BALLISTIC ELECTRON TRANSPORT IN ALUMINUM OXIDE

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by
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Aluminum oxide (alumina) is becoming an increasingly important material in high performance electronics. It is the insulator in magnetic tunnel junctions used for MRAM and may allow for the fabrication of solid state qubits based on Josephson junctions. In this thesis I have used ballistic electron emission microscopy (BEEM) to study the physical and electronic structure of alumina.

BEEM’s high spatial resolution ($\sim 1 \text{ nm}$) was exploited to study the alumina surface where clusters of chemisorbed oxygen were observed. The overall behavior of these clusters helped piece together the electronic structure of the material, in addition to the oxidation process itself.

While the data from the oxide surface studies can be interpreted under the standard set of assumptions people generally impose on BEEM (i.e. no scattering) the data obtained when the oxide is buried cannot. In the latter case the signal levels are too low to ignore scattering.

Before the spectra of buried oxide films could be interpreted, scattering needed to be understood. Scattering in BEEM is nothing new. Kaiser and Bell (BEEM’s inventors) did the experiment nearly a decade ago when they injected holes into a Au base and collected electrons with n-type Si. The essential physics behind the scattering process was properly described in their work. However, fits to data using their theory failed at electron energies above 1.3 eV. By properly accounting for the density of tunneling states, the Kaiser-Bell approach can be modified to correctly describe the data at higher electron energies.

Once simple systems could be reliably fit, scattering BEEM could be used to
study alumina. In the case of hole injection, a higher turn on voltage (relative to Au on Si) is observed which is described by an inelastic scattering process. In the case of electron injection, the same scattering is present and is observed because the alumina attenuates the otherwise dominant unscattered signal.

Scattering also effects spin transport. As scattering increases, the polarization of a ballistic electron beam becomes diluted. This is observed as the fading of contrast in magnetic images as alumina forms between two ferromagnetic layers.
BIOGRAPHICAL SKETCH

Andrew Charles Perrella was born on February 8th, 1976 in Nyack, NY. In 1994, after 18 years of growing up in New York he graduated from Nyack High School and headed west to the University of Illinois (Urbana-Champaign). In 1998 he graduated from Illinois with a B.S. in physics, and headed back east. He was married to Fern Lan Siew that summer, and the two moved to Ithaca to attend Cornell. In the spring of 2004, almost six years later, he received a Ph.D. in Physics.
To Fern, Kathryn, Irene and Charles
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When I first arrived in Bob Buhrman’s group, I was placed under Bill Rippard where we both worked on BEEM. I often say that the very first experiment we did together was the best experiment and I should have quit while I was ahead. Instead I studied with Bill until he graduated in 2001. The last project we began together was studying aluminum oxide films. Two papers and a conference proceeding resulted from these experiments. At that time I had learned everything everything I knew about BEEM from Bob and Bill, and my task was continue with the oxide studies until our understanding of the material was as complete as possible. In reality, the three of us had misinterpreted our original results, as discussed in Chapter 5, and I have spent the last year and a half trying to resolve exactly what is happening in these systems.

During that time it was necessary to understand BEEM in greater detail. Since Bill’s departure, Bob and I have dealt with scattering in BEEM which can no longer be ignored in systems with low signal levels. Hopefully this adds to knowledge base of the group and students after me won’t have to spend time misinterpreting the signals they measure. Although he left the lab in 2001, Bill remained incredibly helpful and a critical resource for myself and Bob. Specifically he talked me through repairs of old BEEM when I encountered situations that had not come up when we were working together. Hopefully I will be just as helpful to the two that continue the BEEM legacy.

I now leave the project in the hands of Phil Mather and John Read. Phil joined the project as the laboratory in D7 was beginning to expand. He was instrumental in the design and construction of prep II and new BEEM. I owe him a great debt, not only for helping to obtain data, but for maintaining an energy level that I have never seen in a human being. No setback we ever had phased him. Not once. Every
challenge was met with an immediate response. John joined the group about a year ago, and is the one that I have already handed old BEEM over to. His systematic and methodical approach will benefit him more than he knows. Not only is it good scientific practice, but a trait necessary to balance out his colleague. As a team these two will have a skill set which would be difficult for anyone to reproduce. It is my pleasure to leave this project in the hands of these two capable and talented individuals.

The Buhrman group as an entity has always had a comradery which has only grown during my years here. All of those in this group, both past and present, have been helpful. Preeti Chalsani and Nathan Emley have overlapped with me the most and their friendship and knowledge have helped me through both expected and unexpected ordeals.

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The members of my committee, Dan Ralph and Piet Brouwer, along with our postdoc Ilya Krivorotov, provided me with a generous amount of academic and intellectual support. Their knowledge has been a great asset to myself and Bob in thinking about the physics behind all of the work contained in this thesis.

Of course Bob has had the greatest influence over these last few years. It was rather by accident that I stumbled upon his group in what might have been the single greatest example of dumb luck in my life. We have very compatible styles and over the course of my studies here I could not have asked for a better person
to work with. I found that over the years, whether willingly or not, I have acquired many of his traits.

Finally, the support I have received from my family can not be described. I have had many unexpected hurdles to jump during these last few years and I would not have survived (literally) without my parents, my sister, and of course my wife.
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CHAPTER 1
Introduction

1.1 Introduction

In the world of oxides there is only one king, silicon oxide. It is the material responsible for the success of silicon in the electronics industry. It hangs from the walls of European cathedrals and lines the canyons of Manhattan. No single oxide effects both science and civilization as profoundly as silicon oxide. However, as electronic devices evolve in the twenty first century, a second oxide is emerging as the clear runner up. As lower power circuits require higher and higher resistances, aluminum oxide (Al$_2$O$_3$) is coming into its own in the device community. It is the insulator of choice for magnetic tunnel junctions (MTJ) and superconducting Josephson junctions (JJ). Additionally, as silicon technology pushes below the 70nm node, gate oxides will approach 1nm where tunneling can result in leakage currents that are unacceptable. To counter this, higher K dielectrics like aluminum oxide are being considered as replacements [1, 2]. In addition to the promising electrical properties of this material, aluminum oxide is easily grown by depositing metallic aluminum and exposing it to oxygen. This allows for the incorporation of aluminum oxide into industrial process lines where throughput is paramount.

All of these modern applications of aluminum oxide require detailed knowledge of its structural and electronic properties. While pure sapphire, or α aluminum oxide is known to be an ideal insulator in the bulk with a band gap greater than 8 eV, the electronic structure of amorphous Al$_2$O$_3$ is the subject of intense research.
It is well known that Al$_2$O$_3$ is amorphous when formed by thermal oxidation of thin ($<1$nm) deposited aluminum. Since this is the process which is most appealing to device manufacturers, it is important to understand the detailed electronic structure of amorphous Al$_2$O$_3$ to determine how or if it can be controlled.

1.2 Types of aluminum oxide

There are over twenty-five known forms of aluminum oxide and hydrated aluminum oxide compounds that have been reported. There are also many naming conventions that are used when referring to aluminum oxide. Alumina is a common term that is often used with reference to aluminum oxide or aluminum oxide compounds. Some reserve it strictly for sapphire, while others apply it more liberally to include all forms of Al$_2$O$_3$ as well as hydrated aluminum oxide and compounds that form with aluminum oxide. In this text the term alumina will refer to aluminum oxides with the chemical formula Al$_2$O$_3$, both crystalline and amorphous. The next few sections will discuss some of the more common or relevant forms of aluminum oxide. Originally, the Greek letter system in naming aluminum oxide was designed to correspond to the relative abundance found in nature[3]. $\alpha$-alumina being the most abundant, $\beta$ the next and so on.

1.2.1 Alpha

The most abundant and stable form of alumina is known as $\alpha$-alumina or corundum. While corundum is never considered a gemstone, the two forms of corundum are. Sapphire is undoped corundum and ruby is corundum doped with chromium. Besides being valuable as gems, the two are also important to the laser and optics community. The discussion of $\alpha$ alumina in this text will stick strictly to sapphire.

Sapphire has rhombohedral crystal structure with fifteen atoms per primitive
Figure 1.1: The crystal structure of corundum (sapphire). The bonds between aluminum and oxygen are shown in (a). Alumina can also be represented as a hexagonal close packed structure (hcp) as shown in part (b). The dashed line indicates a hexagonal plane.
unit cell (three groups of Al$_2$O$_3$). Each aluminum atom is bonded to six oxygen atoms and each oxygen atom is bonded to four aluminum atoms. Half of the bonds are 1.86 Å long and the other half are 1.96 Å long [4]. Figure 1.1 (adapted from ref.[5]$^1$) shows the unit cell (a) and the O-AL bonds. The crystal can also be described as hexagonal close packed (hcp). Figure 1.1(b) shows approximately 13 Å of oxide using the same unit cell with a dashed line to indicate the orientation of the hexagonal planes. The short, strong bond lengths make it very hard, second only to diamond in naturally occurring minerals. Sapphire is therefore an important material to the ceramics industry, as well as to the others mentioned before.

Optically, sapphire is transparent, so therefore must have a band gap much greater than the energy of visible light. Figure 1.2a shows the band structure of sapphire as calculated by Godin [4] using a tight binding model. Figure 1.2b shows the calculated density of states (DOS) using the same formalism and shows a direct band gap of 8.8 eV.

These calculated results agree well with the calculations of Batra [6] and the experimental results from ultraviolet (UV) absorption [7]. Many experimental results however, show structure in the gap of sapphire. This can certainly be attributed to defects in the crystal, but as Guo et al.[8], Gignac et al. [9] and Godin[4] have shown, surface states can exist inside the bulk gap. These can be seen when measuring the electronic properties of sapphire. In electron energy loss spectroscopy (EELS) measurements by M.J. Plisch [10], sub-gap structure is observed in both the amorphous alumina as well as sapphire. However it is unclear what the exact nature of these states are. It is possible that they are due to a reduced density of extended states as compared to the conduction band, entirely due to surface states, or localized states in the sapphire due to defects. As will be

$^1$3D graphics were generated at the Naval Research Lab’s Crystal Structure Database http://cst-www.nrl.navy.mil/lattice/index.html using the data from reference [5]
Figure 1.2: The band structure (a) and the DOS (b) of sapphire as calculated by Godin [4] using a tight binding model.
discussed later in the case of $\gamma$-alumina, introducing defects lowers the calculated band gap by a few eV, however there are still clearly observed sub-gap states. Regardless of the exact nature of the states that exist within the gap, alumina in all of its forms are fantastic insulators. Measurements of bulk sapphire yield a dielectric constant of 12.3 and a resistivity of $1 \times 10^{11} \Omega \cdot \text{cm}$ at 500°C [3].

As will be discussed later, the perfect crystalline insulator known as sapphire is not what forms when deposited aluminum films are thermally oxidized. It is important however, to understand these ideal properties because it is these bulk properties that make this material promising for applications in device electronics. As with all materials it is believed that as thin oxides can be made purer and purer, the electrical properties will begin to approach the bulk values.

1.2.2 Beta

$\beta$-alumina refers to compounds of aluminum oxide with alkaline oxides. Examples include $K_2O \cdot 11Al_2O_3$ and $Na_2O \cdot 11Al_2O_3$ [3]. Since $\beta$-alumina contains elements other than aluminum and oxygen, it is not really true alumina by the definition used in this text. It is reasonable to assume that there are no alkaline contaminants in the alumina used in devices since all thin films are grown in ultra high vacuum (UHV) conditions which will be discussed later. $\beta$-alumina is only worth mentioning here because of it’s abundance and therefore importance to the ceramic and aluminum refining communities.

1.2.3 Gamma

With the exception of alpha and amorphous alumina, $\gamma$-alumina is the only other flavor of aluminum oxide which has received significant attention by physicists. $\gamma$-alumina contains the same ratio of Al to O atoms as $\alpha$-alumina but has a tetragonal structure where there are 8 cation vacancies for every 160 atoms.
The chemical formula is typically written as □_{2/3}Al_{21/3}O_{32} where the □ represents a vacancy. Samples of γ-alumina can be formed by reactive sputtering, anodic oxidation, electron bombardment of alumina powder or by the thermal oxidation of aluminum foil in air followed by a 873 K anneal for 24 hours [12]. The first of these methods is of interest to the device community since it is possible to deposit thin films of alumina with this method. The γ phase is meta-stable and upon heating will eventually form the thermodynamically stable α phase [13]. Because the γ to α transition needs heat and/or pressure to occur at a measurable rate, the properties of γ alumina are important to understand as typical thin film deposition methods will undoubtedly produce alumina with defects.

Perhaps the most important effect of the vacancies is a reduction of the band gap from 8.8eV to under 5 eV. Figure 1.3a shows xray photoemission spectroscopy (XPS) and DOS calculations for γ-alumina [11].

The substantial reduction in the gap is shown in Figure 1.3b. Here the results from figure 1.2b (thick line) are overlayed on the results shown in figure 1.3a for the γ-alumina with two tetragonal (tt) vacancies (thin line). Calculations of the γ-alumina DOS are more varied than those for α-alumina. Gutierrez et al. [11] report a gap of 4 eV but admit that their density functional technique (DFT) calculations underestimate the gap, the same technique resulted in a gap of 6.3 eV for α-alumina. Similarly, using a local approximation density functional theory (LDA) Mo et al. [14] report a gap of 5.13 eV and 6.29 eV for γ and α phase respectively. The only experimental results that have been reported are EELS measurements by Ealet et al. [12]. While a measured gap of 8.7 eV is claimed, there is obvious structure inside the gap. The authors attribute this to surface states but there is little evidence to substantiate that claim over other possible sub gap states or even a reduced gap itself. While the exact reduction of the gap
Figure 1.3: (a) XPS measurements and calculated DOS for $\gamma$-alumina obtained from reference [11]. (b) A comparison of the calculated band gap for $\gamma$-alumina (thin line) from (a) and $\alpha$-alumina (thick line). The $\alpha$-alumina data was taken from figure 1.2b. The reduction in the gap from almost 9 eV to 5 eV is due to the increased disorder (vacancies) of the $\gamma$-alumina.
might not be clear, one thing the calculations clearly show is that introduction of vacancies results in a smaller band gap. The fundamental result is that as more defects are introduced into the system, alumina becomes a less ideal insulator.

1.2.4 Amorphous

The pinnacle of disorder in a system is when the structure is amorphous. In amorphous alumina (a-alumina) the Al$_2$O$_3$ stoichiometry still exists, but there is no long range crystal structure. The lack of long range order makes it very difficult to calculate band structure. As of this writing no theoretical papers exist that attempt to calculate the band structure of a-alumina. This lack of theoretical work on a-alumina makes it an unappealing system to study but in this case nature gives us no choice. It is well established that ultra-thin (<1nm) alumina barriers are amorphous. Using both XPS and high resolution transmission electron microscopy (HREM) Snijders et al. [15] demonstrated that films oxidized at room temperature were predominately amorphous, regardless of thickness. An increasing percentage of $\gamma$ phase was observed with increasing oxidation temperature. After prolonged oxidation at 773 K the films eventually became crystalline ($\gamma$-alumina), however in all cases the first nm of oxide was always amorphous. Jeurgens et al. [16] from the same group as Snijders at Delft used thermodynamic arguments to explain why the thin junctions are more stable in the amorphous phase. Their analysis showed that the amorphous metallic interface is lower in energy than a crystalline metallic interface. In bulk alumina, however, the crystalline phase is lower in energy which means that a critical thickness exists below which the amorphous phase dominates. This thickness ranged from .5 nm to 4 nm depending on the orientation of the underlying metallic film.

The room temperature thermal oxidation of aluminum is a self limiting process, where the oxide creates a shield as it forms. The self limiting occurs between 1.5
- 2 nm [17]. This is well within the thickness range where amorphous structure dominates, so any oxides formed by this process will be amorphous regardless of how thick the initial aluminum film was. On the other extreme, about .5 nm of deposited aluminum is needed to form a spatially complete barrier [18]. This places a very small window on the range of oxide thicknesses that can be studied using room temperature thermal oxidation, all of which will have amorphous structure. It is oxides in the .5nm to 1.5 nm range that are used in technologically relevant MTJs and therefore are the subject of most current tunnel junction research efforts [19]. This thesis will also be restricted to amorphous oxides in the aforementioned thickness range. Through both BEEM measurements performed here at Cornell, and other data taken from the literature the electronic properties of amorphous alumina will begin to emerge.

1.3 Aluminum oxide in electronics

1.3.1 Magnetic tunnel junctions

By the fall of 2003, alumina tunnel junctions have shown promise in device electronics as the barrier material in magnetic tunnel junctions (MTJs). IBM, Motorola and Seagate have all placed intense research efforts into MTJ systems.

Figure 1.4a shows a cross sectional schematic of a simple ferromagnet - insulator - ferromagnet MTJ. A typical four point measurement setup of the same MTJ is shown in figure 1.4b. In a MTJ spin polarized electrons tunnel through the oxide from one ferromagnetic electrode to another. The rate of tunneling, and hence the measured resistance of the MTJ depends on the relative alignment of the two ferromagnets. If the two magnetizations are aligned, the device is in a low resistance state. If the two magnetizations are anti-parallel, the result is a high resistance state. In practical devices, one ferromagnet is usually pinned with an
Figure 1.4: A typical cross section (a) of a MTJ and that same tunnel junction in a simple four point measurement setup(b). Typical resistance vs. applied field curves for a tunnel junction patterned into a $2 \times 1$ $\mu$m ellipse. When the magnetizations of the two layers are parallel, the device will be in its lowest resistance state. When the magnetizations are anti-parallel the device will have its highest resistance. *Data Courtesy of G.D. Fuchs*
antiferromagnet and the other ferromagnet is free to switch magnetization. Figure 1.4c shows the resistance versus applied magnetic field (R vs. H) curve for a typical MTJ with a fixed bottom layer and a free top layer. The solid black line shows the resistance as the field is swept from negative 1kOe to positive 1kOe, the dashed line shows the scan in the opposite direction. Initially the device is in an aligned, low resistance state. As the field is swept past 0 and into positive applied field, the free layer switches while the fixed layer remains. The device is now anti-aligned and in a high resistance state. Eventually as the external field overcomes the exchange biasing from the anti-ferromagnet, both layers are switched, the device is aligned and the resistance is low again.

Typically in applications the fixed layer will always remain with one magnetization and the free layer will switch, this will provide the necessary two states, ultimately a binary 1 or 0. One measure of a MTJ that is always important is the relative difference in signal level between the two states or $\frac{\Delta R}{R} = \frac{R_{\text{high}}}{R_{\text{low}}} - \frac{R_{\text{low}}}{R_{\text{high}}}$ where $R_{\text{high}}$ is the highest (mis-aligned) device resistance and $\Delta R = R_{\text{high}} - R_{\text{low}}$ where $R_{\text{low}}$ is the lowest (aligned) device resistance. The example in figure 1.4c has a $\Delta R$ of about 14%. The greater the $\Delta R$ the easier it will be to determine which of the two states the device is in.

Each specific device will have its own requirements on the performance of the MTJ. For example, Seagate has been developing MTJs as hard drive read heads. In this application the free layer is designed to switch, and thus the device resistance, as the hard drive media it is reading exerts a magnetic field of alternating orientation on the free layer. Essentially the MTJ is acting as a binary magnetic field sensor. Their requirement is that the total resistance of the junction is relatively low ($\sim 50 \Omega$) and an area less than $1 \mu m^2$[19]. This means that the resistance area product $(RA)$ should be around $50 \Omega \cdot \mu m^2$. The $RA$ product is a useful property
of a MTJ because it allows one to predict the total resistance of a MTJ which has identical material thicknesses, but a different area. The $RA$ product is dominated by the electronic structure of the barrier material, which is one of the reasons why the electronic properties of alumina are of great interest.

IBM and Motorola are pursuing MTJs for a different reason. Their goal is to build magnetic random access memory (MRAM). The goal of MRAM is to create fast, non-volatile memory. A MTJ lends itself nicely to non-volatile memory because the state of the device is stored in the magnetic moment of the free layer. Hence, when the power to the device is turned off, the state of the device remains. This is in contrast to complementary metal oxide semiconductor (CMOS) devices which require power to retain information. While storage of information is identical to the way a hard drive stores data, the reading and writing of the data is completely different. Instead of having a read head, write head and spinning media, MRAM will have each MTJ wired directly to a read and write circuit. Thus, no moving parts and the potential for fast operation. The requirements on MTJs for MRAM are that each device have a resistance on the order of $1k\Omega$. This is to ensure that the transistors required to read and amplify the MTJ receive a signal of a few $\mu A$ [20] when the device is biased with voltages on the order of a few mV. Another important property is that the MTJs be as small as possible so they can be packed together with the greatest possible storage density. Once again it is important to understand properties like $\frac{\Delta R}{R}$ and the $RA$ product so useful devices can be designed and produced.

Each part of a MTJ, such as the magnetic switching or the anti-ferromagnetic exchange biasing, is an area of research for scientists and engineers. In this thesis the thrust will be to understand the electrical properties of the alumina tunnel barrier.
1.3.2 Superconducting Josephson junctions

In addition to its success in MTJs, alumina is also the insulator of choice for superconducting Josephson junctions (JJ). Because of their ability to perform at THz switching speeds, JJ have shown promise in high speed memory [21] and computation applications[22]. Despite the very desirable operational speeds, JJ have yet to be incorporated into widespread high performance electronics. Due in part to it’s own limitations but also because of how successful silicon has been, both functionally and economically.

There is one emerging technological application that may finally place JJ at the top of the device electronics world. The computational speed that could be achieved with a functioning quantum computer is mind boggling and has caught the attention of private industry, academics and government agencies. A comprehensive review of quantum computing is beyond the scope of this (or perhaps anyone’s) thesis, but it is important to know that the fundamental component of the quantum computer is the quantum bit or qubit. While conventional computation requires bits with two states, corresponding to a 1 and 0 like the MTJ example above, qubits also have two basis states but are allowed to exist in any superposition of these two states. Many techniques and systems, such as nuclear magnetic resonance (NMR) of fluid cells [23]or the trapping of atoms with lasers[24], have been used to make elaborate qubits (for a concise review see ref. [25]). In order to produce a real computational machine, the elaborate systems must be forgotten and a scalable, solid state system must be realized.

