneal). This clustering of the DOS to a lower value demonstrates both that the oxide has becomes much more homogenous, and that the band tails have been removed: there are fewer available states on average, and the presence of areas with many available states that might create leakage channels in a fully formed tunnel junction is dramatically reduced. While electron bombardment improves the electrical structure of naturally oxidized AlO$_x$, the greatest changes occur with UHV annealing. The thermal treatment forms a better ordered, more homogenous oxide from the initially disordered, inhomogeneous film. In the case of an aluminum film, *ex situ* plasma oxidized, and later annealed upon reintroduction to UHV to several 100° C to remove adsorbed water, regions of differing local conductance were found via CITS. These regions were attributed to regions of crystalline and amorphous AlO$_x$ [26]. In this work, at the highest anneal temperature, the reduction of the spread in DOS values also points to a shift of the AlO$_x$ from a disordered state to a more ordered crystalline form.

It is important to note that CITS is a measurement that differs somewhat from an average multiple $I_t(V_t)$ curves taken at a single fixed location as in figures 5.13 and 5.11, and hence is indicative of slightly different electronic properties as well. When taking STS curves at a fixed location, one is able to verify that no cluster has appeared and no current spike indicating film degradation has occurred during measurement. However, with CITS verification of the local oxide status is
not possible after each $I_t(V_t)$ curve is acquired. Hence, unstable film regions are measured as well. Thus, the spread of the DOS values measured during CITS data acquisition is also an indication of film stability. Negative DOS values which would otherwise be unphysical are due to a change in the oxide during measurement resulting in a current spike, and hence the relatively high incidence of such values in the as grown and FGEB films are indications that these films are not as stable against the high density of tunnel current injection required for STS measurement as the annealed films.

Note that the temperatures required to enact changes in the physical or electronic structure of the oxide are much higher than those successfully utilized in device fabrication. Precise timing and/or thermal cycling may need to be employed in order to produce a combination that will yield the desired results for the oxide layer and simultaneously not be prone to interlayer diffusion problems. Perhaps rapid thermal annealing is a possibility to achieve these requirements.

5.8 Stress Effects

I alluded to the differences in film stability across the various treatment methods above. One of the simplest manners to quantify which films are to most susceptible to instability and stress effects is to repeatedly scan the same region and note how the film surface evolves.

The upper images in figure 5.16 (a), (b), and (c) are initial BEEM images taken on the surface of 375°C annealed, as-grown, and FGEB samples respectively and show a lower density of chemisorbed clusters; dark regions in the BEEM scan. Subsequent scans, the lower images of figure 5.16 (a), (b), and (c) reveal a stress-induced accumulation of such clusters. These stress effects can cause the motion
Figure 5.16: Stress induced oxygen cluster formation. Upper BEEM images are initial scans and lower images are subsequent scans for 375°C annealed (a), as-grown (b), and 10 V FGE (c) samples after the time noted. The FGE sample is extremely quick to degrade, indicating that oxygen is only weakly stabilized in the uncovered barrier. As-grown films exhibit cluster formation on a slower time scale. Annealed films are the most resistant to cluster formation, showing the movement of clusters across the surface, but no accumulation as scans progress.
of a cluster to a more stable position as oxygen vacancies are generated under the tip. While the un-annealed sample (b) accumulates an increasing number of clusters with scanning time, annealed samples (c) exhibit only the motion of an approximately constant density of clusters, demonstrating that the annealed oxide is resistant to STM stress effects. However, a notable feature of the FGEB samples is they are particularly quick to degrade; usually forming chemisorbed oxygen clusters shortly after I began examining a region with STM, indicating that when oxygen has been forcefully driven into the oxide it is unstable against electronic stress. The fact that many new clusters appear in the lower semicircle form is an indication that they were formed as the tip scanned over that region. As the scan proceeds from top to bottom, a cluster that was not initially imaged, and suddenly appeared as the tip passed over that region, would form such a half moon shape. Any fresh spot in the oxide exhibits approximately the same cluster density, whereafter new surface oxygen clusters will appear during subsequent imaging.