Josephson junctions lend themselves nicely to qubits. They are solid state devices which can be patterned in parallel and can exhibit robust quantum mechanical behavior. A very complete review of JJ in quantum computation was written by Makhlin et al. [26]. The two basic configurations of JJ as qubits is
shown in Figure 1.5. Figure 1.5a shows an example of a charge-based JJ qubit.

Figure 1.5: Examples of two superconducting qubit geometries, the charged based JJ qubit (a) and the flux based JJ qubit (b).

In this circuit the top superconducting lead can be thought of as a reservoir of Cooper pairs which are allowed to tunnel into the island (bottom electrode). By properly tuning the gate voltage $V_g$ to balance out the equilibrium charge on the island, an energy situation can be created where 1/2 extra cooper pair is an energy maximum, and 0 and 1 extra cooper pair are the energy minimums or basis states. The amount of charge on the island is then always measured to be a superposition of the 0 or 1 extra cooper pair energy levels.

Figure 1.5b shows a simple example of a flux JJ qubit. The phase difference ($\varphi$) across the smaller (SQUID) loop is related to the flux $\phi_2$ through the big loop. The energy of the system is related to the phase where the minimum energy is when $\varphi$ is 0 and the maximum energy is when $\varphi$ is $\pi$. The flux through the smaller loop $\phi_1$ allows for the tuning of the equilibrium energy. Thus the double well potential (two state system) can be centered around an arbitrary value.

In both cases the Josephson tunneling which is critical to the performance of
the device is governed by both the superconducting phenomena and the electrical properties of the oxide. It is therefore essential to understand properties like the barrier height, distribution of channels and continuity in space.

1.3.3 High K dielectrics

The idea behind using higher K dielectrics in silicon technology is simple. The capacitance of a simple parallel plate system containing a dielectric is written as

\[ C = K \frac{A \epsilon_0}{d} \]

where \( A \) is the area of the plates, \( d \) is the distance between the two plates, \( K \) is the dielectric constant and \( \epsilon_0 \) is the permittivity of free space [27]. As technology pushes required device sizes smaller and smaller the area of gate capacitors must of course decrease. This however changes the capacitance, and to compensate \( d \) must also decrease proportionally to maintain the same electronic properties of the gate. As device dimensions get smaller than 70nm, the thickness of the SiO\(_2\) becomes less than 1.5nm [1]. With thicknesses this small direct tunneling through the gate becomes significant and can result in unacceptable leakage currents. High leakage currents mean devices consume more power than necessary, and therefore a solution must be found. SiO\(_2\) typically has a value of \( K = 3.8 \) where thin alumina films have a value of \( K \sim 10 \) depending on the details of the alumina. This means that for the same area and the same capacitance value, the distance between the plates can be about 2.5 times larger for the alumina capacitor than for the silicon oxide capacitor.

Figure 1.6 demonstrates this thickness advantage gained by using alumina. Since the tunneling current is exponentially dependant upon thickness and decreases by about 1 order of magnitude per Å of additional thickness, a big reduction in the leakage due to tunneling can, in principle, be obtained by simply changing dielectric materials.
Figure 1.6: The advantage of using alumina as a dielectric (b) is that the same capacitance can be obtained as a thinner SiO$_2$ based device (a). As high performance electronics demand the SiO$_2$ thickness to be less than a nm, tunneling becomes a substantial source of leakage current. The exponential dependence of tunneling on thickness means the thicker alumina barriers will have substantially less leakage do to tunneling.

BEEM does not really offer a way to probe the dielectric constants. Nonetheless, information we can obtain about the electrical and growth properties of the material will only help those who are trying to engineer devices using alumina.

1.4 Summary

In order to create useful electronic devices each and every component of that device must be understood. In the case of MTJs the magnetics and the barrier must be studied. For JJ, the superconducting phenomena and barrier properties are equally important, and for high K dielectrics the electrical and growth properties of alumina are the key pieces. In all cases knowledge about the detailed electrical and physical properties of alumina are important. In this thesis I will focus on putting together a picture about those two essential properties of this versatile material.
CHAPTER 2
Experimental Procedures

2.1 Introduction to BEEM

Developed in the late 1980’s by Kaiser and Bell, ballistic electron emission microscopy (BEEM) is an unmatched tool for probing both the energy and spatial dependant transport of hot electrons in thin films [28]. Figure 2.1a shows a standard BEEM setup where a conducting film is grown over a semiconducting substrate. The excellent (∼ 1nm) spatial resolution is achieved by rastering a scanning tunneling microscope (STM) tip over a conducting (usually multilayer in our samples) thin film in constant tunnel current (I_t) feedback mode. This produces a topographic, or STM image. As we will see later, the STM signal is really a convolution of the topography, tip density of states (DOS) and sample DOS. However, the dominant effect is almost always the topography so the STM image will be interpreted as a topographic map of the film surface unless otherwise noted.

Figure 2.1b shows a one-dimensional energy diagram for BEEM. When the STM tip bias (V_t) is negative, electrons are injected into the sample. In our experiments the first part of the multilayer (base) that is deposited on the semiconductor (collector) is gold. The gold - semiconductor (either n-type Si or GaAs) interface forms a Schottky barrier (Φ_b) which acts as a detector for hot electrons. Only those injected electrons that satisfy both energy and any applicable momentum constraints are collected in the substrate and recorded as BEEM or collector current (I_C). All other tunnel injected electrons are collected in the base as tunnel
Figure 2.1: (a) The experimental setup for BEEM. Contact is made to the metal surface (base) to allow feedback for an STM tip operating under constant tunnel current conditions. When the metal is grown on a semiconducting substrate (collector), the resulting Schottky barrier acts as a hot electron detector. The collector current (BEEM) can be measured by making ohmic contact to the back of the substrate. The result is the ability to simultaneously acquire two images. The first being the STM or topographic image, the second being a map of ballistic transport in the film. Besides being able to measure transport with spatial resolution, energy dependence can also be obtained. The one-dimensional energy diagram in shown in (b). Electrons transport through the base and those which reach the Schottky barrier with energy $> \Phi_B$ can be collected. The energy of the ballistic electrons can easily be set by adjusting the tunnel voltage ($V_t$). The contacts to the base and the collector are also shown.
current $I_t$. As we will see in Chapter 3, scattering greatly reduces the number of electrons that contribute to $I_C$, therefore the BEEM image will be interpreted as a spatial map of ballistic electron transport unless otherwise noted. The energy dependence of $I_c$ can be measured by simply adjusting $V_t$. Figure 2.2 shows the energy dependant response of $I_c$ for a simple Au-Si Schottky diode. Here current begins to flow once the tip bias exceeds the Schottky barrier of this system at 0.8 eV.

![Graph showing collector current vs. negative tip bias](image)

**Figure 2.2**: $I_c$ vs. $V_t$ for a 130 Å Au on Si(111) film. The turn on at 0.8 V is a direct measure of the Schottky barrier height.

### 2.1.1 Sample requirements

The Ph.D. thesis of M.K. Weilmeier [29] contains a complete listing of what properties are important for a good BEEM sample. One worth mentioning with regard to alumina studies is the zero bias resistance (ZBR) of the sample, which must be sufficiently high, $> 2 \text{G}\Omega$. In order to understand why the ZBR is so important it is helpful to visualize the sample - measurement circuit as shown in Figure 2.3. Here the sample is effectively replaced with a capacitor and a resistor ($R_s = \text{ZBR}$).
A possible source of noise, the effective capacitance can be reduced by reducing the size of the STM contact area [29]. In our samples it only plays a role when the tunnel current experiences an effectively high frequency AC signal, such as a sudden spike. For all samples studied under reasonable acquisition conditions (<1 ms per pixel) the capacitive coupling can be ignored.

Figure 2.3: The equivalent circuit diagram for the BEEM measurement system. The sample can be thought of as a resistor and a capacitor in parallel placed between the two pre-amps. The zero bias resistance (ZBR) must be high enough to prevent an electron reaching point A from leaking back through the sample to the STM pre-amp.

$R_s$ on the other hand can contribute to the noise of the system for several reasons. The first reason is the Johnson noise contribution of $R_s$. The Johnson noise current due to $R_s$ is proportional to $\frac{1}{\sqrt{R_s}} [30]$. For a pixel acquisition rate of 100 Hz, a 10 fA (typical current values for MTJ samples discussed later) noise level requires a value of $R_s > 100 \text{M}\Omega$. A second reason is that while the virtual
grounds of the STM and BEEM pre-amps should be identical, in reality they will always be off by a few µV. This is the case for any real circuit. In order to keep the current flow between the two pre-amps below that same 10fA, \( R_s \) needs to be greater than 1GΩ. Finally, a very simple argument involving parallel resistors can be made which requires an even higher \( R_s \). Imagine an electron that is injected into the substrate and arrives at point 'A' in Figure 2.3. In order to reach ground, the electron must choose a path that goes through the BEEM feedback resistor \( R_2 \) or a path back through the sample (\( R_s \)) and through the STM feedback resistor \( R_1 \). In both the microscope built by M.K. Weilmeier and W.H. Rippard (old BEEM)[29] and the VT400 built by RHK Technologies (new BEEM)\( R_1 \) and \( R_2 \) have nominal values of 100 MΩ and 1GΩ respectively. Ideally we want an electron sitting at point 'A' to choose a path through \( R_2 \) so we can record it as BEEM current. That means \( R_s + R_1 > R_2 \). The Schottky diodes which are fabricated for use as BEEM detectors in this thesis typically have \( R_s \) values of a few GΩ. This still allows some current to escape, but insures most of the injected electrons are collected.

Since all of the samples in this thesis were grown on Schottky diodes, it doesn’t seem that sample ZBR should be a problem. In fact, for our technique it is not, however other attempts at using BEEM to study alumina have tried to avoid using the Schottky barrier. A sketch of the BEEM setup used by Kurnosikov et al. [31]is shown in Figure 2.4a. Here the authors attempted to put the STM pre-amp on the top lead of a MTJ, and the BEEM pre-amp on the bottom lead. The corresponding energy diagram in Figure 2.4b shows how this type of measurement should work in theory. The electrons from the tip are tunnel injected directly into the top lead the same way they would be injected into the base. Of these injected electrons, those whose energy is greater than the oxide barrier height \( \Phi_{\text{ox}} \) can overcome the
Figure 2.4: (a) A schematic of the BEEM experiment published by the Eindhoven group [31]. No Schottky barrier is used so the only resistance between the two pre-amps is the tunnel junction. The energy diagram (b) suggests that in theory this setup should yield a direct measurement of the alumina barrier height, $\Phi_{\text{ox}}$. Experimentally however, the ZBR of such samples is too low and sufficient signal to noise is not possible without unpractically small device areas.
barrier and be transmitted into the bottom electrode where they can be collected as BEEM current. Without worrying about practical measurement issues, it seems that this approach would yield a direct measurement of $\Phi_{ox}$ much the same way standard BEEM yields a direct measurement of $\Phi_B$. The major problem with this approach is that the resistance of thin alumina barriers is far too low. Typical RA products for thin tunnel junctions, as mentioned before, can range from 100 $\Omega \mu m^2$ to 10 k$\Omega \mu m^2$ depending on the thickness of the oxide [19]. In order to achieve the same 2 G$\Omega$ resistances that are required for the diode samples these tunnel junctions would have to have areas on the order of 5-10 nm$^2$ which would be impossibly small to fabricate. Of course without the Schottky barrier detector, the transmitted signal will be higher, but even if the tunnel junction has an average transmission coefficient of 0.1 (i.e. 100 pA for 1 nA of $I_t$), these tunnel junctions would need resistances on the order of 100 k$\Omega$, or areas less than 0.1 $\mu m^2$. Still too small a device to practically fabricate and study with an STM.

Despite the resistance and noise issues discussed above, Kurnosikov et al. [31] still attempted to make these measurements. They evaporated their leads through shadow masks and did not pattern their devices in any other way. This made their device resistances very small and noise issues a real problem. In private communications with one of the authors they did not disclose what their device resistances were, but did admit to noise being a problem. Two attempts were made to address the noise issue. One was to scan with an AC signal and use a lock-in to detect the collector current, and the other was to scan with a high tunnel current, 40 nA. The former method introduces capacitance issues discussed above, and the 40 nA of tunnel current is an order of magnitude greater than what most people would use when doing STM. The very high tunnel current raises the concern of unwanted tip touches, since the mean tip sample spacing is closer, or damage to
the oxide because of much higher current densities, about $4 \times 10^6$ A/cm$^2$ for $I_t = 40$ nA. The images published by Kurnosikov et al. are of poor quality and it is difficult to determine what is being measured. However, since Kurnosikov and co-workers are the only other group who have attempted studying alumina with BEEM, their results are the only ones which can be directly compared with the work presented in this thesis.

Needless to say, because of the experimental problems encountered by trying to do BEEM directly on an oxide, the Au-Si Schottky diode remains a critical component of the instrument, even for studying oxides. In this thesis I will only use samples with Schottky diodes that have a ZBR of 2 GΩ or greater. All other thin films which are to be studied are grown on top of these diodes.

2.1.2 Sample fabrication

All of the sample preparation procedures for Si substrate samples are identical to those used by both Weilmeier and Rippard [29]. The process for GaAs substrates parallels the Si process and is illustrated in Figure 2.5. The process begins with a n-type GaAs wafer which is .36 mm (.015”) thick (Figure 2.5a). Resistivity of these wafers is around 5 Ω·cm, which is similar to the Si wafers. Two inch diameter wafers are the most common, but certainly there is no reason to use any particular diameter. Three inch wafers would be better due to greater die yields than the two inch variety.

The GaAs wafers are cleaned with a 120 second dip in 10:1 water:ammonium hydroxide and then placed in a plasma enhanced chemical vapor deposition (PECVD) machine where 500 nm of SiO$_2$ is deposited (Figure 2.5b). Photoresist is spun on the oxide (Figure 2.5c). The exposure is done with the contact aligner using the same mask as the Si, namely 100 µm × 100 µm devices with 7.056 mm center
Figure 2.5: The fabrication procedure for creating sample die from GaAs wafers. A bare GaAs (a) wafer is covered with 500nm of PECVD SiO$_2$ (b). Photoresist is spun on the wafer (c) and patterned into 100 $\mu$m $\times$ 100 $\mu$m devices (d). The SiO$_2$ is etched through (e) and the photoresist is lifted off(f).
to center spacing. The resist is developed (Figure 2.5d) and the oxide etched in buffered oxide etch (HF, NH₄ and water) for 4 min, or until the devices look clear under the microscope (Figure 2.5e). Ohmic contact on the backside of the wafer is not done by ion implanting, rather 500 nm of Au is evaporated on the backside of the wafer (Figure 2.5f). The wafers then go through a hot plate anneal, ramping to 350 °C in 30 min, then back down at the same rate. The process window is huge on the last step, all that is required is the Au mixes with the GaAs.

The GaAs die are then ready for metal deposition just like the Si die. Immediately before they are introduced to the chamber the GaAs die are cleaned with a 1 minute dip in 2:1 water:ammonium hydroxide followed by a 1 minute rinse in isopropyl alcohol. This standard procedure typically leaves a monolayer of oxide on the surface.

2.1.3 UHV requirements

All of the experiments in this thesis have been fabricated and measured under ultra high vacuum (UHV) conditions (< 5 × 10⁻¹⁰) torr. The exception, of course, is when thin films are exposed to a controlled dose of oxygen. Because Iₑ is so sensitive to scattering, it is imperative to keep the systems clean to avoid unwanted oxidation or gas adsorption. This is especially important when we examine highly reactive surfaces like aluminum which can begin to deteriorate after a few days, even in UHV. A sample sitting at 5 × 10⁻¹⁰ Torr experiences a dose of 8 µTorr · sec every day. This is equivalent to 8 monolayers of gas hitting the surface everyday. The sticking coefficient of oxygen on aluminum is .016 [32], this means that if the partial pressure of oxygen is 1/5 the total pressure of 5 × 10⁻¹⁰ Torr, 2 - 3 percent of the surface becomes covered per day. Of course if the pressures involved are 10 times higher, 20-30 percent of the surface is covered and the sample becomes unusable very quickly. Samples with generally non-reactive surfaces, like Au, are
pretty safe. Many of the tunnel junction samples we will talk about are coated with copper. This provides reasonable sample lifetime with good growth properties on transition metals.

As a general rule, Cu or Au coated samples remain clean for months. Cobalt surfaces are usually debris free for one or two weeks. Aluminum samples will begin showing signs of changes after only a few days, however oxidized surfaces remain for several weeks since the controlled oxygen exposure is usually many orders of magnitude greater than the exposure they receive in UHV.

2.2 Capabilities and limitations of BEEM

2.2.1 Sensitivity

Every measurement technique has its strengths and weaknesses. In BEEM, the defining strength is the spatial resolution with which it can measure transport in a thin film. The details of the momentum distribution, along with its importance, have been debated since the earliest days of BEEM. The two lines of thought regarding the electrons which are ultimately collected as $I_e$ are that they either must be unscattered hot electrons focused to within 6° of normal [28] or that each interface creates a uniform momentum distribution around the Fermi surface [33]. In any case, achieving nanometer resolution with in BEEM images is quite common. This kind of spatial resolution of electron transport is not achievable with any other technique, especially for buried interfaces. While it is also quite commonplace for an STM to achieve atomic resolution images (both old BEEM and new BEEM have done so), atomic resolution has never been observed in BEEM images.

Besides the unmatched spatial resolution, BEEM has the advantage of only collecting hot electrons. Because the electrons are tunnel injected into the sample,
and every layer of the sample, including the substrate, has the same Fermi energy, the electrons which comprise \( I_c \) are truly ballistic. This is in contrast to a technique like conducting tip atomic force microscopy (AFM) where changing contact resistance could alter the ratio of ballistic to diffuse electrons. The advantage of a purely ballistic electron distribution is that it is accurate to think of the electrons as free moving through the simple energy diagram of Figure 2.1b. Among other things this allows for direct measurements of ballistic attenuation lengths and transmissivities of interfaces [34].

Lastly, the \( 10^{10} \) gain of the BEEM pre-amps allows for \( I_c \) detection of 50 fA while scanning and 1 fA while taking IVs through the use of signal averaging. This means the study of films with a total ballistic transmission of \( 5 \times 10^{-5} \) for the former and \( 1 \times 10^{-6} \) for the latter is possible when using 1 nA of tunnel current. This type of sensitivity is extremely important in the study of alumina where the current levels are typically on the order of tens of fA.

2.2.2 Compatible energy range

One of the great benefits of using the Schottky barrier as the detector in BEEM is, as mentioned above, the ability to only collect hot electrons. However this comes at a cost. Because the turn on for a Au-Si Schottky barrier detector is 0.8 eV (Figure 2.2) BEEM is blind to any features below this energy. That means oxides with barriers less than 0.8 eV, or DOS effects in metals near the Fermi energy cannot be measured. In theory it is possible to reduce the Schottky barrier and still maintain the proper noise requirements by changing Schottky barrier materials and going to low temperatures, but that will be discussed in the next section. For room temperature studies, little can be done to study both the spatial and energy dependance of transport at energies below 0.8 eV. In fact, due to the turn on of the Au-Si detector, most multilayer systems can only be studied at energies greater
than 1 eV.

Besides the lower limit set by the Schottky barrier there is a practical upper limit to the detectable energy range as well. This is less of an issue when studying practical systems as typical devices usually operate between a few mV to a few V, however it remains a limitation. The upper limit to the energy range arises from several sources. One of the common culprits is surface deformation at high bias. In this case large mounds develop on the surface under the tip if the bias is too high. These mounds create a situation where the nature of the sample, especially in multilayers, becomes unknown. Thus, any data taken over these large defects can’t be accurately interpreted. The large mounds usually act in a way to reduce $I_c$, but that is not necessarily the case. For Au coated samples this can happen at tip biases around 2-2.2 V, Cu coated samples are a little more sturdy (2.5 V), while Co samples are typically stable when scanned at 3 V although they deteriorate beyond that. Another artifact of high bias is a rolling off of $I_c$. This generally occurs around the same bias one may start to build mounds. This also prevents the direct interpretation because it may be unclear what is causing the effect.

A thorough discussion of these and other high tip bias effects can be found in chapter 6 of Hans Hallen’s thesis [35] and won’t be duplicated here. However, it is important to note that the energy band in which BEEM can effectively study thin films at room temperature is between 1 and 3 eV.

2.2.3 Injected distribution

It would be convenient if an STM tip injected all of the electrons with energy $eV_t$, but that is not the case. Thermal spreading, the exponential voltage dependance of tunneling, and electric fields generated at the tip all cause the injected electrons to have a distribution in energy. Since only those electrons which are greater than
the Schottky barrier are collected, understanding the energy dependence of the injected electrons is an important component in calculated BEEM spectra. Figure 2.6 helps illustrate this effect. The Fermi energy of the tip is raised by an energy eV\textsubscript{t} above the Fermi energy of the sample when a negative tip bias V\textsubscript{t} is applied. The convention used in this thesis will be to set the Fermi energy of the sample to 0. Since all the states in the tip below eV\textsubscript{t} are also occupied, electrons with energy ε greater than 0 will have some probability f\textsubscript{T}(ε) of tunneling from the tip to the sample. It is worth pointing out that electrons with ε < 0 won’t tunnel from the tip to sample because the states below the Fermi energy of the sample are occupied. Therefore only electrons with ε > 0 will contribute to the tunneling current.

There are many theories that can be used to calculate the distribution of tunneling electrons. Since the detailed structure of an STM tip is not known, and probably will never be, one must make assumptions in order to come up with an algebraic expression for the tunneling distribution. These assumptions are based on both educated physical guesses as well as the ability to actually do the calculation. One of the simplest approaches is to assume the tip and the surface are two infinite planes. This planar model is used by Kaiser and Bell [28] in their calculations. The idea that a very sharp tip might somehow be modelled as a plane seems ungrounded, however on the scale of atoms, a plateau with a thousand atom radius is essentially infinite while still macroscopically sharp. The theory used for calculations in this thesis however is the same as that used by Ludeke and Bauer [33]. The model, which was originally developed by Lang et al. [36] in the early days of STM, describes the tip as a plane with a single atom adsorbed on it.

Figure 2.7 shows a cartoon illustrating this model. The rationale behind using
Figure 2.6: When the Fermi energy of the tip is raised $eV_t$ above the Fermi energy of the sample ($\varepsilon = 0$), all electrons in the tip with energy greater than 0 will contribute to the tunneling current with some probability defined by equation 2.1.

Figure 2.7: The model used by Lang[36] in deriving equation 2.1. The STM tip is modelled as an infinite plane with a single atom adsorbed on the surface.
this model is that since tunneling is exponentially dependant on distance, whatever
point is closest to the sample will contribute to the vast majority of the tunnel
current. The general rule of thumb is an order of magnitude reduction in tunnel
current for every angstrom of additional distance. Therefore an atom 2 Å in di-
ameter adsorbed on a plane will contribute 100 times the tunnel current than any
of the atoms that make up the plane itself. While it is just as unlikely to have a
perfect plane, as it is to have a perfect plane with a single atom adsorbed on it,
it is quite likely that the tip will have grains and defects. Whichever atom on a
grain or defect is closest to the sample will contribute to tunneling. Modelling it
as a single atom on a plane makes the mathematics approachable. The final form
of this distribution becomes the manageable equation 2.1.

\[ f_T(\varepsilon) = \frac{be^{b(\varepsilon - eV_t)}}{1 + e^{(\varepsilon - eV_t)/k_BT}} \]  (2.1)

The energy term \((\varepsilon - eV_t)\) takes care of our requirement that \(\varepsilon = 0\) is the Fermi
energy of the sample. When one uses the Fermi energy of the tip as \(\varepsilon = 0\) the term
\((\varepsilon - eV_t)\) is simply written as \(\varepsilon\). The expression in the denominator is simply the
Fermi function and allows for states to be thermally populated at energies higher
than the tip bias. The normalization constant, \(b\), is determined by integrating \(f_T\)
over all energies. It can also be written as \(b = |\ln(0.5)|/E_{1/2}\). In this form it is
easy to think about what it means physically since \(E_{1/2}\) describes the amount of
energy spreading in the electron distribution. The greater \(E_{1/2}\), the more smeared
out in energy the distribution will be. Figure 2.8a. shows equation 2.1 plotted out
for several values of \(E_{1/2}\) for a tip bias of -2V. An important point to bear in mind
is that the function \(f_T(\varepsilon)\) is properly normalized when integrating over all energies,
however in the case of BEEM we will require a constant tunnel current and the only
allowed energies are \(\varepsilon = 0\) to \(\varepsilon = \infty\). When \(E_{1/2}\) is small relative to the tip bias, say
.14eV when $V_t = -2V$, the distribution is tightly focused and normalization is not a problem. However when $E_{1/2}$ approaches the tip bias as is the case for the solid line in Figure 2.8a ($E_{1/2} = 1eV$), $f_t(\varepsilon)$ is expecting a contribution from electrons with $\varepsilon < 0$, which are unavailable. Nothing changes in the functionality, however the distribution must be re-normalized so that a constant number of electrons is delivered by $f_T$ regardless of tip bias and $E_{1/2}$ values. This can all be done numerically and the graphs in Figure 2.8a all represent the same total number of electrons.

Figure 2.8b shows the calculated BEEM IVs using the tip distributions shown in Figure 2.8a using the Ludeke - Bauer formalism [33]. As one might imagine the smaller $E_{1/2}$, the more focused the distribution is at higher energy, and therefore the higher the collector current. The absolute scale is somewhat arbitrary so a value of 1 for the highest signal was chosen. Since many factors can contribute to the size of the signal, no insight into the value of $E_{1/2}$ can be obtained by comparing relative signals. The effect of varying $E_{1/2}$ on the energy dependence is shown in Figure 2.9. Here all of the curves correspond to the same values of $E_{1/2}$ as stated in Figure 2.8 and have been scaled to a value of 1 at -2V. Only the dashed line ($E_{1/2} = .14eV$) shows a measurably different energy dependence with a sharper turn on and an earlier change to a linear response. Fits to data suggest a value of .28 eV or greater. This was confirmed by Ludeke and Bauer [33] who have published fits using values for $E_{1/2}$ of both .28eV and .54eV. Because the overall magnitude isn’t helpful in determining $E_{1/2}$ and energy dependence only gives a lower limit, we can’t really nail down reasonable values with data until the discussion of scattering BEEM in Chapter 3.
Figure 2.8: (a) The effects of increasing $E_{1/2}$ on the electron population tunneling from the tip to the sample at $V_t = -2$V. As $E_{1/2}$ increases the electron distribution becomes more smeared out. All of the curves are normalized to contain the same total number of carriers. (b) The effects changing $E_{1/2}$ has on the collector current signal level. The current was normalized so $E_{1/2}=0.14$ eV had a maximum value of 1pA. It is possible that by varying $E_{1/2}$ over a large range, the collector current can be changed by up to a factor of 2. This suggests that BEEM current can be tip dependent. The legend in (a) for $E_{1/2}$ values still applies.
Figure 2.9: The effects changing $E_{1/2}$ has on the collector current energy dependence. The collector currents for each value of $E_{1/2}$ was normalized to 1. Only the most focused electron distribution ($E_{1/2}=0.14$) is measurably different. No value of $E_{1/2}$ can shift the turn on voltage.

For now it may be useful to compare the Lang [36] formalism to the tunneling distribution developed by Young [37]. The expression is derived by Taylor expanding the one dimensional Fowler-Nordheim expression for tunneling from a tip through vacuum to a metal.

\[
I_t = I_0 e^{-2\kappa (e - eV_t)} \left\{ \frac{e^{-eV_t}}{1 + e^{\frac{eV_t}{k_B T}}} \right\} \tag{2.2}
\]

\[
\kappa = 0.51 \sqrt{\phi(eV) \text{Å}^{-1}} \tag{2.3}
\]

Here $I_0$ is a normalization constant, $\phi$ is the work function of the tip, and $F$ is the electric field at the tunneling point in $-V/\text{Å}$ (e- ejection). For tungsten $\phi = 4.7 eV$. $\kappa$ whose only physical component is $\phi$ describes how far the tip wave function extends into vacuum. The higher $\phi$, the less the wave function extends.
into vacuum. Comparing the coefficients in the exponents allows us to relate the
electric field density to the energy spread $E_{1/2}$ of Lang’s formula.

$$E_{1/2} = .319F$$

(2.4)

For $E_{1/2}$ in eV, $F$ is in $\text{-V/Å}$. This means that typical values for $E_{1/2}$, .28 to
.54 eV, correspond to fields of .9 to 1.6 V/Å respectively. Fields of this magnitude
are certainly possible at the end of an STM tip. For typical tunneling conditions
an average field of a few volts over 6-10 Å is standard, which allows for higher
fields at the sharp tip. One thing that comes out of this formula which may not be
intuitive is that the sharper the STM tip, the more spread out the energy of the
injected electrons. It would seem then that there is a compromise between having
a tip with good spatial resolution and poor energy resolution and visa versa. In
reality, once $E_{1/2}$ is greater than .28 eV, additional spreading does not affect the
energy dependence of the signal, so having a sharp tip with good spatial resolution
is not detrimental. Additionally, since the energy dependence is not measurably
different, Figure 2.8b suggests that changes in the tip state could account for
changes in the value of $I_c$ by up to a factor of 2. Of course such tip switches
correspond to changes in the shape of the tip and should therefore be detectable
in the STM image.

2.3 Variable temperature BEEM

2.3.1 The variable temperature advantage

One of the main limitations to Old BEEM is that it only operates at room tem-
perature (RT). For the most part, the relevant systems that are used in devices
must operate at RT and so therefore RT studies of these devices is both useful and
relevant. However there is still an advantage in being able to vary the tempera-
ture of the sample. Because the Au - Si Schottky barrier degrades after long time exposure to temperatures above 450 K, there is little to be gained by studying these systems at higher temperatures. At lower temperatures however, there are significant gains to be made by lowering the temperature of the sample. The most important aspect of lowering the sample temperature is the ability to use lower Schottky barriers, and thus extending the energy range that can be studied. The ZBR ($R_S(V = 0)$) of the Schottky barrier can be written as [29]

$$R_S(V = 0) = \frac{k_B e^{\frac{\Phi_b}{k_B T}}}{q A^* T^2}$$

(2.5)

Figure 2.10: The Schottky barrier height required to produce samples with a minimum ZBR of 2GΩ vs. measurement temperature.

Here $q$ is the electron charge, $\Phi_b$ the Schottky barrier, $A$ is the area of the device, $A^*$ is the modified Richardson constant which has a value of 110 A/(cm²K²)
for Si, \( k_B \) is Boltzmann’s constant and \( T \) is the temperature. Assuming a constant area of 100 \( \mu \text{m} \times 100 \mu \text{m} \), our standard device size and about the limit for how small we can go before creating a situation where aligning the tip to the sample is impossible, we can plot the Schottky barrier height which is required as a function of temperature for a minimum ZBR of 2 GΩ. This plot is shown in Figure 2.10, along with markers as to what metal - Si interface gives that Schottky barrier height. Metal - Si data was taken from Zse [38], except for Ti-Si which came from reference [39]. The advantage to cooling the sample is clear, readily available metals can be used to form lower Schottky barriers that would serve to extend the relevant energy range for BEEM measurements.

Other advantages for cooling the sample come from simply studying systems at different temperatures. The study of magnetics, insulating barrier heights and attenuation lengths at different temperatures can lend insight into the physics of each of those systems. Additionally, the behavior, both electrically and physically, of surface adsorbates (Chapter 4) at different temperatures can also aid in their identification. Both by measuring different properties versus temperature, and by simply reducing their mobility so definite areas of the surface can be studied for longer periods without alteration.

It is worth pointing out here that although it is useful to cool the sample, there is very little to be gained by cooling the tip. Figure 2.11 demonstrates this point. In Figure 2.11a the electron distributions for a tip at 300mK and at RT are plotted. As one would expect the Fermi function limits the population of electrons at energies higher than \( eV_t \). The 300 mK tip has a sharply focused distribution with an exponential tail. Conversely the tip at RT shows a more rounded peak with electrons populating energies above \( eV_t \). \( E_{1/2} = 0.28 \text{eV} \) for both tips. It would seem that the very sharp peak in the cooler sample would produce sharper IVs,
Figure 2.11: The effects of temperature on the tunneling distribution (a) and the $I_c$ vs. $V_t$ curves (b) corresponding to the tunnel distributions in (a). Since the major features of the tunnel distribution are determined by energy, not temperature, there is no improvement in the energy resolution of BEEM by operating at lower temperatures.
however Figure 2.10b shows that the temperature of the tip is irrelevant to the collected BEEM signal.

2.3.2 The two system advantage

The obvious advantages to having a variable temperature (VT) system made the decision to obtain one easy. Because old BEEM would have been impossible to retro-fit with a cryo system, and it would be imprudent to alter a well functioning instrument anyway, by the fall of 2000 the decision was made to add an additional BEEM instrument to the laboratory in D7 Clark. Once the funding was secured, the decision had to made between purchasing a system or making a new one from scratch. Building a system was not considered a primary option since old BEEM took years to complete. Certainly we could have learned from previous experiences but implementing the VT would have required a lot more engineering than simply duplicating old BEEM. If a suitable VT system could be purchased that would be the desired route. In the fall of 2000 no company made VT BEEM systems. Only two companies, Omicron and RHK Technologies, made VT UHV STM systems. Since BEEM is an extension of a STM, it seemed possible to have the appropriate BEEM electronics outfitted to the existing STM platforms. Omicron could deliver an STM/BEEM system but would not yield on two important design requirements.

The first was that the STM was to be made of non-magnetic material. This was to prevent magnetostriction effects when an external magnetic field was applied. This problem exists in old BEEM due to the fact that the head is made of super invar. While it is possible to scan with old BEEM under a magnetic field, it is simple enough to avoid the same problem. The second, and more important requirement, was that the instrument needed to take samples of the identical size (7mm x 7mm die) as old BEEM. There are several advantages in having two machines which can look at the same exact samples. For one thing, identical samples
should yield identical results. Therefore the calibration of the two machines can be checked with respect to one another. While an obvious statement, this would be impossible without compatible systems. Secondly, the same sample fabrication and transportation system could be used in conjunction with both instruments. This enables a single UHV environment where samples can be fabricated and moved from one machine to the other without breaking vacuum. Additionally the tooling is made simpler since a single system of tools can handle the load for both instruments. Since RHK was willing and able to meet our specifications, new BEEM would be a modified version of the RHK VT400 UHV STM.

2.3.3 Integrating the RHK VT400

Because of RHK’s ability to adapt their system to handle our current samples, no modifications to old BEEM would be needed. This enabled the new floor plan of D7 to take shape while data was still being taken on the old system. Figure 2.12 shows a layout of the old (a) and new (b) floor plan. The original layout included old BEEM and a x-ray photoemission spectroscopy (XPS) system as measurement stations and a fabrication chamber (prep I) with six thermal evaporation sources. The new layout involved moving the ESCA XPS to another part of the room where it would no longer be in mechanical contact with the two BEEM systems and the two fabrication chambers (prep I and prep II). In-situ transfers are still possible from the either prep chambers to ESCA through a portable turbo pumping station. New BEEM and a second prep chamber (prep II) would be added to the east side of the load lock in a mirror image configuration to old BEEM and prep I.

As the new configuration unfolded, prep II and new BEEM were assembled together but not connected to the existing, and working, part of the system. Once everything was ready to go the two were connected and the ability to transfer samples in UHV from either fabrication chamber to either microscope was realized.
Figure 2.12: The old configuration (a) and the new configuration (b) for the laboratory in D7 Clark Hall. In order to achieve a two instrument, fully in-situ configuration, the new fabrication chamber (prep II) and microscope (new BEEM) replaced the ESCA system. The expanded BEEM setup contains nine evaporation sources and 2 sputter sources along with oxidation and nitridation capabilities. Total UHV transfers from one microscope to the other are possible. Vacuum transfers can still be made to the ESCA XPS system by mating a vacuum pumping station to the center load lock.
The only modification to the existing chambers (old BEEM and Prep I) was the spatula and spring clip [29] sample transfer system was replaced by forks which moved pucks around. A drawing of the basic puck is shown in Figure 2.13. The change was made because the RHK system only accepts pucks with the dimensions shown in Figure 2.13b. Therefore a fork - puck system had to be implemented in the load lock and Prep II. In order to make the entire system compatible, forks were installed in Prep II and old BEEM. While special RHK pucks are used in new BEEM, pucks with spring clips attached are used everywhere else. This enables the original sample holder and mask system [29] to be used in the fabrication of samples, the function of the wobble stick in old BEEM to remain unchanged, and the ability to transfer throughout the system. Additionally the finicky spring clips where no longer fixed in the chamber and were readily taken out of vacuum so repairing them does not require a vent.

2.3.4 Additional fabrication capacity

In the original configuration of the laboratory in D7 (Figure 2.12A) the sole fabrication chamber was Prep I. Prep I has the capacity for six thermal sources, and one spare 6-inch flange that could potentially be used for a sputter source. While it seems that ability to evaporate six different kinds of thin films would be enough, there is always tremendous benefit in adding growth capacity. While it is obvious that additional sources can be used to test the effects of new elements or alloys, there is also a great advantage in using additional sources as backups to existing ones. This increases throughput by eliminating the need to vent if a source runs out. Since new BEEM would need a staging area in UHV to take samples from the fabrication pucks and place them on the scan pucks, an additional chamber between the load lock and new BEEM was a necessity. It was obvious from the
Figure 2.13: A drawing of the UHV transfer pucks (a) and the cross sectional dimensions (b) used in the BEEM system. Pucks can moved anywhere in the chambers and are highly adaptable. As long as the base is made in this geometry, any type of attachments can be added to the top.

beginning that this chamber could double as both a staging area and a new growth system.

A drawing of prep II is shown in Figure 2.14. Since the needs of the experiment, and use of the chamber could change over time, the concept behind designing Prep II was to achieve maximum adaptability and scalability. This was accomplished by fitting ten 10-inch flanges on the two ends of the chamber. The 10-inch flange was chosen over smaller sizes because bigger pumps could be attached, bigger gate valves could be used to allow full wafer processing (3” and possibly 4” with a load lock re-design), and we already possessed several thousand dollars worth of 10-inch
Figure 2.14: A drawing of prep II. Scalability and symmetry were paramount in the chamber design. The right hand side of the chamber is dedicated to sample growth. There are 3 e-gun sources, with the room for 3 k-cell sources on the bottom flange. Two sputter guns are mounted on the center of the chamber across from the nitrogen cracker. The left side of the chamber is reserved for sample staging.
cluster flanges that could be used to add attachments to the chamber. Eight 6-inch ports circle the center of the chamber. Originally these ports were to allow the addition of sputter guns to the chamber, but they have done more than that. Finally, on the surface area of the chamber which was not occupied by ten or six inch ports, a dozen 2.75-inch ports were added to serve as housings for gauges, a Ti-sub pump and other support instrumentation. As of fall 2003, to the western most 10-inch flange is attached to the load lock via a gate valve. A turbo pump and ion pump are attached to the top and bottom western flanges respectively. The staging area for new BEEM samples and tips occupy the remaining two flanges on that side. Attached to the bottom flange on the eastern side is an evaporation flange with three E-guns currently installed and the capacity for three additional k-cell sources. The rest of the eastern flanges are used for transfer arms and viewports. A nitrogen cracker has been installed on one of the center 6-inch ports. This allows for atomic nitrogen to be injected into the chamber to allow the growth of nitrides. Two sputter guns have also been added to the center ring of 6-inch ports. This brings the grand total number of working sources in the system to eleven with room to grow.

2.4 Summary

I have always found it fascinating that such a large amount of overhead is required to study things which are so small. It is quite remarkable that the large vacuum chambers and all of their parts house the smallest of tips to study layers of atoms at the nanometer scale. However, as you have read in this chapter, it is all a necessary part of running controlled experiments. When done properly, BEEM is an unmatched tool for spatial resolution of ballistic transport in thin films. However to achieve this, there are certain experimental concerns that need to be
understood and dealt with. In this chapter I have laid out the overall experimental setup(s) which were used to properly execute BEEM experiments. While most of the data that I took personally came from old BEEM, the additional capacity of new BEEM and prep II are in their infancy of utility. The scalability, flexibility and capacity of both the new and old system will prove to be a powerful tool for research.
CHAPTER 3
Ballistic Electron Scattering

3.1 Introduction

In a typical BEEM experiment, such as those described in this thesis, an n-type semiconductor substrate is used as the collector. In order to be measured as a collector current, carriers must travel through the bulk of the semiconductor to the BEEM pre-amps. This condition limits the carriers that are collected to electrons. Holes would recombine quickly in the substrate. So, as mentioned earlier, typical scanning conditions for BEEM use a negative tip bias to inject electrons into the base. These hot electrons can then be collected. Using a positive tip bias injects electrons into the tip, and therefore holes into the base. In order to collect these holes directly one needs to use a p-type semiconductor. This hole collecting BEEM or h-BEEM was demonstrated by Bell et al. [40] and serves as a good tool for direct measurement of the valance band Schottky barrier height. However the use of a p-type semiconductor is not the only way to record BEEM current with a positive tip bias. In the case of n-type substrates, injected holes can scatter and form a population of hot electrons that can then be collected. As you might expect this scattered BEEM (sBEEM) has a substantially lower signal level than a standard BEEM measurement. An example of sBEEM is shown in Figure 3.1 for 130 Å of Au evaporated on two different n-type substrates, GaAs and Si. While it may be difficult to see in the GaAs data, both the GaAs and the Si data show a ratio of direct to scattered (RDS) signal of about 20:1 at $|V_t|=1.8V$. The energy
dependance of such a simple system has been explained by Bell et al. [40] as a single free electron scattering event. Neidermann et al. [41] investigated the problem for PtSi and found results that agreed with Bell. In both experiments an RDS of 10:1 for Si(100) was measured. Additionally, both investigations have encountered two major problems with this theory. The first is explaining the correct magnitude of the signal, which Bell et al. calculated to be 10 times less than what they actually measured. The second is the energy dependence at bias voltages above 1.5 eV.

![Figure 3.1: Positive and negative tip I\textsubscript{c} vs. V\textsubscript{t} for 130 Å Au on n-type Si(111) (dashed line) and n-type GaAs (solid line). The ratio of BEEM to scattered BEEM (sBEEM) is 20:1 at |V\textsubscript{t}|=1.8V. Since the n-type substrates can only collect electrons, the sBEEM signal is the result of holes scattering to electrons.](image)

As the amount of scattering in a thin film increases, and the magnitude of I\textsubscript{c} decreases, the effects of sBEEM become more and more important. As we will see in the later chapters that deal with oxides, the very small signal levels that are measured warrant a proper understanding of the scattered signals. In this chapter I will explore the scattering mechanism described by Bell et al. and the effects it has on the distribution of electrons and holes after one or more scattering events.
Once these electron distributions are known it is straightforward to calculate $I_c$.

3.2 Ballistic scattering mechanism

3.2.1 Auger like scattering

There are several ways in which scattering can either create or alter the BEEM spectra. In pure sBEEM (positive tip bias), an injected distribution of holes scatters to an electron population. If the electron population has some constituents with sufficient energy, they can contribute to the collector current. When a negative tip bias is applied, scattering can effect the signal by taking an injected electron distribution and scattering it down to a distribution of holes as well as a distribution of electrons with lower energy. In this case, the new electron distribution can still have constituents with sufficient energy to overcome the Schottky barrier.

In order to calculate what these distributions will look like, we must consider the behavior of a single set of carriers involved in the scattering process.