A model for this process of stress induced oxygen liberation from the oxide barrier layer is shown in figure 5.17. The high local current density destabilizes oxygen from the barrier, after which it will combine with other chemisorbed oxygen on the surface. This other oxygen may not have been localized sufficiently strongly at a particular region on the surface to be imaged by the STM tip, but is rather pushed around as the tip passes over. The new cluster is then stabilized on the surface at the vacancy site and appears in subsequent BEEM images.

A primary problem for AlO\textsubscript{x} based MTJs is time dependent resistance drift (TDRD), which always produces a lowering of the resistance as devices are stressed in accelerated aging tests [27]. This local destabilization of oxygen in uncovered barriers may be an indication of the processes through which TDRD occurs.
Figure 5.17: Stress induced cluster formation in AlO$_x$ barrier layers. The high tunnel current density is sufficient to destabilize oxygen from the barrier layer under the tip, whereby it forms a chemisorbed O$_2^-$ cluster stabilized on the surface over the generated vacancy.
5.9 Conclusions

While FGEB and annealing the AlO$_x$ barrier layer prior to deposition of the top electrode are not standard procedures in tunnel junction formation, the use of top electrodes with a higher $\phi$ than the metal immediately under the oxide layer, and of mild annealing ($= 400^\circ$ C) after top electrode deposition are common approaches for JJs and MTJs respectively. The STS results reported here indicate what effects these approaches have on the electronic properties of the barrier. The use of a top electrode with a higher $\phi$, drives more chemisorbed oxygen into the oxide, filling vacancy sites [11]. This removes low energy states from the oxide and increases the tunnel barrier height. Mild annealing of tunnel barriers with symmetric electrodes can have a similar effect by more uniformly distributing chemisorbed oxygen that the deposition of the metallic over-layer may trap at and near the top of the oxide layer [28]. Thus, electrode oxidation, caused by over-oxidation and reaction with the chemisorbed layer in favor of enhanced oxidation of the AlO$_x$, is reduced. This also removes low energy states from the oxide and raises the barrier height. Thermal annealing also lowers atomic disorder in the barrier. While BEEM studies of buried layers indicate that the barrier layer is spatially rather uniform after the deposition of the top electrode onto the chemisorbed oxygen covered oxide surface, it may prove advantageous to process the oxide layer by FGEB or thermal annealing prior to this deposition step. Indeed a preliminary study has already found that as much as a factor of ten reduction of 1/f resistance noise amplitude in Al/AlO$_x$/Al junctions can be effected by FGEB of the oxide layer. [11]
References for Chapter 5


CHAPTER 6

SCATTERING AT FERROMAGNETIC – SEMICONDUCTOR INTERFACES

6.1 Introduction

In addition to being a charged particle, the electron contains a small magnetic moment in its spin. Devices that employ spin as well as charge effects, utilizing magnetic channels paired with conventional electric signals have been the subjects of extensive study [1]. Integration of simultaneous electric and ferromagnetic doping in semiconductors has proven difficult to accomplish at room temperature, leading to strong interest in efficient methods for injection of spin polarized electrons into semiconductors as an alternative manner in which to create a spin polarized electric current. In the eventual device, spin injection, manipulation, and detection should take place via electrical means, as opposed to working with the much more space consuming circularly polarized light sources. An important advance towards robust electrical injection that circumvents the fundamental problem of the conductivity mismatch between ferromagnets and semiconductors resulting in very low injection efficiencies [2], is to utilize the Schottky barrier formed at the ferromagnet - semiconductor interface [3, 4] to avoid polarization quenching ohmic transport across the interface. The magnetic tunneling transistor [5] is one important device incorporating such a Schottky barrier that demonstrates an electrical means of injecting spin-polarized electrons into a semiconductor. A high quality, spatially homogenous, and uniform barrier formed on GaAs with minimum electron scattering present at the interface is highly desirable. As GaAs has three different conduction band minima (CBM) which occur at different points
in momentum space, each with a distinct Schottky barrier height (see figure 6.1), ballistic electron emission microscopy (BEEM) collector current ($I_c$) as a function of tunneling bias ($V_t$) gives insight into the nature of scattering at the metal / semiconductor interface. The mechanism by which scattering affects the BEEM $I_c(V_t)$ spectroscopy is detailed in Chapter 3, however here I will just state that each additional CBM provides an additional contribution to the BEEM current, and hence the relative weights of these additional contributions, which depends upon the degree of scattering into off-center CBM, affects the curvature of the $I_c(V_t)$ spectra.