Figure 3.2a shows the case of a positive tip bias (sBEEM) scattering event. An electron is injected into the tip, and conversely a hole with energy and momentum $(E_0, k_0)$ is injected into the base. An electron whose energy is greater than $E_0$ and less than the Fermi energy, can scatter, lose energy and fill this hole state. This will leave a hole state with energy and momentum $(E_1, k_1)$ at an energy above $E_0$. Energy conservation demands that for any electron that fills the hole state, another electron will gain energy and be excited above the Fermi energy. This will also leave a vacant hole state with energy and momentum $(E_2, k_2)$ and create an electron with energy and momentum $(E, k)$. It is these electrons which can be collected if $E$ is greater than $\Phi_b$. This type of scattering is analogous to the Auger process in which an empty core state is filled by an electron with greater energy and consequently ejects an electron whose energy can be measured thereby
Figure 3.2: (a) The Auger-like scattering process for the case of hole injection into the base (positive tip bias). A hot hole injected into the base \((E_0, k_0)\) can scatter down to the Fermi level \((E_1, k_1)\). The energy lost in the process is used to excite an electron hole pair \((E, k_2)\) and \((E_2, k_2)\) respectively. If the electron created in the process \((E, k)\) has energy greater than \(\Phi_B\), it can be collected and recorded as BEEM signal. (b) The similar process for the case of electron injection (negative tip bias). In this case a hot electron injected into the base \((E_0, k_0)\) can scatter down to the Fermi level \((E_1, k_1)\). The energy lost in the process can excite an electron hole pair \((E_2, k_2)\) and \((E, k)\) respectively. One or both of the final state electrons \((E_1, k_1)\) and \(E_2, k_2)\) can be collected if their respective energies are greater than \(\Phi_B\).
revealing the energy difference of the final and initial states.

An identical process can occur for the case of an injected electron (Figure 3.2b). Here an injected electron with energy and momentum \((E_0, k_0)\) can lose energy and scatter down to an electron with energy and momentum \((E_1, k_1)\). Again, energy conservation demands that an electron from below the Fermi energy is excited with the same gain in energy that was lost by the incident electron. This excited electron has energy and momentum \((E_2, k_2)\) and leaves a hole below the Fermi energy with energy and momentum \((E, k)\). It is useful now to introduce a naming convention. Instead of referring to carriers as 'electrons with energy \(E\)' or 'holes with energy \(E_2\)', I will simply write them as 'E electrons' or 'E holes'. So, in the case of a negative tip bias, the \(E_1\) and \(E_2\) electrons contribute to the scattering signal so long as their energy exceeds the Schottky barrier. In reality the signal will be a convolution of the injected distribution with the \(E_1\) and \(E_2\) electrons.

The initial distribution of injected electrons and holes was worked out in the last chapter. Therefore, if the relationship between in the incident carriers (\(E_0\) electrons or holes, depending on the situation) and the final carriers that are to be collected (\(E\) electrons in sBEEM, or \(E_1\) and \(E_2\) electrons in the case of negative tip) is known, the distribution of collected carriers can be worked out and the BEEM spectra can be calculated. In order to have a concrete example, I will work out the relationship between injected holes and collected electrons as shown in Figure 3.2a.

Conservation of energy in this scattering event demands

\[
E_0 - E_1 = E_2 - E
\]

Likewise, momentum conservation demands
The vector diagram for equation 3.2 is shown in Figure 3.3. Here the circle represents the fermi surface. This will be useful to consider when we integrate over all available states. From these two relationships we can invoke Fermi’s golden rule [42] to determine the rate, \( R(k) \), at which \( E \) electrons are generated.

\[
\mathbf{k}_0 - \mathbf{k}_1 = \mathbf{k}_2 - \mathbf{k}
\]

(3.2)

\[ R(k) = \frac{2\pi}{\hbar} \sum_{k_1, k_2, E_1, E_2 < E_f} |M|^2 \delta(E_0 + E - E_1 - E_2) \delta_{k_0 + \mathbf{k} - k_1 - k_2} \]

(3.3)

In this equation \( M \) is a matrix element that depends on momentum transfer \( \mathbf{q} = \mathbf{k}_0 - \mathbf{k}_1 \). Bell et al. note that for an unscreened free electron Coulomb interaction \( M \propto 1/\mathbf{q} \), but also note that metallic screening takes away this singularity. Following the arguments in [43] the relationship can be written as \( M \propto 1/(\mathbf{q}^2 - k_f^2)^{1/2} \) where the Fermi momentum, \( k_f \), is generally much greater than \( \mathbf{q} \). Therefore \( M \) can be treated as a constant. Equation 3.3 can be worked out in the following manner \(^1\). First we can rewrite the momentum part of the delta function.

\(^1\)The details of the math here were worked out with the help of P.W. Brouwer
\[ \delta_{k_0+k-k_1-k_2} = \delta(\text{solid angle}) \frac{1}{|k+k_0|} \delta(|k+k_0|^2 - |k_1+k_2|^2) \]  

(3.4)

Defining \( \phi = \) the angle between \( k_1 \) and \( k_2 \), \( \theta = \) the angle between \( k \) and \( k_0 \) and invoking the law of cosines, equation 3.4 becomes

\[ \delta_{k_0+k-k_1-k_2} = \frac{\delta(\text{solid angle})}{|k+k_0|} \delta(k^2 + k_0^2 + 2kk_0 \cos \theta - k_1^2 - k_2^2 - 2k_1k_2 \cos \phi) \]  

(3.5)

The conservation of energy term in equation 3.3 allows us to write \( k^2 + k_0^2 = k_1^2 + k_2^2 \) which simplifies the expression.

\[ \delta_{k_0+k-k_1-k_2} = \frac{\delta(\text{solid angle})}{|k+k_0| \cdot |k_1| \cdot |k_2|} \delta(\cos \phi - \frac{kk_0}{k_1k_2} \cos \theta) \]  

(3.6)

The solid angle term in the equations above is not something that needs to be calculated since it will not be energy dependent. This constant term can be combined with all other constants outside the summation. Then, writing the sum as an integral we have

\[ R(k) = \text{Const.} \int_{k_0^2}^{k_2^2} \frac{dk_1^2}{|k+k_0|} \int_{k_3^2}^{k_1^2} dk_2^2 \delta(k_0^2 + k^2 - k_1^2 - k_2^2) \times \int_{-1}^{1} d \cos \phi \delta(\cos \phi - \frac{kk_0}{k_1k_2} \cos \theta) \]  

(3.7)

The integral over \( d \cos \phi \) is trivial since the coefficients in front of the \( \cos \theta \) term are all magnitudes and therefore positive. Likewise, the integral over \( dk_2^2 \) is simply one so long as the condition of \( k_1^2 < k_2^2 \) and \( k_1^2 > k_0^2 + k_2^2 - k_1^2 \) is met This allows us to re-write the limits for the integral over \( dk_1^2 \)

\[ R(k) = \text{Const.} \frac{1}{|k+k_0|} \int_{k^2+k_0^2-k_1^2}^{k_2^2} dk_1^2 \]  

(3.8)
Defining $\alpha$ as the angle between $\mathbf{k}$ and $\mathbf{k}_0$ the integral can be evaluated, the law of cosines can be employed and the expression can be written in terms of energies

$$R(\mathbf{k}) = \text{Const.} \frac{2E_f - E - E_0}{\sqrt{E_0 + E + 2\cos \alpha \sqrt{EE_0}}} \quad (3.9)$$

It may seem a little sloppy to simply pile all of the constant terms together, however that constant term includes two terms which have not been calculated, the matrix element $M$ and the solid angle contribution to the $\delta$ function in equation 3.6. Calculating these two terms are beyond the scope of this thesis. Equation 3.9 is similar to the expression derived by Bell et al. [44] for the similar process shown in Figure 3.2b. Their result for the rate of hole production was

$$R(\mathbf{k}) = \text{Const.} \frac{E + E_0 - 2E_f}{\sqrt{E_0 + E + 2\cos \alpha \sqrt{EE_0}}} \quad (3.10)$$

We will continue sticking to the case of Figure 3.2a and use equation 3.9 for $R(\mathbf{k})$. In order to calculate the distribution of electrons generated by hole injection we must determine the branching ratio, $R_b = \hbar R(\mathbf{k})/\Gamma_{\text{ee}}$. Here $\Gamma_{\text{ee}}$ is the lifetime of a given electron which is dominated by electron - electron scattering. Of course the lifetime of an electron is related to rate at which they scatter, which is also related to the rate at which they are generated since the carriers in question are all created by scattering. $\Gamma_{\text{ee}}$ is found by integrating the scattering rate over all k-space.

$$\Gamma_{\text{ee}} = \hbar \int_{E_f}^{2E_f - E_0} \frac{d^3k}{(2\pi)^3} R(\mathbf{k}) \quad (3.11)$$

Here the limits are given in energy as the integral in k-space is easier to solve in energy space after the angular terms are dealt with. Doing this, it is straightforward to show that
$$\Gamma_{ee} = \text{Const.}(E_0 - E_f)^2 \quad (3.12)$$

As you might suspect, this is also the expression for $\Gamma_{ee}$ if equation 3.10 is used instead of equation 3.9 for the scattering rate. Bell et al. [44] calculate the branching ratio’s effect on the collector current by integrating over all available k-space and including the term directly into their expression for $I_c$. I feel it is more useful to put the branching ratio into a form that will allow us to directly operate on the injected distributions of both the holes and the electrons. To do this we can simply integrate the branching ratio over all $\alpha$ and leave the energy terms. Doing this allows the branching ratio for the scattering of injected holes to electrons to be written as

$$\text{BR}_{h\rightarrow e} = \text{Const.} \frac{2E_f - E - E_0}{(E_0 - E_f)^2} \quad (3.13)$$

In the case of injected electrons which can scatter to other collectable distributions (Figure 3.2b), the branching ratio can be calculated in the same manner as equation 3.13. The final result is

$$\text{BR}_{e\rightarrow e} = \text{Const.} \frac{E_0 - E_1}{(E_0 - E_f)^2} \quad (3.14)$$

Equations 3.13 and 3.14 are general results, but simplify further under our convention of $E_f = 0$ for the sample. With these two equations all that is needed is a little bookkeeping and the distribution of electrons and holes can be tracked for an arbitrary number of scattering events. For a hole of injected energy $E_0$ the energy, $E$, of the electron generated has a minimum value of 0 and a maximum value of $-E_0$. This is shown in Figure 3.4. In order to determine the population of electrons at a given energy $E$, the contribution from all holes with energies less than $-E$ must be summed.
Figure 3.4: A reproduction of Figure 3.2a with the intermediate steps removed. Electrons which are excited during the scattering process are allowed to have any energy between the Fermi energy of the base (E=0) and -E₀ as indicated by the shaded area below the electron. When calculating the population of electrons at a given energy E, the contribution from all holes with energies less than -E must be summed.

3.3 Effects of scattering

3.3.1 Scattering and the electron distribution

I will continue the discussion of scattering by again considering the condition shown in Figure 3.2a, namely injected holes under conditions of positive tip that scatter to electrons. Because the tunnel distribution is highly focused around the Fermi level of the electron source, in this case the base, the population of holes will be highly concentrated near the Fermi level of the sample. Figure 3.5 shows the case of injected holes (solid line) for a tip bias of +2V and an E₁/₂ of .28 eV. Because scattering will reduce the population of carriers at higher absolute energies (as measured from the Fermi Energy), there are two effects working against collecting
electrons. The first is simply the high concentration of holes with energy > \(-\Phi_B\), and the second is the effect of scattering. The final result of the latter effect is shown in Figure 3.5. Here the dashed line represents the effect of applying equation 3.13 to the solid line in Figure 3.5. It is clear that the population of electrons with \(\varepsilon > \Phi_B\) is less than the number of holes with \(\varepsilon < -\Phi_B\), and both are clearly less than the number of electrons with \(\varepsilon > \Phi_B\) that would be injected with a tip bias of -2V (see Figure 2.8a). The magnitude of \(I_c\) that results from each of these conditions will be discussed in the next section.

![Figure 3.5](image)

**Figure 3.5:** The injected hole distribution (solid line) for a tip bias of 2V and \(E_{1/2} = 0.28\) eV. Applying equation 3.13 to this distribution gives the electron distribution shown by the dashed line. The scattered distribution contains many more carriers near the Fermi level than the injected distribution. In order to show the presence of carriers with energies above the Schottky barrier, the x axis needs to be changed (Inset).

The second type of scattering which can alter BEEM spectra is when an injected electron population is scattered down in energy (Figure 3.2b). Figure 3.6 shows the effect of applying equation 3.14 to an electron distribution injected from
a tip biased at -2V with a value of $E_{1/2} = 0.28$ eV. It is perhaps more obvious to see in this case, rather than the last one, that the effect of scattering is to shift the carrier populations closer to Fermi level. As was the case before the population of electrons with $\varepsilon > \Phi_B$ is much less for the scattered electrons than it is for the injected electrons. Furthermore, the electrons are assumed to scatter isotropically, where as the injected beam is highly focused, thus creating a large disparity in the number of electrons that are collected from each distribution. In the next section the relative $I_c$ signal levels resulting from each scattering process will be compared, however the real situation is not so simple. For one thing, Figure 3.6 assumes that every electron scatters exactly once. This is something that is impossible in a simple mean free path picture where the $I_c$ is proportional to $e^{-t/\lambda}$ where $\lambda$ is the mean free path and $t$ is the film thickness. This is because if $t = \lambda$, about a third ($e^{-1}$) of the electrons don’t scatter and the signal collected would be a mixture of both the injected and scattered signals. The fact that the injected distribution is focused at a higher energy means that even though the injected distribution has been reduced to a third of its original value, it will still contribute more to $I_c$ than the scattered distribution. If the film thickness is $2\lambda$ then only 14% of the initial injected beam (IIB) remains, however keeping track of the scattered electrons quickly becomes more difficult. About 63% of the original scattered distribution (40% of IIB) will also scatter again, however 63% of what remained of the injected beam (23% of IIB) will scatter for the first time and replenish some of the lost scattered electrons. The bottom line is that after 2 mean free paths, 14% of IIB remain unscattered, 46% of the electrons have scattered once and 40% have scattered twice.
Figure 3.6: The injected electron distribution (solid line) for a tip bias of -2V and $E_{1/2} = 0.28$ eV. Applying equation 3.14 to this distribution gives the resulting electron distribution shown by the dashed line. As was the case in Figure 3.4, the effect of scattering is to increase the carrier population near the Fermi energy, and decrease the number of high energy hot electrons.

In order to write down what the total electron distribution is for $t = n\lambda$ seems like simply a matter of bookkeeping. It is. However there is one caveat that must be dealt with before we can start simulating the total distribution for an arbitrary number of mean free paths. The caveat is that every time electrons scatter down to other electrons, a hole population is created, likewise, when holes scatter up to electrons they also leave a population of holes whose energy approaches the Fermi energy. So it is a matter of bookkeeping, however after one scattering event, one must keep track of the electron and hole population applying equation 3.13 when switching carriers and 3.14 when scattering down to like carriers. Specifically consider the case where electrons scatter down to other electrons (Figure 3.2b), the resulting distribution (Figure 3.6) is also accompanied by a distribution of holes created in the scattering process. Both the electron and hole populations are capable of scattering again, creating new populations of each. Figure 3.7 shows this
process for an injected electron beam and two scattering events. As one might expect, the more scattering that happens, the more the two distributions mirror each other. Eventually all that is left of the hot carriers will be large populations of electrons and holes near the Fermi level where they are now able to relax by phonon scattering.

Figure 3.7: On the left is the injected electron distribution for a tip bias of -2V. If every electron scatters, the resulting electron distribution is shown with the solid line and the resulting hole distribution is shown with the dashed line. Each of these distributions which were created after one scattering event can scatter into a new distribution of holes and electrons. The electron distribution shown for two events is the sum of applying equation 3.14 to the electron distribution after one event, and equation 3.13 to the hole distribution after one event. The hole distribution after two events is calculated in a similar fashion.

One note about Figure 3.7 is that each distribution assumes all of the carriers from the previous distribution scatter. While this is useful for seeing the effects of scattering, the total electron distribution will be a convolution of many distributions. It turns out that there is a way to write down an expression for an electron distribution after an arbitrary number of mean free paths that takes into account the distributions that contribute and properly weights them.
To begin, let $y_k(\varepsilon)$ represent the distribution of electrons as a function of energy above the fermi energy (i.e. the solid lines in Figure 3.7 show $y_0(\varepsilon), y_1(\varepsilon)$, and $y_2(\varepsilon)$). Calculating $y_k(\varepsilon)$ follows the bookkeeping rules described earlier for keeping track of electron and hole populations and properly applying equations 3.13 and 3.14. The total electron distribution $Y(\varepsilon)$, for a film of thickness $t=n\lambda$ can then be written as

$$Y(\varepsilon) = \frac{y_n(\varepsilon)}{2}(1 - e^{-1})^n + \left(\frac{n}{n-1}\right)\frac{y_{n-1}(\varepsilon)}{2}(1 - e^{-1})^{n-1}e^{-1}$$

$$+ \left(\frac{n}{n-2}\right)\frac{y_{n-2}(\varepsilon)}{2}(1 - e^{-1})^{n-2}e^{-2} + \ldots + y_0e^{-n} \quad (3.15)$$

The scattered distributions ($y_k(\varepsilon), k \neq 0$ are all divided by a factor of two. This is done because eq. 3.13 and 3.14 assume isotropic scattering of the electrons. Hence, half the electrons are lost since they are moving away from the Schottky barrier. The coefficients for each of the terms are simply the binomial expansion coefficients ($\binom{n}{k}$). Figure 3.8 shows the results of applying equation 3.15 for different values of $n$. After $n=4$ the distributions look very similar and have the characteristic of scattered distributions, namely few high energy electrons and many more electrons near the Fermi energy. However, proper treatment of the initial distribution results in the focus near $V_t$ remaining even after the beam has travelled 3 mean free paths. In the next section we will see what this means to the BEEM spectra, but one can certainly anticipate that it can only result in higher signal levels and an energy dependance that resembles direct BEEM spectra rather than the sBEEM spectra seen in Figure 3.1.

It should be stated here that for an initial injection of holes, equation 3.15
Figure 3.8: Figure 3.7 shows what happens to an injected electron distribution if all the carriers scatter. In reality, not every carrier will scatter. If one assumes $e^{-1}$ electrons scatter after one event (for example one mean free path), then the actual distribution will be a convolution of distributions resulting from a different number of scattering events. The proper bookkeeping is explained in equation 3.15. Shown above is the result of applying equation 3.15 for different values of $n$.

can also be used. However if one assumes holes have the same mean free path as electrons, every mean free path the holes travel through, $1 - e^{-1}$ of what remains from the original injected hole distribution scatters up to electrons for the first time. Again, it is all a matter of bookkeeping and one must take care to apply equation 3.15 appropriately.

By now we have established a proper and complete description of scattering due to attenuation in a free electron metal. This will turn out to be a very important thing to consider when thinking about low signal level BEEM spectra, as we will see in the discussion of alumina spectra. There are still a couple of components missing from the theory that are important to keep in mind. First of all, everything assumes we are dealing with a free electron metal, this is not reality when talking about ferromagnets or even the noble metals. Secondly, the formulas above do not
deal with interfacial scattering. This type of scattering is significant at interfaces like Cu - Co [34] where it can reduce the ballistic current by an order of magnitude. These effects and others may alter the distribution of electrons in both energy and momentum in ways not described here. However it is likely that all types of scattering will act upon the injected distribution in a similar manner to what has been described above. Specifically the focus of electrons at higher energy will be lost in lieu of a larger population of electrons near the Fermi energy which are undetectable by BEEM.

3.3.2 Scattering and the BEEM signal

In their description of BEEM spectra, both Ludeke-Bauer [33] and Kaiser-Bell [28] derive analytical expressions for $I_c(V)$. This is certainly useful when considering contributions from an injected source that is also described by an analytical expression. However for the scattering distributions that are determined by numerically evaluating equations 3.13 - 3.15, it is impossible to write down an analytical term. In this thesis we will find it useful to calculate $I_c$ by considering what happens when an arbitrary distribution encounters the Schottky barrier. Since our derivations of equations 3.13 and 3.14 assume isotropic scattering, it is more appropriate to calculate BEEM spectra in the Ludeke - Bauer framework because it assumes isotropic scattering at the base - collector interface. In reality both theories describe the BEEM spectra well and could be employed. The term from the Ludeke-Bauer theory that is needed here is the collection efficiency of the semiconductor - metal interface which, using our coordinates reduces to

$$\frac{\varepsilon - \Phi_B}{E_f + \varepsilon}$$

(3.16)

It may seem like we can set $E_f = 0$ and further simplify this expression, how-
ever that is not accurate. The expression is derived by taking the ratio of the free electron density of states for Si and Au \(^2\). Since a value of \(E_f\) is needed we use 5.5 eV which is the value for Au.

Figure 3.9: The scaled \(I_c\) vs. \(V_t\) curves calculated using the injected electron distribution shown in Figure 3.6 (dashed line) and the scattered electron distribution shown in Figure 3.5 (solid line). Notice the apparent late turn on and increased curvature at low bias for the positive tip signal.

It is now a straightforward task to generate theoretical \(I_c\) vs. \(V_t\) curves for BEEM. For each value of \(V_t\) an injected electron distribution is generated. We keep the direct signal or have it scatter. If \(V_t\) is positive, a distribution of electrons can also be generated as described above. In either case we take a distribution of electrons and apply equation 3.16 for each value of \(\varepsilon\) greater than \(\Phi_B\) and sum the result. Using an arbitrary scale factor, \(R\), which is the same for every point, \(I_c\) vs. \(V_t\) can be calculated for an infinite combination of scattering possibilities.\(^3\) Using

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\(^2\)For a complete description of how the Ludeke - Bauer formalism is applied see McNabb [45]

\(^3\)Here the actual current level is based on a number of things besides simply \(V_t\). Interfacial
this method to calculate $I_c$ vs. $V_t$ will prove to be useful and adaptable to a wide variety of systems.

To begin with, let us consider the case of positive tip bias (Figure 3.2a). In order to generate $I_c$ vs. $V_t$ curves we follow the method described above for the electron distribution shown in Figure 3.5. One point worth mentioning is that after a single scattering event under these circumstances, the electron distribution is already heavily weighted with lower energy electrons. Therefore, including more scattering or properly applying equation 3.15 to these electrons won’t substantially change the energy dependence as the distribution will continue to gain lower energy electrons. This is in contrast to applying formula 3.15 to an injected distribution originating from a negative tip bias where scattering does have an impact since it serves to shift the focus of electrons away from higher energies while creating lower energy electrons. Figure 3.9 shows the calculated curves for sBEEM (solid line) and an unscattered BEEM signal (dashed line). The two curves have been scaled so they have an arbitrary maximum value of 1 pA/nA. The noticeable difference in the energy dependence is that the sBEEM signal has a more gradual onset or turn-on. Bell et al. [43] show that this turn on has a $(eV_t - \Phi_B)^4$ dependence at the turn-on rather than the $(eV_t - \Phi_B)^2$ seen in the BEEM signal. Both curves then become linear at high bias, however while in theory the BEEM signal continues as a straight line indefinitely $^4$, the sBEEM signal will begin roll off. Figure 3.10 shows the sBEEM signal from Figure 3.9 extended to 3V. As you can see, the calculated signal begins to roll off dramatically beyond 2V. The physical picture behind this can be understood by considering the injected hole distribution in Figure 3.5. Since a majority of the carriers are already near the Fermi level, bringing

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scattering, elastic scattering, inelastic scattering, momentum scattering, impurities, tip conditions... the list goes on. While Ludeke-Bauer[33], Kaiser-Bell[28], and Neidermann [41] all try to correctly predict what these values should be, none have succeeded. Instead, the use of an overall scale factor allows one to concentrate on the energy dependence.

$^4$As stated in chapter 2, there is a practical maximum to the magnitude of $V_t$ of any sign
the tip bias to higher and higher values only extends the tail of the distribution. This means that increasing the tip bias does not add substantially more carriers which contribute to the collector current. This is in contrast to negative tip bias where the electron distribution is focused near $V_t$.

![Graph]

Figure 3.10: The calculated $I_c$ vs. $V_t$ taken out to a high positive bias. Because the initial hole distribution is focused near the Fermi level, with only a small tail at high bias, increasing the tip bias does not significantly increase the number of high energy carriers. The result of this is the roll-off shown in the figure. However, this effect is not observed and is one of the problems with the Kaiser-Bell [43] model for scattering.

Measurements done with positive tip bias agree well with the theoretical predictions for the turn on region. The model is used to fit positive tip data for a simple 130 Å Au on Si sample in Figure 3.11 a (data shown in circles). Using a value for $E_{1/2} = 0.28$ eV the turn on region is well explained by the data. The only free parameter used in this fit was an overall scale factor. However the free electron scattering theory breaks down at higher bias. Figure 3.11b shows the best fit to
Figure 3.11: The calculated $I_c$ vs. $V_t$ (line) and the data for 130 Å of Au on Si. The theory and the data agree near the threshold (a), but diverge at higher bias (b).
the same sample taken out to higher bias, again allowing the scale factor to be the only free parameter. There are two major areas where the theory breaks down. The first area is in the overall size of the reverse signal. Our results show a ratio of BEEM to sBEEM of 20:1 at $+/- 2$ V. The results originally obtained by Bell et al. [43] show a ratio of BEEM to sBEEM of 10:1 at $+/- 2$ V. The theory predicts a ratio of 100:1. Neidermann et al. [41] were also unsuccessful in predicting the absolute magnitude of $I_c$ in of their PtSi thin films. Calculating the magnitude of this signal won’t be attempted in this thesis, however this observation indicates that the scattering mechanism is much more efficient than predicted by free electron theory. This could be because the process is universally more efficient (i.e. more electrons scatter than predicted), or the process more efficiently scatters hot holes to hot electrons (i.e. the scattering matrix elements are energy dependent). Both of these explanations would decrease the ratio of BEEM to sBEEM. The second area where the theory breaks down is in the inability to fit the data at higher bias. The data shown in Figure 3.11b shows a linear region that grows much faster that the theory predicts and no sign of the roll off predicted in Figure 3.10.

One way to see what might be happening in the Au/Si system is to check the Bell-Kaiser theory with an actual free electron metal. The only realistic free electron metal that can be used is Al. Ideally one would like to grow Al directly on Si so it could be compared with the Au/Si system. This turned out to be experimentally impossible. Al/Si Schottky barriers were poor, virtually Ohmic, which caused signal to noise issues that could not be solved by simply cooling the sample. Fortunately Al on GaAs(100) formed a good Schottky barrier which is well fit to the Ludeke-Bauer theory using a barrier height of 1.07 eV. This kept the measurement instrument limited. The results are shown in Figure 3.12. Figure
Figure 3.12: Positive and negative tip $I_c$ vs. $V_t$ for 150 Å of Al on GaAs (a). The ratio of BEEM to sBEEM is 94:1 at +/- 2V, which is close to what Kaiser and Bell [43] predict for a free electron metal. (b) The energy dependence predicted by the model (solid line) also more closely matches the data (open circles). Al is a free electron metal and unlike Au, has no d-states.
3.12a shows both the positive and negative tip data for 150 Å Al on GaAs. The first striking observation is that the ratio of negative tip to positive tip is 94:1 at +/- 2V which is very close to what is predicted by the free electron picture. In order to test the energy dependence fits were done to the positive tip data. The fits and a close up of the data is shown in Figure 3.12b. While the theory agrees well with the data, it is clear that the signal to noise ratio does not allow the energy dependence to be tested as rigorously as one would like.

Thus, while we may not have a clear insight yet as to the disagreement in the energy dependence of the Au data, the Al/GaAs sample clearly shows that the Auger like scattering process is the primary source of the sBEEM signal. The data suggests that higher scattering rate in the Au system (and hence higher sBEEM signal) is due to some contribution from d-state scattering which is not present in the Al.

As for the energy dependence disagreement between the free electron theory and the Au data, there are a few possible explanations. The two major issues that we will address are: 1. The value of $E_{1/2}$ is much too small; 2. The DOS of the metal that we inject into must be taken into account since the surface we inject into contains both extended states and surface states. Both of these states can scatter into a collected signal, however only the former contributes substantially to the negative tip signal.

To address point No. 1, it is easy to see why using a larger value of $E_{1/2}$ would help the free electron theory more accurately describe the data. A beam that was spread out more would produce a higher population of electrons above the Schottky barrier after the scattering process. This would not only create a larger signal, but delay the roll off effect. Figure 3.13a shows the results of fitting the data allowing for 2 free parameters: the overall scale factor and $E_{1/2}$. The fit is a
perfect match to the data, but with a value for $E_{1/2}$ of $5.5 \times 10^{10}$ eV. Using equation 2.4 this translates to an effective field of $17 \times 10^{10}$ V/Å at the end of the tip. This field is roughly eleven orders of magnitude greater than what one would expect a normal material to withstand. Clearly increasing $E_{1/2}$ brings the theory closer to the actual results, but fields this high are not physically justifiable. Ludeke and Bauer [33] claim that a value of .54 eV is at the high end of what is is reasonable according to their fits. Keep in mind however that Figure 2.9 showed that once $E_{1/2}$ is increased beyond .5 eV there is no difference in the negative tip spectra that Ludeke and Bauer would have used to test their theory. Unfortunately without a good way to directly measure $E_{1/2}$, it will remain a debatable number. It cannot be a free parameter in the fits since it will explode beyond reason, and certainly cannot be the single reason why the theory breaks down.

In order to address the second possibility, we must first measure the DOS of the Au surface we are tunneling into. Fortunately an STM provides us a way of measuring the exact density of states that we are tunneling into. Scanning tunneling spectroscopy (STS) is performed by measuring the tunnel current vs. tip bias for a fixed tip sample distance. This is performed by demanding a specific tunnel current (usually 1 nA) at a specific tip bias and then turning off the feedback during the data collection, then re-establishing that specific tunnel current before the next measurement. Once the $I_t$ vs. $V_t$ is obtained the total density of states can be calculated, or at least approximated, by using the following from Chen [37]

$$\text{DOS} \propto \frac{dI_t/dV_t}{I_t/V_t}$$

(3.17)

The DOS data obtained from a 250 Å Au on Si film is shown in Figure 3.14. The Lang tunneling theory [36] uses a constant DOS to determine the electron distributions shown before. While this may be fine near the Fermi level, it is clear from
Figure 3.13: The result of fitting the 130 Å of Au on Si data (open circles) using the Kaiser-Bell model (solid line) with two free parameters, and overall scale factor and $E_{1/2}$. The fit agrees reasonably well with the data but the value of $E_{1/2}$ was $5.5 \times 10^{10}$ eV which corresponds to a physically un-reasonable field of $17 \times 10^{10}$ V/Å.
Figure 3.14 that the total DOS begins to increase at higher biases. These states can be either surface states or extended states, the STS measurements cannot distinguish between the two. However both types of states can be initial states for the scattering process described above. In order to account for these new states, the tunneling distribution (equation 2.1) was used but the populations were weighted by the DOS of states shown in Figure 3.14. The resulting electron distribution is shown as the solid line in Figure 3.15. Here a value of \( E_{1/2} = 0.29 \) eV was used and the tip bias is 2V. The dashed line shows the result of using equation 2.1 without the weighting. Both tunneling distributions have been properly normalized so the sum total of carriers is the same. While the difference in the two distributions seems subtle, the effects on the sBEEM signal is significant. The results of using the weighted distributions to generate sBEEM spectra is shown in Figure 3.16. The data is shown in circles and the solid is the theory. Two free parameters were used in this fit, an overall scale factor and \( E_{1/2} \). The fit shows exceptional agreement with the data in all aspects for a value of \( E_{1/2} = 0.29 \) eV. This value of \( E_{1/2} \) is quite reasonable as it falls within the range proposed by Ludeke and Bauer [33] and corresponds to an acceptable electric field of 0.9 V/Å at the tip. The data and theory in the turn on region as well as the high bias (\( V_t > 1V \)) region are perfectly matched. There is no sign of roll off and unlike Figure 3.11b the curvature is identical.

Using the DOS weighting technique does more than just allow us to fit sBEEM data. Perhaps most importantly the proper explanation allows us to retain the key physics from the free electron picture, namely the effects of Auger like scattering. It also gives insight into the role of surface states. Clearly we can conclude that they play a significant part in the tunneling current, but we can also state that they are capable of being the initial state in the scattering process described above.
Figure 3.14: The density of states for 130 Å of Au on Si(111) as measured by scanning tunneling spectroscopy (STS).

Figure 3.15: The injected hole distribution as calculated using the Lang theory [36] (dashed line) and the corrected distribution (solid line) calculated by weighting the Lang distribution with the measured DOS for a Au surface (Data from Figure 3.14) for a tip bias of 2V. Both distributions have been normalized so the total number of carriers is the same. The corrected distribution has a higher population of injected carriers near $V_t$ which results in a higher sBEEM signal.
One point worth mentioning here is that the contribution of surface states to the tunneling current may also help explain the roll off effect sometimes observed in negative tip bias spectra. Since the surface states can only contribute to a scattered signal, which is always much less than an unscattered signal, tunneling into a higher percentage of surface states will result in a suppression of the direct BEEM signal.

![Graph](image)

**Figure 3.16:** $I_c$ vs. $V_t$ data (open circles) from a 130 Å of Au on Si(111) and the corresponding one parameter (scale factor only) fit (solid line) using the corrected injected hole distribution.

### 3.3.3 Effects of multiple scattering

If we wish to include the effects of scattering discussed above on the overall BEEM signal, then equation 3.15 allows us to properly account for an injected electron distribution after an arbitrary number of scattering events. As mentioned in the
last section, one can also take into account these multiple scattering events for an initial injected hole distribution. The only caveat to the latter case is that scattering both giveth and taketh away to the sBEEM signal. Scattering is needed to generate electrons from the initial holes, but too much scattering and the signal disappears. Assuming electrons and holes have the same attenuation length, and that the scattering occurs as carriers transport through the bulk of the material, the result of multiple scattering is a thickness vs. current plot that deviates from a simple exponential decay. Figure 3.17a shows the effects of scattering on collector current for positive (solid) and negative (dashed) tips. The signal level is calculated at +/- 2V. The dotted line shows a simple exponential decay and all curves have been normalized to a maximum signal level of 1 which occurs at the non-physical thickness of 0. For the most part, proper bookkeeping reveals that a negative tip signal deviates only slightly from a simple exponential dependence. The only problem that would arise in calculating attenuation lengths from negative tip data using a simple exponential decay is that $\lambda$ would be 1.08 times larger than its actual value. The positive tip case decays much more slowly than both the simple exponential and the negative tip cases. For thicknesses between 1-6 $\lambda$ the decay is essentially exponential, but using a simple exponential fit to determine attenuation length would result in a $\lambda$ that was 1.3 times the actual value. Of course it is clear that after this region the shape of the curve is much more complicated than an exponential decay. While the magnitude of the signal is continuously decreasing with thickness, the thickness dependence changes. One consequence of having the positive tip signal decay more slowly than the negative tip signal is that if the initial positive tip signal is smaller, some amount of scattering will result in equal signal strengths.
Figure 3.17: (a) The calculated signal for $I_c$ as a function of scattering events for a tip bias of -2V (dashed line), and +2V (solid line). The negative tip signal decays more slowly than a simple exponential decay (dotted line). The positive tip signal decays much more slowly than the negative tip signal indicating that eventually the two signals will be equal (this depends on initial conditions). The positive tip, negative tip and simple exponential decay signals were normalized to a maximum value of 1. (b) The resulting BEEM and sBEEM $I_c$ vs. $V_t$ curves. The forward and reverse signals were both normalized to a maximum value of 1. Increased scattering has no effect on the positive tip signal. For the negative tip signal, a slight increase in the curvature after the turn-on is the only significant feature. No amount of electron - electron scattering can shift the turn-on for either tip bias.
The energy dependence of multiple scattering effects is shown in Figure 3.17b. The forward and reverse signals have both been normalized to a maximum value of 1 for all of the plots. The most noticeable feature is that the energy dependence of the positive tip signal remains effectively unchanged upon additional scattering events. Neither the turn on nor the curvature shows substantial change. This is not surprising when one considers the shape of the electron distribution after one scattering event from injected holes (Figure 3.5). After this initial scattering event the distribution is already heavily weighted with low energy electrons. Additional scattering will result in nearly identical distribution, only with less high energy constituents. This is in contrast to the negative tip situation where several scattering events (Figure 3.8) are required to remove the initial focus of electrons around $\varepsilon = eV_t$. As the process unfolds, not only does the magnitude of the signal change, but so does the energy dependence. The turn on of the signal, however, does not change.

3.4 Summary

In later discussions of oxide transport, proper understanding of scattering effects is essential. Through BEEM and sBEEM measurements on simple systems we have verified that the free electron Auger like scattering process is the key factor in producing a sBEEM signal. Modifying the tunnel distribution through inclusion of DOS effects, the basic theory first developed by Kaiser and Bell can be used to achieve exacting fits to the experimental data. Additionally, this effect has been applied to both negative and positive tip measurements in order to determine the effect multiple scattering events has on the collector current. The result of multiple scattering is that the sBEEM signal decays more slowly than the BEEM signal, providing a means for the two signals to have similar magnitudes after sufficient
scattering events. Multiple scattering also effects the energy dependence of the BEEM signal to a small degree, but does virtually nothing to the sBEEM signal in that same regard. The turn on in both cases is unaffected by inclusion of multiple scattering terms. This allows us to interpret any change in the turn on to be a result of the sample’s fundamental electronic properties.
CHAPTER 4
Aluminum Oxide Surface Studies

4.1 Introduction

Much information about the electronic and physical structure of a material can be gained by combining both BEEM and common STM techniques such as STS. Therefore, a good place to begin is with alumina on the surface of the sample in question. In this chapter I will describe studies of the alumina surface, what can be learned from them and what artifacts need to be avoided. Information gained from these studies will help us start piecing together a picture of the detailed electronic properties of alumina.

4.2 Features of the alumina surface

We begin our discussion of the alumina surface by considering both BEEM and STM images of samples with an oxidized aluminum surface. Figure 4.1 shows simultaneously obtained STM (a) and BEEM (b) images of a Au 110 Å / Cu 12Å/ Co 12Å/ Al 8Å evaporated multilayer where the top Al layer was exposed to 20 mTorr of high purity (99.9985%) O₂ for 60 seconds. From this point forward, instead of quoting the pressure and time for a given oxygen exposure, only the total dose will be given. We have oxidized samples under a variety of pressure and time combinations and have found that total dose is the only important parameter. In these studies it is meaningful to quote the dose in units of mTorr · sec. Therefore,
Figure 4.1: Simultaneous STM (a) and BEEM (b) images of a Au 110 Å / Cu 12Å/ Co 12Å/ Al 8Å evaporated multilayer where the top Al layer was exposed to 20 mTorr of high purity (99.9985%) O₂ for 60 seconds. The arrows in both images point to identical spots on the sample indicating that areas which contain surface adsorbates (a) correspond to regions of low BEEM current (b). For these images, $I_t = 0.1\ nA$ and $V_t = -1.8V$. 
the sample in Figure 1 has a dose of 1200 mTorr · sec, or 1.2 Torr · sec \(^1\). We will learn in the next chapter that a dose of 30 mTorr · sec is the minimum dose required to form what we measure electrically as a fully formed oxide. Discussion of the dose and what is meant by a fully formed oxide will be the topic of Chapter 5. To continue, the images in Figure 4.1 are representative of samples with a complete Al layer (> 5 Å on a Co lead [46]) and a dose of this order of magnitude. The first striking feature about the alumina surface is that it is relatively rough. Over the 75 nm x 75 nm scan shown, there are peak to valley height changes of almost 3nm. This is about a factor of 5 higher roughness than one would measure in an all metallic sample or even a sample where a top lead was deposited over the alumina [46]. Additionally the surface is covered with numerous clusters which are measured as raised features in the height image. I will show later that these clusters are chemisorbed oxygen which stick to a fully formed oxide by absorbing electrons. In the BEEM image these clusters are associated with regions of attenuated current. An example of which is indicated with the arrow in Figure 4.1. Careful observation will reveal that there are some clusters which appear on the BEEM image, but can’t be seen in the STM image. This is simply a result of the color scale drowning out features. Clusters which appear in the bottom of valleys may still have an absolute height which renders as black on the color map.

As will be discussed later, cluster size and density are correlated with oxide thickness. However, the properties of these clusters are quite similar from sample to sample. Figure 4.2 shows STM (black) and BEEM (grey) line traces for two different samples. Figure 4.2a is data taken from a Au 110 Å / Cu 12 Å / Co 12 Å / Al 8 Å (0.3 mTorr · sec) sample. As you can see, in this case there are two well defined clusters roughly 5 nm wide. The cluster on the left is approximately

\(^1\)The Langmuir, L, is sometimes used to describe doses. One Langmuir is equivalent to a monolayer of gas hitting the surface of a metal and is approximately equal to a dose of 1 µTorr · sec.
Figure 4.2: Simultaneous STM (black) and BEEM (grey) scope traces of clusters on alumina for: Au 110 Å / Cu 12 Å / Co 12 Å / Al 8 Å (0.3 mTorr · sec) (a) and 110 Å / Cu 12 Å / Co 12 Å / Al 8 Å (lab air for one hour)(b). In thinner oxides (a), clusters appear on the surface as pancake shaped puddles of oxygen 2.5 - 7.5 Å tall (1-3 monolayers) and roughly 10 times as wide. These clusters always correspond to depression in the BEEM signal. On thicker oxides (b), the clusters have the same general shape, but cover a greater percentage of the surface. In these cases the peaks in the BEEM signals correspond to areas where the alumina is exposed.
5 Å tall, and the one on the right is about half that size corresponding to two and one monolayers of oxygen respectively. To within our ability to measure, clusters on every sample share these features. They are predominately pancake shaped puddles of oxygen 1-3 monolayers thick and about 10 times wider than they are tall. Likewise, the BEEM signals associated with the clusters show up as flat depressions directly correlated with raised areas in the STM image. Figure 4.2b contains data from a sample with a much thicker oxide (110 Å / Cu 12 Å / Co 12 Å / Al 8 Å lab air for one hour). This sample shows that the clusters are, on average, wider, taller and more closely packed. The cluster on the right hand side of the image is 3 monolayers tall and nearly 10nm wide. In this sample, instead of the clusters showing up as depressions in the BEEM trace, the bare alumina appears as bright spots since the surface is almost entirely covered. As you can see from these line traces, the clusters are easy to pick out when both the STM and the BEEM images are examined simultaneously.

This last observation brings us to an important point. The combination of BEEM and STM is much more powerful than either tool alone. This fact has proven to be invaluable in the study of the alumina surface. To illustrate this point consider the STM images in Figure 4.3. Figure 4.3a is an image taken by Kurnosikov et al. [47] at Eindhoven and shows the STM image of a plasma oxidized sputtered aluminum film. Figure 4.3b is a closeup of the sample shown in Figure 4.1 (originally published in ref. [48]). Both STM images show qualitatively the same features. Clusters, including the very unique features of half clusters which will be discussed later (circled in each image), cover both films. The difference in the size scale of each image can be attributed to the smaller sputtered grains versus the larger evaporated grains. While it is great that these two STM images of alumina appear qualitatively the same, looking at the STM images alone makes it
Figure 4.3: STM images of the alumina surface taken by our group (b) and Kurnosikov et al. [47] at Eindhoven (a). Both STM images show qualitatively the same features, including clusters and the very unique features of half clusters. The smaller grain size seen in (a) is most likely the result of sputtering versus our larger grains from evaporated Al.
difficult to determine exactly what those prominent features might be. As a result, Kurnosikov and his co-workers came up with a much different conclusion than we have as to the nature of the prominent cluster features, and therefore the electrical structure of the alumina surface. They concluded that these prominent features were regions of apparent height increase due to a local increase in the DOS. This interpretation of the data led them to conclude that these spots of increased DOS were places where the film was beginning to fail electrically and that they were in fact imaging the early stages of dielectric breakdown.