In this chapter, I will start with a discussion of the long studied and highly nonuniform Au–GaAs system before moving on to address BEEM measurements of Fe, Co$_5$Fe$_5$0, and Ni$_8$1Fe$_1$9 (Py) films deposited on a GaAs substrate to give nanometer resolved evaluation of hot electron transport across the Schottky barrier. Sputter deposited NiFe films show the least amount of scattering and high-
est hot electron transfer ratio. A set of very interesting preliminary measurements of MBE deposited Fe films provided courtesy of Brian Schutlz and Chris Palmstr{$\textsc{phi}$}m at the University of Minnesota will also be described.

### 6.2 Sample Fabrication

I fabricated the samples in this study through either sputter deposition or thermal evaporation. First, I prepared a backside ohmic contact for BEEM current collection via deposition of a thick 75 nm Au layer and subsequent annealing to $\sim 350^\circ$ C for $\sim 1/2$ hour to promote Au - GaAs alloying. GaAs substrates were first etched in an ammonium hydroxide : water (1:6) solution for 90 s, followed by an isopropanol alcohol rinse, after which they were transferred into either a sputter deposition chamber or a UHV evaporation chamber (in the case of only Au deposition only). I sputtered deposited samples of Fe, CoFe, or NiFe in layers of 15, 25, or 50 Å in a chamber with a base pressure of $\sim 3 \times 10^{-8}$ Torr, at an Ar sputtering pressure of 1 mTorr. Next, I deposited layers of Cu (20 Å) and Au (50 Å) to prevent oxidation of the ferromagnetic materials upon air transferring them to the UHV system for BEEM measurements. Fe films were only coated with Au. GaAs – Au only samples were grown in UHV at a base pressure of $\sim 2 \times 10^{-10}$ Torr and immediately transferred into the STM / BEEM chamber for data acquisition.

Substrates for MBE grown films were fabricated at the University of Minnesota. They were first annealed to $610^\circ$ C to remove surface oxide, then a GaAs buffer layers ($\sim 1$um) was grown at $580^\circ$ C to ensure a clean interface. Following this, Fe (15, 35, or 50 Å) and then 100 Å of Au were deposited. In-situ low energy electron diffraction (LEED) measurements demonstrate epitaxial growth with good
ordering. X-ray diffraction shows both Fe and Au films are epitaxially oriented in the (001) direction.

6.3 Au–GaAs Interfaces

While GaAs substrates have a strong advantage for BEEM in that they allow the collection of electrons via several different CBM, an important drawback is present as well. The Schottky barrier (SB) serves as the crucial part of the system, and a spatially homogeneous barrier is highly desirable as any variation present in the barrier complicates understanding of any structures of interest grown upon it. While the Au - Si system forms an excellent basis for devices, the long ballistic attenuation lengths of Au cannot be utilized with such success for films grown on GaAs substrates due to the high degree of inhomogeneity of this Schottky barrier (see figure 6.2). This SB inhomogeneity in the otherwise ideal Au system has been observed in many studies [7–10] and attributed to Ga diffusion into the Au and As segregation at the interface [9] or a similar multiphase structure at the interface [10].