To see how the data could be interpreted in this fashion we need to consider what happens to the STM tip when it encounters surface features and regions of increased DOS. In a constant current feedback mode, the STM tip will withdraw when the tunnel current increases in order maintain the feedback conditions. This means that the recorded STM image will indicate a tip withdraw when the tip encounters a feature, the tunnel gap closes and $I_t$ increases. Because $I_t$ is exponentially dependant on the tunnel gap, this is usually the dominant effect and is the reason why STM images are often interpreted as topographic images. However, a local increase in the density of states will also result in increased $I_t$ and a tip withdraw. It is possible for these effects to appear as regions of apparent height on the surface. To illustrate this, Figure 4.4 shows what the STM image (b) looks like under the two different sample conditions (a). The upper sample in Figure 4.4a has an adsorbate while the lower sample has a small region of increased DOS. Since the STM line trace in Figure 4.4b is a recording of the tip height, both the upper and lower images appear qualitatively the same. While arguments can be made that the DOS effects could not result in such large amplitude apparent height variations, the bottom line is that the STM picture alone does not always allow for unambiguous interpretation. This is where the additional data obtained by
Figure 4.4: STM (b) and BEEM (c) line traces for the samples shown in (a). Under constant current feedback conditions a surface adsorbate (upper) and local region of increased DOS (lower) will result in a tip withdraw and qualitatively look identical. However a surface adsorbate will result in a decrease of BEEM signal, while an area of increased DOS will result in an increase in BEEM signal. The two techniques used together can more accurately determine the nature of features than either technique alone.
BEEM comes into play. From our discussion of scattering in the last chapter it is well established that any kind of scattering results in a greatly attenuated BEEM signal. A surface adsorbate (Figure 4.4a upper) would have an extra interface and therefore more scattering. Hence the BEEM signal for a surface adsorbate would appear as a current depression as shown in the upper line trace of Figure 4.4c. In contrast to that, a region of locally increased DOS would have better conductivity and therefore result in an increased BEEM signal as shown in the lower line trace of Figure 4.4c. Knowing both pieces of information allows us to clearly identify the clusters as surface adsorbates, where as the authors of reference [47] did not have the benefit of the BEEM measurements and were susceptible to mis-interpretation.

Figure 4.5: Scanning under constant current feedback conditions is possible through a thin insulator as long as the electron relaxation time is faster than the feedback system. The ability to scan with $I_t = 0.1 \text{ nA}$ but not with $I_t = 1 \text{ nA}$ indicates that the lifetime of electrons in oxides states is between 0.1 and 1 nsec.

By this time we have seen several images of the alumina surface. It is a reasonable question to ask how it is even possible to scan an insulator since $I_t$ needs to flow through a conductor. One possibility is that electrons tunnel inject directly into the conduction band of the oxide and flow into the base electrode. Another possibility is that electrons tunnel inject into localized states in the oxide and then relax to the base where it is easily collected. This process is sketched out in
Figure 4.5. In the first case it is straightforward why scanning is possible. The second case is only possible if the relaxation time is much faster than the STM feedback acquisition time. As mentioned earlier, feedback for both old and new BEEM takes place on the order of msec. Typical lifetimes for excited electrons in such a thin (< 2nm) insulator are on the order of nsec. Clearly the process of relaxing down to the Fermi surface is fast enough to allow feedback. It is possible to put a number on this lifetime by considering our typical scanning conditions ($I_t \approx 100$ pA and $V_t \approx -2$ V). For $I_t = 1$ nA, one electron arrives at the surface every $10^{-10}$ sec. That means for $I_t = 100$ pA, one electron arrives at the surface every nsec. Since we can scan with $I_t = 100$ pA we can conclude that the lifetime of electrons in oxide states is less than 1 nsec. Imaging can be done at virtually any voltage although scanning with a higher $I_t$ often damages the surface, presumably because of charging. Since a value of $I_t = 1$ nA will usually damage the surface, we can say that the lifetime of an electron in an oxide state is longer than 0.1 nsec. Of course, as one would expect, the thinner oxides (< 5 Å) can handle the higher tunnel currents, indicating the lifetimes in thin oxides are shorter than in the thicker oxides.

Since much about a material can be learned from surface studies, it is important to be able to distinguish the true surface from adsorbates. Then, once it has been established that the alumina surface contains these clusters it is possible to begin accurate characterization, not only of the surface below the clusters, but also of the clusters themselves.

4.3 Identification of the clusters

It may appear that these surface adsorbates are an external item that makes study of the oxide difficult. They do in fact make measurements a delicate operation,
but these clusters are an important part of the alumina system. Understanding the clusters will add insight into both the electronic structure of the alumina as well as the oxidation process itself.

4.3.1 Cluster mobility

The first clue that these clusters were attached to the surface, and not part of the surface itself, came when watching a series of scans one afternoon. Two consecutive images showed identical features with the sole difference of an added cluster in the second. Figure 4.6 shows these particular BEEM images taken from a Au 110 Å /Cu 12Å/ Co 12Å/ Al 8Å which was exposed to 0.3 mTorr·sec of oxygen. Both images were taken over the same location with \( I_t = 100 \) pA and \( V_t = -2.8 \) V. The image in 4.6a was taken 5 minutes before 4.6b. Because we are using BEEM images, clusters appear as black spots. Although we are not interested in absolute values of collector current at this point, it turns out looking at BEEM images makes it easier to identify and follow cluster behavior than looking at STM images. This is simply due to the fact that the contrast in current is much greater than the contrast in topography, especially since the alumina surface is rough. The white circle in Figure 4.6b shows a cluster that does not appear in Figure 4.6a. Because STM/BEEM are essentially static measurements, it would be impossible to determine if this cluster moved from another place on the surface, or simply formed in that spot. It is possible to conclude that these clusters are mobile in the sense that they can move around and/or form and disappear. Further inspection of the two images reveals several places where the clusters either formed, or disappeared. Some features indicate that the clusters formed, then disappeared during a few line traces (several seconds). These transforming features appear as partial clusters. There are two well defined half clusters circled in Figure 4.2a and 4.2b and a few partial clusters can be seen in Figure 4.6. These are easily identifiable
as features where one or both vertical edges are perfectly straight lines.

Figure 4.6: Two consecutive BEEM images of a Au 110 Å /Cu 12Å/ Co 12Å/ Al 8Å which was exposed to 0.3 mTorr · sec of oxygen. Both images were taken over the same location with \( I_t = 100 \) pA and \( V_t = -2.8 \) V. The image in (a) was taken 5 minutes before (b). The only difference in these images is the presence of a cluster in (b, white circle) which is not present in (a). This was the first evidence we had that these clusters are mobile.

While there is not hard and fast rule as to what the clusters do and don’t do, generally clusters tend to form under the tip. This is especially apparent when taking spectroscopy measurements. In these situations the tip is held at a fixed location and after a few minutes of taking IVs one is guaranteed to have a cluster appear eventually. This may be a result of the tip pumping energy into the system, the clusters requiring excess electrons in order to form, or the migration of negatively charged clusters to regions of high positive field on the surface\(^2\). To test the hypothesis that clusters migrate towards the tip (or form under it) the tip in these measurements has a large negative field so the surface just below the tip will have a large positive field.

\(^2\)The tip in these measurements has a large negative field so the surface just below the tip will have a large positive field.
following experiment was done. A 50nm x 25nm area was scanned on the sample shown in Figure 4.6 for several hours at $I_t = 100$ pA and $V_t = -2.8$ V. A wide image, 150nm x 150nm, was taken of the area before and after the concentrated scans. The results are shown in Figure 4.7 with (a) being the 'before' image and (b) being the 'after' image. The dashed box indicates the area where the concentrated scans took place. There is a clear accumulation of clusters under the area the tip was scanning, lending evidence to the claim that these clusters are in fact mobile surface adsorbates rather than areas of increased DOS. Both STS and BEEM spectroscopy can be employed to further understand the nature of these clusters. As discussed earlier, one major advantage a BEEM system has over other techniques is the ability to determine DOS and transport properties at a very specific location. Although this will prove to be quite valuable, great care must be taken when acquiring both STS and BEEM spectra. Charge build up and burning out the surface are some of the things which can happen, however the main problem is the mobility of clusters. While taking spectra over the bare alumina surface, clusters can appear under the tip during a measurement. On the same note, while taking spectra over a cluster it can disappear leaving the nature of what each curve measured undetermined. Although it is tedious, the one way to work around this intrinsic difficulty is to verify the nature of the surface with a line scan, take about a minute worth of data, then verify the nature of the surface again. This process can be repeated to obtain good statistics for signal averaging and the instant the surface changes the measurements can be stopped. The plots in Figure 4.8 were taken using this technique. 4.8a shows the DOS results taken over the alumina (solid) and a cluster (dashed). To begin with, the alumina has states to within .5 eV of the Fermi energy. Beyond this, signal to noise became to small to distinguish any features. Conversely, the cluster clearly shows no states below
Figure 4.7: The mobility of the clusters is demonstrated in these before and after BEEM images of a Si(111)/Au (11 nm)/Cu (1.2 nm)/Co (1.2 nm)/Al (0.8 nm) that was exposed to 0.3 mTorr·sec of high purity O$_2$. The image in (a) was taken with $I_t = 0.1$ nA and $V_t = -3.0$V and shows a uniform density of clusters. The image in (b) was taken at the identical location with the identical parameters as (a), but after scanning the 50 x 25 nm$^2$ area (inside the dashed box) for several hours, and shows the accumulation of clusters in the region where the STM was scanning.
1.5 eV above the Fermi energy. While it may not be obvious, the data in 4.8b agrees completely with this observation. Injection into the alumina (solid) results in a typical BEEM IV with a turn on at the Au/Si Schottky barrier of 0.81 eV. This metallic behavior is what one should expect since the oxygen exposure is 100 times lower than that required to create a full barrier [49]. The cluster performance is a little more interesting. The turn on appears at the same $-V_t = 0.81$ V as the solid line and it begins to look as if the two curves will follow each other. At $-V_t = 1.5$ V however the amplitude quickly dies off. We know from the images that the clusters must have a lower collector current at $-V_t \approx 2.0$ V since they appear as dark areas in the BEEM images. The roll off is explained by considering the condition of constant $I_t$ during BEEM spectroscopy. Initially, the tip cannot inject $I_t$ into the cluster because there are no states available (4.8a). Therefore $I_t$ must be delivered to the alumina below the cluster or directly to the Al underneath the oxide. This is why the two BEEM spectra appear identical below $-V_t = 1.5$ V. Once $-V_t > 1.5$ V the tip is able to inject into cluster states. The low value of $I_c$ at the cluster sites indicates that the states in the cluster are highly localized and do not extend into the alumina underneath. This is further verification that these clusters are indeed surface adsorbates. To identify the nature of these chemisorbed clusters we first consider the experimental conditions in which they appear. The density of clusters found on the surface increases with increasing oxygen exposure, as does the oxide thickness. While newly deposited, un-oxidized Al has no clusters, samples exposed to high oxygen doses or to the atmosphere show nearly complete coverage. Certainly in the latter case a number of gases could chemisorb onto the alumina surface, but in the cases where the clusters appear when dry oxygen is admitted into UHV chambers which have with a base pressure $< 3 \times 10^{-10}$ Torr, the reasonable choices are reduced to atomic and molecular oxygen. Finally, these
Figure 4.8: Spectroscopy data taken over a cluster (dashed) and the bare oxide surface (solid) for a Si(111)/Au (11 nm)/Cu (1.2 nm)/Co (1.2 nm)/Al (0.8nm) sample exposed to 0.3 mTorr·sec of high purity O₂. (a) shows the differential logarithmic conductivity (proportional to the density of states). (b) shows BEEM spectroscopy taken over the same locations.
surface clusters, while stable in UHV at 300 K, are also quite mobile, indicating that the binding energy of this chemisorbed oxygen is somewhat less than 1 eV.

An analytical scanning transmission electron microscopy study of oxygen contained in nanopores that have been formed in amorphous alumina tunnel-barrier layers by radiation damage[10], which locally reduces the oxide and diffuses the Al away from the electron beam, is helpful in identifying the absorbed species. Electron energy loss spectroscopy (EELS)[10, 50] has shown that this oxygen exhibits the spectrum seen previously in X-ray near-edge absorption measurements of the “superoxide” formed by chemisorbing oxygen onto alkali metal surfaces[51]. Here the superoxide consists of $O_2^−$ ionically bonded to the alkali surface. The EELS study of the oxygen in the nanopores in the radiation-damaged tunnel-barrier reveals that its lowest unoccupied electron level, the $\pi^*$ orbital, is located 1-2 eV above the Fermi level of the adjacent electrode. This strongly suggests that the adsorbed clusters which exhibit the STM and BEEM spectra shown in Fig. 4.8 are composed of $O_2^−$ with the negative charge indicating an overall negative charge of unknown magnitude, not exactly one extra electron.

4.3.2 $O_2^−$ Cluster Variation

The spectra in Figure 4.7 are typical of all clusters. However, even casual inspection of the images reveals quite a variation in the cluster sizes. It turns out that while the general behavior of the clusters are the same, the details of their spectra can be quite varied. Figure 4.9 shows DOS results taken over five different clusters on three different samples. All of the spectra show DOS that don’t begin until $-V_t > 1$ V. Some have states starting at $-V_t = 1.2$ V (open circles) while others don’t seem to turn on until almost 2V (short dash). There is no correlation between the properties of an individual cluster and its size, position on the underlying alumina, alumina thickness or the density in which clusters form around it. There
must, of course, be a reason the \( \text{O}_2 \) clusters behave differently. It is possible that clusters with different amounts of excess electrons have DOS turn ons at different values. The more free electrons present on the cluster, the harder it is to inject another. Of course if charge density plays a role into how hard it is to add an electron, both the excess charge and total cluster volume would be important. If one wanted to seriously study these oxygen cluster nanoparticles, their mobility would need to be decreased. Low temperature measurements would certainly be useful.

Figure 4.9: The DOS results from STS measurements taken over five different clusters from three different samples showing the variability in DOS turn-on. Some have states starting at \(-V_t = 1.2\) V (open circles) while others don’t seem to turn on until almost 2V (short dash).

Because the DOS turn on points vary from cluster to cluster, it is possible to observe cluster camouflaging at different voltages for different clusters. Cluster camouflaging occurs when one scans with \(-V_t\) lower than the DOS turn on point. Under these conditions the tip tunnels directly into the alumina surface and no cluster effect is seen in the BEEM image. Another way to think about this is to
look at Figure 4.8b. There is a point between $-V_t = 0$ and $-V_t \approx 1.3V$ where the alumina curve and the cluster curve appear nearly identical. In this region, scanning over the cluster would not produce contrast in the BEEM image. Hence, the cluster is camouflaged. Figure 4.10 shows an example of this for a different area on the same sample used for Figure 4.7. The images are shown in order of increasing $-V_t$ with values of 1.5 V, 1.8 V and 2.5 V for (a),(b) and (c) respectively. The white circle in 4.10b indicates a cluster that was camouflaged in 4.10b and the black circle indicates a cluster that was camouflaged in both (a) and (b). The surface images corresponding to (a),(b) and (c) look identical which indicates that these clusters did not spontaneously form. In addition, the order in which they were scanned was (b),(a),(c). This eliminates the possibility that the cluster in (b) formed after scanning (a). An image with $-V_t = 2.5 V$ was taken prior to the three images shown and looks identical to (c). All of the physics that explains cluster camouflaging is contained in Figure 4.8. The point of mentioning it here is to make the reader aware of these artifacts. Additionally, one could study camouflaging in a series of images to determine DOS turn ons for a large number of clusters which could be statistically analyzed. This would certainly be quicker to do for a large number of clusters than taking individual IVs.

4.4 Oxidation and clusters

By this point in the chapter the reader is well aware of the general appearance of alumina surfaces. But what role do these clusters play in the oxidation process and why do they adhere to the surface? To answer both of those questions let us consider the process of low temperature oxidation as described by Mott and Cabrera [52] and shown in Figure 4.11. Oxygen molecules ($O_2$) land on the aluminum surface (a). Since aluminum is a great reducer, and of course oxygen a great oxidizer,
Figure 4.10: Because the DOS for different clusters turns on at different voltages, clusters can appear hidden when the tip bias is less than the turn on energy. Above are three BEEM images from the same sample used in Figure 4.7. The tip bias for each image was -1.5 V, -1.8 V and -2.5 V for (a),(b) and (c) respectively. The white circle in 4.10b indicates a cluster that was camouflaged in 4.10b and the black circle indicates a cluster that was camouflaged in both (a) and (b). The order in which they were scanned was (b),(a),(c) which eliminates the possibility that the cluster in (b) formed after scanning (a).
the first monolayer of alumina quickly forms (b). The next O₂ molecules that land on the surface are also in search of electrons (c). However since the aluminum is already bonded, a new source of electrons must be found. In the Mott-Cabrera [52] model, electrons will tunnel to the oxygen molecule and fill all unoccupied states in order to raise the chemical potential of the molecule to the Fermi energy of the alumina. The presence of the now negatively charged molecules on the surface creates and electric field (d). The smaller, lighter aluminum atoms then diffuse through the alumina along this field (e). Once there is a fresh source of aluminum, more oxide can form (f). This process has several striking features. One feature is that since the electric field will be strongest where the oxide is thinner, the oxide grows more quickly in the thin spots. This will result in a relatively uniform oxide. A second feature about this model is that as the oxide gets thicker, the aluminum diffusion will drastically slow down and the oxidation rate will self limit between 15 Å and 20 Å [17]. It is this property of the oxidation process that will give us insight into the role of the clusters.

4.4.1 Cluster density and oxide thickness

To begin, consider the oxygen molecules landing on an inert surface such as gold, they would quickly obtain electrons to balance the Fermi levels as described above. Even though the oxygen molecules would now have an overall negative charge, a metal such as gold would quickly screen any such charge and there would be no net field to hold the molecules on. Eventually these molecules would desorb into the UHV surroundings leaving the surface bare, which is what is observed. In alumina the situation is very different. XPS studies have shown that the alumina formed in by room temperature thermal oxidation of deposited alumina has oxygen vacancies [53]. As with SiO₂, these vacancies will result in fixed positive charge in the oxide above the Fermi energy. When the oxygen molecule lands on the surface it has
Figure 4.11: The oxidation process of alumina. Oxygen molecules ($O_2$) land on the aluminum surface (a). The first monolayer of alumina quickly forms (b). The next $O_2$ molecules that land on the surface are also in search of electrons (c). The presence of the now negatively charged molecules on the surface creates an electric field (d). The smaller, lighter aluminum atoms then diffuse through the alumina along this field (e). Once there is a fresh source of aluminum, more oxide can form (f).
states below the Fermi level of the base. This will result in a flow of electrons from the metal, through the oxide and into the oxygen molecule until equilibrium is established [52]. Figure 4.12a shows the energy diagram for this process. The positive vacancy states and the negatively charged oxygen molecule now have a quasi ionic bond. The $\pi^*$ states measured by STS are shown above the Fermi level in the Figure 4.12a.

The thickness of the oxide will determine the amount of fixed charge per unit area, $\sigma$. Assuming the charge per unit volume of the oxide is constant, the thicker the oxide, the greater $\sigma$. Since the Coulomb repulsion of the negatively charged molecule will act to break it apart, and $\sigma$ will act to hold the cluster together, the thicker oxides should be able to support larger more closely packed clusters. Figure 4.12 (b) and (c) illustrate this point. The thinner oxide (b) has less fixed charge under the the cluster than the thicker oxide (c). Hence (c) can support a larger cluster than (b).

If the oxide is thin, one of two things can happen. Either the aluminum is still mobile through the oxide and the oxidation process continues, or all of the aluminum is used up and the alumina remains thin, limited by the initial source of aluminum. In this second case, even though the oxygen molecule absorbs an electron and leaves a hole vacancy in the alumina, electrons can tunnel into that vacancy from the metal electrode underneath. This would neutralize the quasi ionic bond effect and the oxygen molecules would be free to release into the vacuum environment. What is observed experimentally suggests that this is in fact the case.

Figure 4.13 contains BEEM data from an all metallic (a) sample and a sample with a very thin oxide (b). Figure 4.13a shows a 125nm x 125nm BEEM image of a Au 110 Å /Cu 12Å/ Co 12Å/ Al 4Å sample that has not been exposed to
Electrons from the metal will fill the available oxygen states to establish equilibrium.

States measured by STS

Fixed positive charge in the oxide from oxygen vacancies

Oxygen Molecule

Electrons from the metal will fill the available oxygen states to establish equilibrium

Figure 4.12: When an oxygen molecule lands on the surface of the oxide it will have empty states below the fermi energy [52](a). Electrons will flow from the metal, through the oxide and into the molecule until the chemical potential is at equilibrium (large arrow). Once at equilibrium, the molecule is negatively charged and will be attracted by the fixed positive charge in the oxide. For thin oxides (b), there is less charge per unit area (assuming uniform charge per unit volume) below a cluster than for thicker oxides (c). Hence the thicker oxides can support larger clusters since the fixed charge counteracts the tendency for the clusters to break apart due to Coulomb repulsion.
Figure 4.13: BEEM images of a Au 110 Å /Cu 12Å/ Co 12Å/ Al 4Å sample before (a) and after 1400 mTorr · sec exposure to oxygen. The image was taken with $I_t = 1\text{nA}$, and $V_t = -1.5\text{V}$. The background current in nearly identical in both images (1.1 pA (a), 1 pA (b)) and the oxidized film supports very few clusters. XPS measurements [53] indicate that although oxides this thin do now show the presence of clusters, a large percentage of the surface is covered by chemisorbed oxygen. This suggests that either the clusters are too small (laterally) to be resolved by BEEM or sufficiently thin that the STM tip tunnels directly to the sample underneath.
oxygen. The image was taken with $I_t = 1nA$, and $V_t = -1.5V$. The mean value of $I_c = 1.1\ pA$ and is shown on a black = 0, white = 3\ pA grey scale. Figure 4.13b shows the identical sample after a 1400 mTorr · sec exposure to oxygen. The scan parameters and grey scale are identical. The mean collector current of 1 pA is only slightly less than the non-oxidized case. While the dose is nearly identical to that received by the sample in Figure 4.1, there are far fewer clusters. For this thickness of alumina, 1400 mTorr · sec certainly would react with all the Al creating a layer of oxide between 6 and 7 Å. Although there are only a few clusters visible in the image, XPS studies [53] have shown that for oxides this thin, there is still a large amount of chemisorbed oxygen. This suggests that the model described in Figure 4.12 is valid and the thinner oxides support molecule clusters too small (laterally) to be resolved by BEEM or sufficiently thin that the STM tip tunnels directly to the sample underneath the oxide.