As mentioned in Chapter 3, typically two primary models, either the Bell - Kaiser model (BK / cite), which assumes no momentum scattering at the metal semiconductor interface, or the Ludeke - Bauer (LB /cite) model, which assumes complete momentum scattering, are employed for analysis of BEEM data. Both models give similar behavior, with \( I_c(V_t) \propto (V_t - \phi_b)^2 \), with \( \phi_b \) the SB height around the threshold. They are in fact identical for single zone centered CBM (see Chapter 3), and Hence roughly equitable fits to data result for single barrier semiconductors. However, the situation is different for semiconducting substrates with multiple thresholds such as those available in the case of GaAs. The three
Figure 6.2: BEEM images of Au – Si and Au – GaAs interfaces. The Si system is very uniform and offers a much higher degree of transmissivity as compared with the GaAs substrate. Both films are 135 Å thick. The black to white color scale is 16 pA \ nA for the Si substrate and 4 pA \ nA for the GaAs.
CBM in GaAs Γ, L, X with energetic spacing L-Γ .3 eV and X-Γ .5 eV [6] occur with different directions in momentum space: Γ is centered in the Brillion zone, with a single CBM, while the L valleys occur in the six (001) directions, and the X valleys in the eight (111) directions. As the injected electron momentum distribution will strongly forward focused due to the nature of tunneling (Chapt. 3), with very small momentum components parallel to the metal - semiconductor interface, we expect that in the case of minimal interfacial scattering, transport should be dominated by the Γ valley contribution, while if strong scattering is present, this will no longer be the case and the spectral shape of acquired $I_e(V_t)$ will be markedly different. This difference in spectral shape is shown in figure 6.3, where the total calculated current contributions (Chapt. 3) from each of the valleys have been normalized at 1.6 V to bring out the differences in the curvature of the spectra. I note here that the BK L valley has been left out as it was seen to have minimal contribution (Chapt. 3) and is extremely time consuming to calculate in the fitting procedure.

A clearly apparent difference in curvature is present in this plot, where the LB model produces the appearance of a delay in the BEEM threshold. This delay stems from the fact that the combined effective mass and degeneracy number (4) from the L valleys provides a much greater area for electron collection in the strongly scattered limit than does the single small effective mass Γ valley. I have normalized the two curves to common value to facilitate interpretation of the data, as one of commonly used fit parameters to describe ballistic electron attenuation in traversing the base due to various processes is R, an overall scale factor. While there is some general agreement, it is not always the case that the most highly transmissive regions couple with the lowest degree of scattering (closest to the
Figure 6.3: Normalized BEEM current for Au – GaAs system in BK (dotted) and LB (solid) models. The relatively weak contribution of the $\Gamma$ valley in the LB model as compared with the L valley due to the much higher electron effective mass gives the appearance of a delayed BEEM threshold.
curve laid out by the BK model). This behavior is shown in figure 6.4.

While a model has been developed which allows a scattering parameter that smoothly moves between these two extremes of either complete or no interfacial scattering, predicting absolute intensity, [11, 12] but requiring a rather large number of fit parameters, this model leads to questions as to the uniqueness of the fit. Here, I apply a simplified theory to fit the spectral behavior of $I_c(V_t)$ for the various metal — GaAs interfaces, eliminating many of the aforementioned fit parameters. As described in Chapt. 3, the region of intermediate interfacial scattering between the two gray spectra corresponding to the pure BK and LB models in figure 6.4 (b) can be covered via a weighted sum of the two models. Figure 6.4 (a) shows the directly measured BEEM signal for several various regions distributed across the Au surface. Comparing the overall transmissivity as shown in figure 6.4 (a) with the degree of scattering dictated via the placement of each spectra within (b) shows an interesting correspondence: while the the strongest scattering corresponds to the lowest transmissivity and the weakest to the highest transmissivity, spectra taken in intermediate intensity regions do not always show this correspondence. This may be explained by noting that in a small minority of the lowest transmissivity regions as selected in eg. figure 6.2, the spectra cannot be fit with the well established $\sim 0.9$ eV SB, but rather requires a lower SB and of $\sim 0.8$ eV. These very low SB barrier regions are probably due to the previously mentioned alloying of atomic species at the interface, such as may be employed to form an ohmic contact. Small amounts of interfacial alloying may affect the BEEM transmissivity without dramatically altering the SB barrier height or the degree of scattering at the interface — this behavior was seen in some of the annealed films in the AlO$_x$ studies: annealing at high temperatures sometimes would produce very high
Figure 6.4: Measured BEEM current for Au – GaAs system compared to BK and LB models. Each curve corresponds to a different spot on the surface. (a) shows the overall collector current, while (b) shows each of these curves scaled to the same maximal value at 1.6V. Area between gray curves (pure BK and LB models) is covered by intermediate amounts of scattering. While the most (least) transmissive spectra map to the lowest (highest) amount of scattering, the middle several swap places, indicating that higher interfacial scattering does not necessarily directly correspond to lower transmissivity.
transmissivities, but otherwise unaffected SB heights.

6.4 Sputtered Ferromagnetic Bases

The sputtered ferromagnetic films exhibit SB interfaces that are much more spatially uniform than the evaporated Au films. This behavior is shown in figure 6.5. As Py clearly has the highest transmission (although still considerably less than Au), and maintains a much more uniform SB than Au, it is a promising candidate for a thin interfacial layer to serve as a base for more complicated structures that require a highly uniform interface. While Au is notorious for high mobility and interdiffusion with many atomic species, Co, Fe, and Ni diffuse much less readily, and hence Ga interdiffusion and As segregation is most likely reduced in the presence of these ferromagnets, resulting in a much more uniform barrier than is achievable with Au. The fact that Au – GaAs (and even Au – Si) SB degrade quickly with time, usually only surviving a several days if exposed to atmosphere indicates the highly interdiffusive nature of these contacts. While one might be tempted to point to the more energetic nature of sputter deposition, it has been found that sputtering generally produces Au – Si barriers that are even more prone to interdiffusion, and typically result in such low barriers (and hence zero bias resistances) as to be rendered unusable for room temperature measurements [?]. In addition, Fe films grown via thermal evaporation show similar levels of uniformity indicating that differences in the deposition method are not the dominant effect.
Figure 6.5: BEEM images of ferromagnet–GaAs interfaces. While the evaporated Au interfaces were very non-uniform, these show a much greater degree of homogeneity. (a) is an Fe film, .5 pA \( \text{nA} \) black to white, \( V_t = -1.8 \text{ V} \); (b) is a CoFe film, 3 pA colorscale, \( V_t = -1.8 \text{ V} \); and (c) is a Py film, 8 pA colorscale, and \( V_t = -2 \text{ V} \). Ferromagnetic films are much more uniform than any Au films grown.
6.5 Ballistic Transfer Ratios

In order to remove the thickness dependance and only evaluate the interfacial effects of each of these ferromagnetic metals, the ballistic transfer ratio (BTR), a measurement of the percentage of incident electrons that cross into the conduction band of the semiconductor is utilized. The BTR is calculated through measurements of $I_c(V_t)$ on samples which are identical, except for differing thicknesses of the ferromagnetic base. $I_c(V_t)$ is then fit for an energy dependent attenuation length assuming an exponential decay of $I_c$ with base layer thickness, and to recover the purely interfacial effects, the transfer ratio is calculated from the resultant $I_c$ in the limit that the thickness of the ferromagnetic layer is reduced to zero. This BTR can then be fit for a scattering parameter according to the procedure outlined in Chapt. 3. The results are shown in figure 6.6.

MTT in more detail than before? Cf parkin plots (description)?

describe comparisons of BTR

6.6 MBE and fits

6.7 Tunnel current dependance

Channelling effects due to Au band structure have been invoked to explain the similarities in $I_c(V_t)$ between Si (111) and Si (100) oriented samples in the framework of the BK model (Garcia - Vidal). Garcia Vidal, [100] gap

-30 degrees

Wulfhekel

Spin polarized MTJ vac gap

Naryanamurti
Figure 6.6: Ballistic transfer ratios and scattering fits. Note that Py has by far the highest BTR $\sim 10$ times that of CoFe, and is fit with the lowest amount of scattering.
planar tunneling

6.8 Thickness dependance

MBE and Sputtered films / implications - multiple passes - Stiles paper? - minority / majority differences in propagation?

6.9 Conclusions

AlO$_x$ spin mixing (citation?)
References for Chapter 6