As for the effect of thicker oxides on cluster density, consider Figure 4.14 which contains 100nm x 50nm images from three samples with increasing oxide thicknesses. Each aluminum layer was deposited on a multilayer consisting of 110 Å /Cu 12Å/ Co 12Å. The top aluminum layer and dose are as follows. 7 Å - 0.3 mTorr · sec(a), 7 Å - 1200 mTorr ·sec (b), and 20 Å - $6.3 \times 10^5$Torr · sec (c). The dose in the last sample was achieved by exposing the sample to lab air for one hour. The images clearly show a trend from fewer small clusters, to larger more densely packed clusters as the oxide thickness increases. In 4.14c the surface is almost entirely covered and the bare spots of alumina seem to be the exception rather than the rule. In theory, one could make a series of samples where aluminum was thought to be the limiting factor (i.e. thin films with very high O$_2$ doses) as a calibration set. Then by comparing the cluster density of very thick

\[3\text{The thickness of the oxide is roughly 1.4 times the thickness of the aluminum film when all the aluminum is consumed [10].}\]
Figure 4.14: BEEM images for Al grown on 110 Å /Cu 12Å/ Co 12Å multilayers. The top aluminum layer and dose are as follows. 7 Å - 0.3 mTorr · sec (a), 7 Å - 1200 mTorr · sec (b), and 20 Å $6.3 \times 10^5$Torr · sec (c). The dose in the last sample was achieved by exposing the sample to lab air for one hour. The images clearly show a trend from fewer small clusters, to larger more densely packed clusters as the oxide thickness increases.
(4 nm or more) aluminum films exposed to varying amounts of O₂, a relationship between the oxide thickness and the dose could be made. In practice this would be a difficult task since the first few monolayers of oxide form nearly instantaneously and the very thick oxides are almost completely covered.

4.5 Summary

The examination of the alumina surface ended up providing a rich source of information not only about the electronic structure of the oxide, but also about the oxidation process itself. Through use of combined BEEM and STM, the alumina surface can be shown to contain a sea of O$_2^-$ clusters. The density of these clusters corresponds to the overall oxygen dose, and therefore oxide thickness. The thicker the oxide, the more clusters accumulate.

This observation allows us to see, as well as anyone can, the oxidation process at work. The Mott-Cabrera model of oxidation is supported by the accumulation of oxygen on the surface as the negatively charged molecules await reaction from Al ions buried below the oxide. The electric field formed between the two is sufficient to keep the clusters attached, but weak enough to allow them to move.

It may be possible to use the fact that cluster density is proportional to thickness to measure oxide growth vs. dose by comparing films with Al as the limiting reagent with films that have an infinite supply of Al and varying oxygen doses.
CHAPTER 5

Hot Electron Transport Through Alumina

5.1 Introduction

In the last chapter I reported the results from directly probing the surface of the alumina. These measurements helped us learn about the formation of the oxide, the interaction of oxygen and alumina at the interface, and DOS information of the alumina itself. This chapter will investigate the transport of ballistic current through alumina tunnel junction structures.

Much of the data and qualitative results of the buried tunnel junction BEEM experiments performed by myself, W.H. Rippard and R.A. Buhrman are already published elsewhere [34, 18]. Instead of repeating what has already been written, I will simply summarize the major results of these studies before talking in detail about the ballistic transport properties of alumina in MTJ structures.

To begin with, all of the MTJs that have been studied in this thesis are of the following form, Si(111) / Au / Cu / Co / alumina / Co / Cu. The Au (usually 75 Å) on Si forms the Schottky barrier that is required to do BEEM. The bottom Cu layer, usually 12 Å, is used to seed the Co growth. The top Cu layer (30 Å) has two purposes. The first was insure there was no spin polarized tunneling. In theory tunneling directly into the Co should polarize the tunnel current, although no effect of this sort has ever been detected in our system. The primary importance of the top Cu layer is to slow the effects of aging on the sample. Samples with Co on top tend to have shorter shelf life in the chamber due to the more reactive
nature of Co vs. Cu. For all practical purposes Cu coated samples live indefinitely in UHV. The Co / alumina / Co trilayer is the magnetic tunnel junction that we want to probe. Because Co has a relatively short attenuation length \([49]\), 12 Å of Co is used above and below the alumina. Finally the alumina is made the same way as in earlier chapters. Typically 5-20 Å of Al is deposited and then oxidized with a known amount of oxygen.

![Graph](image)

**Figure 5.1:** \(I_c\) vs. \(V_t\) for MTJ geometry samples with Al thicknesses ranging from 5 to 11 Å and doses spanning 7 orders of magnitude. The thickness of the oxide is clearly different in all of these samples but in each case, likely falling somewhere between 7 to 16 Å. The lack of thickness dependence is a clear sign that we are not measuring tunneling.

The major results of the previous studies were that only 5 Å of deposited Al and 30 mTorr · sec of \(O_2\) exposure were needed to form a spatially complete tunnel junction. Any sample with an Al layer thicker than 5 Å and an oxygen dose greater than 30 mTorr · sec would result in BEEM images and spectra that were nearly identical. Figure 5.1 shows a summary of BEEM spectra taken for samples with
Al thicknesses ranging from 5 to 11 Å and doses spanning 7 orders of magnitude. As already mentioned before, the thickness of the oxide is clearly different in all of these samples but in each case most likely falls somewhere between 7 and 16 Å. The IVs shown in Figure 5.1 don’t only apply to the samples shown, but to any buried alumina sample which had the same metallic multilayers, regardless of Al thickness and oxygen dose. This signature signal earned the name ubiquitous BEEM or simply uBEEM.

The lack of thickness dependence lead us to several major conclusions about our results. One was that the uBEEM signal was clearly not due to tunneling in any way shape or form since that would be highly thickness dependent. A second result was that the attenuation length of electrons transporting through the alumina was longer than could be measured by the range of thickness we probed (5-20 Å). Lastly, fits to a two barrier model indicated that there was a threshold at 1.2 eV which was interpreted as the lowest energy point of the alumina conduction band above the Fermi energy of the sample.

In February of 2003 data was taken that threatened this last result. In this chapter I will discuss the old interpretation, the new data and put together, as complete as possible, a picture of what causes the uBEEM signal.

5.2 The original picture of transport in alumina

5.2.1 The two barrier model

All of the original work described above was done by probing the system with injected electrons (negative tip bias). In doing so the original picture of the alumina system was modelled as a two barrier system. The energy diagram of which is shown in Figure 5.2. This simple model treats the alumina as an insulator with a conduction band $\Phi_{\text{oc}}$ above the Fermi energy of the metal leads that surround it.
Assuming free electron behavior in all of the materials, the transmission through the alumina and into the collector can be written as follows:

\[
\frac{\varepsilon - \Phi_{\text{ox}}}{E_f + \varepsilon} \cdot \frac{\varepsilon - \Phi_{\text{B}}}{E_f + \varepsilon}
\]  (5.1)

Equation 5.1 can then be integrated from \( \Phi_{\text{ox}} \) to \( eV_t \) for every value of \( V_t > \Phi_{\text{ox}} \). Allowing \( \Phi_{\text{ox}} \) to be a free parameter produced excellent fits to the data. Figure 5.3 shows the two barrier fit (+) to a tunnel junction sample with a 6 Å deposited aluminum film exposed to 54 torr • sec of O₂. For comparison, data from an unoxidized sample is shown along with the single barrier Ludeke-Bauer Model (o) from equation 3.16. In the case of the alumina sample, \( \Phi_{\text{ox}} \) was found to be 1.2 V which is what we published [18, 54]. Treating the system as a simple free electron transport problem accomplished a few things. It explained the threshold at 1.2 V and correctly described the energy dependence. The former of these two is important since in Chapter 3 it was pointed out that no amount of elastic electron-
Figure 5.3: The two barrier fit (+) to a tunnel junction sample with a 6 Å deposited aluminum film exposed to 54 torr · sec of O₂. For comparison, data from an unoxidized sample is shown along with the single barrier Ludeke-Bauer Model (o) from equation 3.16. In the case of the alumina sample, Φox was found to be 1.2 eV.

electron scattering can change the apparent turn on voltage. However the simple free electron picture would predict that the ratio of BEEM to sBEEM signal should be the same as for a free electron metal. Therein lies the rub.

5.2.2 Breakdown of the two barrier model

In early 2003, it was pointed out to us by J.P. Pelz of Ohio State that the signal we observed, and the apparent 1.2 eV turn on could be due to photo induced BEEM. The Ohio State data was eventually published in ref. [55] and shows that photons can be created at the vacuum - metal interface by plasmon relaxation and these photons can generate a photo current in the Au-Si diode. The turn on then is due to the band gap of Si which is 1.1 eV, close to our measured turn on. Photon BEEM (pBEEM) would predict two things with regard to the uBEEM signal. The first is that the positive and negative BEEM signal should be much closer in
magnitude than BEEM and sBEEM. The second prediction is that changing the substrate should alter the signal. Specifically, using GaAs with a direct band gap of 1.5 eV should yield a substantially different energy dependence.

In order to check the nature of the uBEEM signal, a typical tunnel junction was grown with Co leads of 12 Å each, and a 10 Å Al layer exposed to 4.5 Torr sec of O₂. Positive and negative tip data was taken and the results are shown in Figure 5.4. The striking symmetry in the forward and reverse signal was instant proof that the simple two barrier model had failed.

Given the fact that photons had contributed to the data in ref [55], we began to test whether or not a photon contribution could be a possible source. One striking difference in the data reported by Heller and Pelz, and our uBEEM signals is that the pBEEM data was an order of magnitude lower in signal than uBEEM. The pBEEM signal level of 3 fA/nA at 1.5 V is consistent with the known efficiencies of the process involved[56, 38]. Additionally, photon production efficiencies and energy dependence should be highly tip dependent [56], which is not something we ever observed in the uBEEM signal.

The substrate dependence was checked by growing a Au 75 Å / Al 15 Å 14 Torr sec / Au 75 Å sample on GaAs (100). Both forward and negative tip data were taken and found to be symmetric, however in order to obtain better signal to noise, negative tip data was collected overnight and is shown in Figure 5.5. Although the energy dependence is slightly different than uBEEM, there is clearly signal below the 1.5 eV direct band gap of GaAs. The difference in shape between using a Si substrate and GaAs substrate can be explained by the different Schottky barrier values (0.9 eV for Au on GaAs). This is further proof that the uBEEM signal is produced by electron collection, not photon collection.
5.2.3 Ruling out bulk electron-electron scattering

From chapter 3 we know that the positive tip signal decays more slowly than the negative tip signal (Figure 3.17a) for electron-electron (e-e) scattering processes. Depending on initial conditions these signals may or may not intersect before signal to noise becomes too low. It seems reasonable then to include multiple elastic scattering events on the list of possible explanations for uBEEM.

However there is one major indicator that e-e scattering alone cannot be responsible for the uBEEM signal. One of the conclusions from Chapter 3 is that while scattering has a strong effect on signal level, it has only a minor effect on the energy dependence. This is only seen in the curvature of the negative tip $I_c$ vs. $V_t$. No amount of scattering can cause a shift in the turn on voltage for either tip bias. Since there is certainly a shift in the turn on voltage for both the forward
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Figure 5.5: $I_c$ vs. $V_t$ for a Au 75 Å / Al 15 Å 14 Torr · sec / Au 75 Å sample on GaAs (100). Forward and negative tip data were taken and found to be symmetric, however in order to obtain better signal to noise, negative tip data was collected overnight. The signal below the 1.5 eV direct band gap of GaAs is further proof that the uBEEM signal is produced by electron collection, not photon collection. This data was taken during a period when the old BEEM op-amp was incorrectly calibrated. The true data should be higher by roughly a factor of 2.

and reverse signal, bulk e-e scattering apparently cannot be used to explain the uBEEM signal.

5.3 The picture of alumina transport

5.3.1 Evolution of the sBEEM signal

We know from previous work (Figure 5.3) how the negative tip signal evolves from an unoxidized tunnel junction sample to one where the barrier is complete. Since no sBEEM measurements were made on such devices during the original studies, it is reasonable to study how the sBEEM signal evolves as the alumina begins to form.

Figure 5.6 shows the BEEM and sBEEM signal from an unoxidized MTJ mul-
tilayer. From the bottom up the metal layers are Au 85 Å / Cu 12 Å / Co 12 Å / Al 6 Å / Co 12 Å / Cu 30 Å. The BEEM signal is of course metallic, with the 0.8 V Schottky turn on. The sBEEM signal is however, uBEEM. The amplitude is just under an order of magnitude greater, but the energy dependence is identical. Figure 5.7 shows the two signals laid on top of each other. The scale for the metallic data (o) is on the left and the oxide data (x) is on the right. The two signals are surprisingly similar, each showing a very definite delay in the turn on voltage. It is difficult to conclude then, that the delayed turn on seen in both the BEEM and sBEEM measurements of MTJs is a result of any band structure properties of the oxide. Specifically the data in Figure 5.7 clearly indicates that overcoming a barrier height is not necessary to produce a delayed turn on as there are no barriers in the all metal samples.

5.3.2 Inelastic scattering and the sBEEM signal

We know that the sBEEM signal can only be generated by a scattering process, therefore we need to look for a scattering process that results in a shifted threshold. In a metallic sample, where there is no barrier, this can be achieved through a scattering process where energy is lost to something other than the electrons.

Up until this point, all of the scattering that we have dealt with has been e-e as per the Bell-Kaiser description of sBEEM [43]. However, consider the process shown in Figure 5.8. This figure is a reproduction of Figure 3.4 with the intermediate holes removed. If the scattering process involves an energy loss (L), then the final energy of the ejected electron cannot be greater than \( |E_0 - L| \) above the Fermi energy. One can anticipate that the loss of energy in a scattering process like this will certainly result in a shifted threshold. Of course, to quantitatively
Figure 5.6: $I_c$ vs. $V_t$ for a Au 85 Å / Cu 12 Å / Co 12 Å / Al 6 Å / Co 12 Å / Cu 30 Å. The BEEM signal is of course metallic, with the 0.8 V Schottky turn on. The sBEEM signal has a different magnitude but identical energy dependence to uBEEM indicating that the sBEEM signal does not evolve like the BEEM signal, and no barrier is required for the delayed turn-on. This data was taken during a period when the old BEEM op-amp was incorrectly calibrated. The true data should be higher by roughly a factor of 2.

work out the effects of energy loss we need to start from energy and momentum conservation and work out what the equivalent of equations 3.13 and 3.14 for an arbitrary amount of energy loss in the process. Doing so result in the following equations for the branching ratios:

$$BR_{h\rightarrow e} = \text{Const.} \frac{2E_f - E_0}{(E_0 - E_f)^2 - \frac{L^2}{2}}$$  \hspace{1cm} (5.2)

$$BR_{e\rightarrow e} = \text{Const.} \frac{E_0 - E - L}{(E_0 - E_f)^2 - \frac{L^2}{2}}$$  \hspace{1cm} (5.3)

Here, equations 5.2 and 5.3 are the energy loss versions of 3.13 and 3.14 respectively. As with the 3.13 and 3.14, these equations can be used for electron to hole scattering (5.2) and hole to hole scattering (5.3). Since all of these samples are made on Au/Si diodes, the Schottky barrier height is fixed to 0.8 eV. Therefore,
Figure 5.7: The positive bias signals from Figures 5.4 (x - right hand axis) and 5.6 (o - left hand axis) laid on top of each other. The energy dependence of the two signals are identical, each showing a very definite delay in the turn on voltage. The data labelled with an 'o' was taken during a period when the old BEEM op-amp was incorrectly calibrated. The true data should be higher by roughly a factor of 2.

The only fit parameters for the positive tip signal are the energy loss (L), and a scale factor. The results of fitting the sBEEM signal for the unoxidized MTJ multilayer is shown in Figure 5.9. The fits are quite good out to 2.5 V for an energy loss of 0.2 eV. For the negative tip data however, this energy loss during the scattering process must also occur if we assume that the electrons and holes behave the same way in a metal. Looking at the actual spectra in Figure 5.6 reveals that in fact there is no sign of a shifted threshold for negative tip bias. This should not be surprising though since it was shown in Chapter 3 that even if a small amount of the injected electron distributions remains after scattering, thus this will dominate the collector current in comparison to the contribution from the scattered electrons. We can now generate a complete model that is used for both the unoxidized samples and the fully oxidized MTJ structures.

For positive tip signals, a single inelastic scattering event is all that is needed.
Figure 5.8: A reproduction of Figure 3.4 with the intermediate holes removed. If the scattering process involves an energy loss (L), then the final energy of the ejected electron cannot be greater than $|E_0 - L|$ above the Fermi energy. This will cause a shift in the threshold.

Figure 5.9 shows the fit to the unoxidized MTJ multilayer, and Figure 5.7 suggests this will work fine for oxidized samples. For the negative tip signal, we use a single electron-electron scattering event with energy loss as described above, however some amount of the injected signal is allowed to leak through unscattered. The ballistic distribution ratio, $D_r$, is then defined as:

$$D_r = \frac{\text{Number of Unscattered Ballistic Electrons}}{\text{Number of Scattered Ballistic Electrons}} \quad (5.4)$$

The total electron distribution that is used in calculating the collector current using equation 3.16 is then described as (Distribution after one inelastic scattering event + $D_r \cdot$ Injected Distribution). Using this fitting formula, the dual polarity BEEM spectra can be fit at once with a single value of L. The results are shown in Figure 5.10. In this fit I have fixed the value of L to 0.21 eV which was what yielded the best fits when only the positive curves were used. The negative tip side then yields a value of $D_r = 6.2$. This means that for every electron in the collected distribution that has scattered, six electrons have not been scattered at
Figure 5.9: The best fit (solid line) to the positive tip data (circles) from Figure 5.6. using an inelastic scattering process. The fit used a fixed Schottky barrier of 0.8 eV and two free parameters, the energy loss and a scale factor. The energy loss for the hole to electron scattering process here was 0.2 eV. This data was taken during a period when the old BEEM op-amp was incorrectly calibrated. The true data should be higher by roughly a factor of 2.

all. Since the injected distribution always contributes electrons of higher energy which are collected more efficiently, it will always dominate the shape of the BEEM spectra until $D_r$ is substantially less than one. As we shall see, changes in energy dependence come when $D_r$ is varied by orders of magnitude. For metallic bases, any value of $D_r$ greater than one properly explains the data. As one would expect from a metallic base, completely ignoring the scattered signal ($D_r \rightarrow \infty$) will fit the data well however using values of $D_r$ below 1 will not. One thing to note is that a separate scale factor was used for the forward and reverse signal. As stated before, many of the constants involved in the scattering process have not been calculated (the solid angle contribution in equation 3.4 for example). This prevents us from extracting useful information from the pre-factors. Instead they are used to simply adjust the magnitude of the calculations to fit the data.
Figure 5.10: Using the energy loss of 0.21 ±1 eV determined from the data in Figure 5.9 and a fixed Schottky barrier of 0.8 eV, we can fit the entire positive and negative tip bias I<sub>c</sub> vs. V<sub>t</sub> for an unoxidized MTJ sample using three free parameters (+/- bias scale factors and the ballistic collection ratio, D<sub>r</sub>). For the negative tip data D<sub>r</sub> = 6.2. This data was taken during a period when the old BEEM op-amp was incorrectly calibrated. The true data should be higher by roughly a factor of 2. For a value of E<sub>1/2</sub> = 0.29 eV, the scale factors are 0.0030 and 0.4518 for negative and positive tip respectively.

This same fit function can now be applied to the uBEEM data of Figure 5.4. The comparison of theory and data for uBEEM is shown in Figure 5.11. Once again a value of L = 0.21 ±1 eV is obtained by fitting only the positive tip side. Then a value of D<sub>r</sub> = .0028 is obtained by fitting the entire dual IV. As before, a separate scale factor for both the positive and negative tip sides are used.

The value of D<sub>r</sub> = 0.0028 is quite revealing. It suggests that for every 1000 scattered electrons in the ballistic distribution, three electrons have gone through the alumina without scattering. It seems that with such a dominant contribution from the scattered electrons, D<sub>r</sub> could simply be set to 0. In fact, that is what is shown in Figure 5.12. In this fit to the data an energy loss of 0.21 eV is also used, but D<sub>r</sub> = 0. In this fit there is only the slightest discrepancy between the
Figure 5.11: Positive and negative bias $I_c$ vs. $V_t$ for a Si(111) / Au 85 Å / Cu 12 Å / Co 12 Å / Al 10 Å - 10 Torr · sec / Co 12 Å / Cu 30 Å. Using the same technique as for the unoxidized sample, the positive tip data alone was used to fit for an energy loss of 0.21 eV. Then the forward and reverse data was fit at the same time to determine $D_r$ which had a value of 0.0028. This means that for the samples with a thin alumina barrier, 3 electrons are collected which don’t scatter for every 1000 electrons that do. Calculations are the solid line and the circles are the data. For a value of $E_{1/2} = 0.29$ eV, the scale factors are .0291 and .1825 for negative and positive tip respectively.

data and the model when $V_t$ is in the range of -1.2 and -1.5 V. As stated before $D_r$ varies over orders of magnitude. For oxides, the data is well described when $D_r$ is between 0 and 0.01.

The results described above suggest that there is very little direct transport in the alumina. Instead, the collector current which is measured in alumina samples is the result of electrons which have undergone an inelastic scattering process. Initially, when the aluminum has no oxygen exposure, the signal can be thought of as a combination of both a ballistic (undisturbed initial injection) signal and the inelastic scattered signal. As the alumina forms, the ballistic contribution is slowly turned off until effectively no electrons make it through the oxide without scattering. To illustrate this point, consider the data shown in Figure 5.13(b) and
Figure 5.12: Fixing the energy loss to 0.21 eV and $D_r=0$ results in good fits (solid line) to the data (circles). The only discrepancy between the data and the model is when $V_t$ is between -1.2 and -1.5 V indicating that the direct signal is only significant in this range.

(d) which is a partial reproduction of data taken from reference [18]. The sample geometry used to obtain data for this figure were identical to the other MTJ samples discussed in this chapter with the oxygen doses of the aluminum layers indicated in the figure. The data in (d) is a blow up of the data circled in (b). Originally this data was interpreted as follows: The inclusion of even the smallest dose of oxygen instantly incorporated scattering centers which attenuated the signal. Additional oxygen slowly made the alumina more opaque to the electrons until an oxide finally formed which only allowed electrons to pass through the material if their energy exceeded the oxide barrier height. One of the major problems with this interpretation is that the same result is expected with respect to the positive tip signal, which is not what is observed. Rather, the positive tip signal (Figure 5.9) indicates that the inelastic process is always in place in these samples.

Under the model that the process is a combination of both a ballistic signal combined with an inelastic scattering signal, the new interpretation is slightly dif-
Figure 5.13: The data shown in (b) and (d) is a partial reproduction of data taken from reference [18]. The sample geometry used to obtain data for this figure were identical to the other MTJ samples discussed in this chapter with the oxygen doses of the aluminum layers indicated in the figure. The data in (d) is a blow up of the data circled in (b). Originally this data was interpreted as the addition of oxygen slowly made the alumina more opaque to the electrons until an oxide finally formed which only allowed electrons to pass through the material if their energy exceeded the oxide barrier height. Under the model that the process is a combination of both a ballistic signal combined with an inelastic scattering signal, the new interpretation is slightly different. In this case, as the alumina forms, the direct signal is gradually turned off ($D_r \to 0$) until only electrons which have undergone an inelastic scattering event remain (a) and (c). The values of $D_r$ used are shown in the legend.
ferent. In this case, as the alumina forms, the direct signal is gradually turned off ($D_r \to 0$) until only electrons which have undergone an inelastic scattering event remain. This is what is shown in Figures 5.13 (a) and (c). For the unoxidized aluminum case, a value of $D_r=6$ is used \(^1\) (dotted line). To parallel the incorporation of more scattering centers (alumina formation), $D_r$ is reduced to 0.5 (long dash), 0.05 (solid), and finally 0 (short dash). The scale factors in the calculations have been adjusted to match the data. As one can see there is a strong agreement between what happens in the calculations as $D_r \to 0$ and what happens in the experiment as the alumina forms.

5.4 The source of inelastic scattering

5.4.1 Phonon excitation

If the scattering process results in an overall energy loss of the hot carriers, then that energy must go somewhere. Two reasonable candidates for a metallic system are phonons and plasmons. We can very quickly rule out the idea of plasmon excitation since for metals, typical plasmon energy are on the order of several volts \(^57\). Plasmon processes are relevant when looking at EELS spectra, however the energetics simply don’t work out in the case where electrons lose a fraction of an eV during the scattering process. That seems to lead one to conclude that the energy loss during the inelastic scattering processes must go into phonon processes.

In order to see how a scattering process could excite a phonon, consider the process shown Figure 5.14. 5.14a shows an ion (open circle) screened by three electrons (dark circles). A hot electron comes in and scatters with one of the screening electrons (b). Now both electrons are hot and leave a hole in the place of the original screening electron (c). This leaves the ion temporarily unscreened so both

\(^1D_r=6\) was the result of fitting our model to the data shown in Figure 5.10
the ion and remaining electrons rearrange to re-establish proper screening. The resulting ion vibration is a possible cause of the energy loss during the scattering of electrons. The very simple explanation depicted in Figure 5.14 gives an idea of how

Figure 5.14: (a) An ion (open circle) is screened by three electrons (dark circles). A hot electron comes in and scatters with one of the screening electrons (b). Now both electrons are hot and leave a hole in the place of the original screening electron (c). The temporarily unscreened ion and the remaining electrons rearrange to re-establish proper screening. The resulting ion vibration is a possible cause of the energy loss during the scattering of electrons.

the scattering of a hot electron can produce a lattice vibration, however the real picture is vastly more complicated. For starters, Figure 5.14 depicts an situation which is initially static. The reality is that the electrons are not of course static and one can only think about the situation in terms of an electron distribution around each ion. Still, the reality is qualitatively identical. The difference is that the when the incoming electron scatters, it will temporarily disturb the electron distribution and the ion will feel a different electric potential. Because the remaining electron distribution will very quickly return to the initial condition, it is important for the scattering event to take place faster than the reparative screening.
Typically, electrons in a metal will screen perturbations on the order of half a femtosecond\(^2\). There is little, if nothing at all, in the literature on how fast the scattering process is. While one would guess it is also on the order of fractions of a femtosecond, it is not important to know the exact values. What is important to know is that the process must be faster than the screening process. I would argue that this must be the case because if the screening process was faster, the hot electrons would never scatter. Instead, they would be perpetually screened and the electrons that they would have otherwise scattered with would be able to move out of the way.

Phonon excitation energies are also much closer in energy to the observed 0.2 eV energy loss. For example, dispersion curves for acoustical phonons in Al [58] indicate values of \(\hbar \omega\) up to 40meV. This specific example falls short by a factor of 5, but there are several possibilities for this. For one thing, there may be more than one scattering event. This is always possible and one can fit the data using \(n=5\) for the number of scattering events although the energy dependence begins to measurable deviate around \(n=4\) (see Chapter 3) for the case of electron injection. Multiple scattering events does not, however, require the presence of an interface which will be discussed in the next section.

Another possibility is that the excitations are of optical phonons, rather than acoustical ones. Optical phonon energies are always greater than acoustical phonon energies, and the only requirement is that the crystal must have a unit cell with more than one atom. This is certainly the case when alumina is present, however it may not be the case in bulk metals. It may be possible though for interfaces to play a role in this scenario.

\(^2\)This is effectively the screening length (\(\sim 0.5 \text{ Å}\)) divided by the Fermi velocity of electrons in a metal (\(\sim 10^6 \text{ m/s}\)).
5.4.2 The role of interfaces

In Chapter 3 it was shown that sBEEM data on gold films were correctly described by the elastic scattering process. In this chapter though, sBEEM in metallic multilayer films clearly showed signs of inelastic scattering indicating that interfaces play a significant role in both the enhancement of scattering as well as the energy loss process. In fact, nearly every sample with an interface that has been studied with sBEEM showed signs of an inelastic process. The exception to this is Cu on Au films which behave nearly identical to Au films. However it is likely that there is much diffusion of Cu and Au [29] so there is not a clear interface in that case.

As for every other interface, it is not surprising that the presence of an interface should enhance the amount of scattering. Previous results have shown that in the case of a Co/Cu interface the BEEM signal is attenuated by a factor of 4 [34] due to band mismatching, hence, increased scattering. Additional scattering enhancements at an interface may also be due to the increased density of electrons which are present to balance out the contact potential. In any case, the presence of an interface certainly increases the amount of scattering. This is seen as both a reduction of BEEM and an apparent enhancement of sBEEM.

As mentioned earlier, interfaces may also explain how optical phonons can contribute to the energy loss. In order to better understand this, consider the simple picture of a real interface shown in Figure 5.15. Figure 5.15a is the cross sectional view of a two metal interface where there is intermixing. The intermixing is relatively small, with only one monolayer containing atoms from each type of metal (indicated by the dashed line). Figure 5.15b shows an idealized version of what this mixed monolayer indicated by the dotted line in (a) would look like in the two dimensional plane. In this two dimensional lattice, there is clearly more than one type of atom per unit cell and thus an optical phonon branch, higher in
energy than the acoustical phonon branch, will be present.

Figure 5.15: (a) The cross sectional view of a two metal interface where there is intermixing. The intermixing is relatively small, with only one monolayer containing atoms from each type of metal (indicated by the dashed line). (b) A simplified version of what the mixed monolayer indicated by the dotted line in (a) would look like in the two dimensional plane. In this two dimensional lattice, there is clearly more than one type of atom per unit cell and thus an optical phonon branch, higher in energy than the acoustical phonon branch, will be present.

5.5 Summary

In this chapter we have really pushed the limits of BEEM. It still remains an unmatched tool for measuring the spatial dependent transport of thin films, but in systems with a large amount of scattering the data is not as straightforward to interpret as in systems which don’t scatter. A domino effect was triggered when our original conclusions about the measured barrier height of the alumina barriers was called into question. Namely, all of the work in Chapter 3 and certainly in this chapter was in response to trying to understand the details of scattering and the BEEM signal. Initially I had thought that all of what we had measured was rendered useless by this smallest of symmetric signals known as uBEEM. While
humbling, the results forced us to better understand the details of our system. In fact, our understanding of the scattering process helped us to create a much simpler explanation of spin scattering which will be discussed in the next chapter.

For the most part the effect of alumina on the ballistic current is understood. There are just two major points which need further theoretical work. The first is to explain exactly the symmetry of the uBEEM signal. This symmetry has been observed in alumina barriers, as well as cobalt oxide barriers grown in a similar way. While scattering is almost certainly the reason behind this, it would be nice to know the solid angle terms and scattering matrix elements which were ignored in Chapter 3. Finally, a more thorough description of the inelastic scattering process would be welcomed. The fact that this is seen in nearly all of our interfaces suggests that there is something fundamental about this energy loss during interfacial scattering, and not simply an experimental artifact. In fact, we may have stumbled upon a way to very delicately probe inelastic scattering processes in thin films. This could prove to be a very useful technique for studying the vibrational modes of molecular systems embedded into metallic films.
6.1 Introduction

Since there is much interest in using alumina for spintronic devices, it is important to understand all of the effects that this material has on spin transport. While our experiments are not sensitive to tunneling (Chapter 5), nor enable us to measure electrons below 0.5 V\(^1\), we can study how the formation of alumina effects the polarization of ballistic electrons. In this chapter I will show that when a ballistic current transports through alumina, the polarization is lost. It is possible for this type of ballistic current to be present in MTJs as a parasitic signal. One possibility is that a ballistic current can transport through the barrier via extended channels, or even tunnel to such states which extend to the other electrode, thus spending some amount of time transporting through the alumina - electrode interface. Since it will be shown that alumina reduces polarization by the same scattering process discussed in Chapter 3, any material which causes scattering may reduce the performance of spintronic devices. The could certainly be the case for ballistic devices which contain nano-oxides.

\(^1\)While high TMR has been observed in MTJ devices operating at low biases, it has been known for quite some time that as the operating bias increases, the TMR decreases until it eventually fades away around .5V [59].
6.2 Polarization measurements with BEEM

6.2.1 Review of spin dependent attenuation in cobalt

In 2000, BEEM was used to measure the spin dependent attenuation length of hot carriers in cobalt [49]. The results of this work indicate that for electrons with energies 2 eV above the Fermi energy, the minority attenuation length ($\lambda_\downarrow = 8\,\text{Å}$) and the majority attenuation length ($\lambda_\uparrow = 21\,\text{Å}$) are different in Cobalt. The consequence of this difference in attenuation length is magnetic contrast in BEEM images. In regions where the magnetic moments are parallel, the collector current ($I_{C,P}$) is higher than in areas where the magnetic moments are anti-parallel ($I_{C,AP}$). Figure 6.1a shows schematically the contrast between aligned layers and mis-aligned layers. The image in Figure 6.1b shows an example of this contrast in a Co - Cu - Co trilayer. Magnetic contrast in Co systems is usually seen on the scale of hundreds of nanometers. It is easy to verify whether contrast is magnetic or not by simply applying an external field. Saturating both layers is the easiest way to accomplish this as one is guaranteed to place the sample into a state where the entire BEEM image takes on the value of $I_{C,P}$. This makes it easy to measure and verify the value of $I_{C,P}$.

A trickier task is to determine $I_{C,AP}$ exactly. In fact, there is no way to put the sample in an anti-parallel state with 100% certainty. Instead, the strategy is to place the sample into a mixed state and find areas of minimum current. While there is no way to prove these areas of minimum current are exactly anti-parallel, it is assumed to be the case as it is often consistent with the calculated values of $I_{C,AP}$ in spin valve samples. It nonetheless remains the major source of error in these measurements.
Figure 6.1: (a) A schematic of ballistic electron magnetic microscopy. When ballistic electrons move through a ferromagnet the attenuation length of the hot carriers is spin dependent. The consequence of this is that when the electrons travel through two ferromagnets separated by a spacer layer, the first layer filters out the electrons with the shorter attenuation length. This means that when the magnetic layers are aligned, the current levels are higher than when they are not. (b) Images of a Co / Cu / Co trilayer. The dark regions are regions where the moments of the two layers are mis-aligned. The bright areas are regions where the two layers are aligned.
6.2.2 Cobalt in the polarizer - analyzer geometry

The magnetic contrast effect seen in BEEM images of spin valve structures allows us to think of the first Co layer as a spin polarizer and the second layer as a spin analyzer (Figure 6.2). The analogy with an optical polarizer - analyzer, where one can gauge the relative angle of the two films based on transmitted intensity, works quite well. There is not a total quenching of the current, nor is the angle of minimum current 90°, however thinking of the two Co layers in this manner is quite useful. Specifically it is possible to write down the current that leaves the first layer and goes into the Cu spacer. Using the results from ref. [49] we can write the polarization entering the spacer layer (P_in) as:

\[
P_{\text{in}} = \frac{e^{-\lambda_1} - \alpha e^{-\lambda_2}}{e^{-\lambda_1} + \alpha e^{-\lambda_2}}
\]

Here \( w \) and \( \alpha \) are the thickness of the first cobalt film and the interface transmission term for the first Co / Cu interface respectively. \( \alpha \) and the corresponding interface term for the second Co / Cu interface, \( \beta \), can be found in either reference [49] or [34] and have a value of .68 and 1 respectively.\(^2\) One minor point of the previous spin valve studies which we can exploit here is the fact that the level of magnetic contrast (\( I_{C,P} / I_{C,AP} \)) is greatest when the two layers have the same thickness. Maximizing the contrast makes the determination of parallel and anti-parallel regions easier and therefore more reliable. Since \( P_{\text{in}} \) can be set by adjusting film thickness, the polarization out of the spacer layer, \( P_{\text{out}} \), can be determined by comparing \( I_{C,P} \) and \( I_{C,AP} \) using the following equation:

\(^2\)As mentioned in [34] the second Co/Cu interface does not have any interface attenuation effects. This is due to the fact that electrons which pass through the first Co/Cu interface have already been selected. Therefore, only those electrons with momentum states that are accepted in both Co and Cu arrive at the second interface.
Figure 6.2: It is convenient to think of the two magnetic films as a polarizer and an analyzer separated by a spacer. The polarizer sets the polarization going into the spacer, and the analyzer measures the polarization coming out of the spacer. This allows one to measure the effects of the spacer on the spins.

\[ P_{\text{out}} = \frac{e^{\frac{-w\lambda}{\tau}} + \beta e^{\frac{-w\lambda}{\tau}} \left( I_{c,F} - I_{c,AF} \right)}{e^{\frac{-w\lambda}{\tau}} - \beta e^{\frac{-w\lambda}{\tau}} (I_{c,P} + I_{c,AP})} \] (6.2)

Equations 6.1 and 6.2 allow us to then determine the effect of the spacer layer on polarization. If \( P_{\text{out}} < P_{\text{in}} \) then it is clear that the spacer layer had a spin scattering effect. In all of the work discussed in this chapter, 18 Å of Co was used in both ferromagnetic layers. This was done to give acceptable current levels, along with reasonable magnetic contrast. The 18 Å of Co fixes the value of \( P_{\text{in}} \) at 71%. As a control, the two Co layers can be separated with a Cu layer. Typically 35 to 50 Å. The resulting measurements indicate that \( P_{\text{out}} = 71\% \) proving that the Cu this thin has no effect on polarization. This is not a surprising result as the spin diffusion length in copper is known to be well over 100 nm [60]. It is a good indication that the polarizer analyzer geometry is a useful tool for examining the spin scattering properties of spacer materials.
6.3 Effects of oxygen on polarization

6.3.1 Including aluminum and oxygen in the spacer layer

In order to test how transporting through the thin layers of oxidized Al effects spin we will begin by imbedding 10 Å of Al in the middle of a 44 Å Cu spacer layer. Then, as controlled doses of oxygen are be administered prior to the deposition of the top Cu and Co layers, the effects of the forming alumina layer on spin transport can be determined. Figure 6.3 shows the sample configuration for the spin mixing samples.

There are a few reasons why aluminum was imbedded into a Cu layer, rather than simply growing the Al directly on the bottom Co lead and then growing the top Co lead directly on top of the Al. The first reason is due to the lack of contrast in all of the MTJ samples. It is possible that shadowing during our sample growth could result in ferromagnetic coupling of the two magnetic leads, therefore killing all magnetic contrast in the BEEM images. This effect is eliminated by making the spacer thicker as has been shown before in spin valve samples. Secondly, the Co/Cu interface terms in equations 6.1 and 6.2 could conceivably be different for different interfaces. Instead of duplicating previous work [46, 49], it is simple enough to duplicate the Co/Cu interface configuration.

All of the samples in this chapter have the form depicted in Figure 6.3b. From top to bottom the metal layers are Co 18Å/ Cu 22Å/ Al 10Å/ Cu 22Å/ Co 18Å/ Cu 12Å/ Au 75Å/ Si(111). The Cu / Au bi-layer on the bottom serves the same function here as with the tunnel junction samples. Namely the seeding of Co growth and the formation of a Schottky barrier for the Cu and Au respectively. The center Al layer was exposed to varying doses of O₂ prior to deposition of the top Cu and Co leads.
Figure 6.3: (a) The schematic for testing the effects of alumina formation on spin transport. A 10 Å layer of Al, which experiences controlled doses of oxygen, is embedded in a copper spacer layer separating two 18 Å Co films. (b) The BEEM energy diagram for the same experiment.
6.3.2 Extracting polarization information from images

Before I discuss the quantitative results of alumina formation on spin transport I will begin by reporting qualitatively what happens. Figure 6.4 shows 800nm x 800nm BEEM images taken with $V_t = -2V$ and $I_t = 1nA$ for three separate samples. All samples have the form described above with oxygen doses of 0 (a and b), .075 mTorr · sec (c) and 30 mTorr · sec (d). The images in (b),(c), and (d) have been fourier transformed and reconstructed after filtering out signals with high spatial frequency. For comparison, (a) is the unprocessed version of (b). The high spatial frequency signal is not magnetic in nature [46] and makes it more challenging to determine regions of parallel alignment and antiparallel alignment as the contrast fades. The linear grayscale is 0-1 pA, black to white, for (b),(c) and (d). The images show a fading of the contrast as the oxygen dose increases. Eventually, once the barrier is fully formed (d), the image is void of any magnetic contrast. There is a notable reduction in the average signal level as would be expected [18], in addition to the reduction of the contrast. One may argue that the signal level in (d) is so small that the blacked out image reveals nothing about the state of magnetic signals in the sample. It is a simple matter to adjust the color scale to verify the lack of contrast. Figure 6.5a shows the same image as in Figure 6.4d. Below it, Figure 6.5b, the color scale has been amplified to 0-100fA, white to black. The image clearly lacks any of the the long range magnetic contrast seen in Figures 6.4b and 6.4c. Further evidence that there is no magnetic contrast in these images comes from the lack of response to an applied magnetic field, both qualitatively in the images as well as quantitatively in the signal levels.
Figure 6.4: BEEM images from samples whose Al received doses of 0 mTorr · sec (b), 0.075 mTorr · sec (c) and 30 mTorr · sec (d). The images in (b),(c), and (d) have been Fourier transformed and reconstructed after filtering out the high spatial frequency signals which are not magnetic in nature. For comparison, (a) is the raw data for (b). The linear grayscale is 0-1 pA, black to white, for (b),(c) and (d). The images show the fading of the large scale magnetic contrast as the alumina forms. All data was taken with $V_t = -2$ V and $I_t = 1$ nA.
Figure 6.5: The image in (a) is identical to the image in Figure 6.4d. For this low signal level the color scale is not very revealing. In order to see more clearly that there is no large scale magnetic signal, the greyscale was decreased to 0-100fA, white to black. The small scale contrast seen in this images and others like it do not change in magnetic field.
6.3.3 Effects of oxygen dose on spin transport

The observation that contrast fades with oxygen dose is a nice way to qualitatively see the effect of alumina formation on spin transport. However, the equations above let us go into the images and determine quantitatively what the polarization loss is as a function of oxygen dose. Figure 6.6 shows the effects of oxygen dose on the polarization leaving the spacing layer for 2V electrons. As stated above, the 18 Å thick Co top lead sets the polarization of ballistic electrons going into the spacer at 71%. This is the polarization which is measured by the analyzer layer if one looks at a sample with the Cu/Al/Cu spacer layer mentioned above without an oxygen dose, or if the spacer is simply Cu and contains no Al. The incorporation of even the slightest oxygen however, as an immediate impact on the spin transport properties of the spacer layer. The first two data points show an output polarization of 52% and 45%. Using the sticking coefficients measured by Zhukov, Popova and Yates [61], this corresponds to 0.3 and 1 monolayers of oxide respectively. By the time the oxide is fully formed at a dose of 30 mTorr · sec, all spin information leaving the spacer layer is lost. This is not surprising given the images in Figure 6.5.

It was shown before [18] that as the oxygen dose increases, the transmissivity decreases. As seen in the last chapter this is explained by the introduction of scattering centers and the onset of inelastic scattering which effectively shifts the threshold voltage. The loss of transmissivity is not any different in these samples and is directly correlated with the loss of polarization. Figure 6.7 shows a plot of the
Figure 6.6: $P_{\text{out}}$ vs. oxygen dose. The plot qualitatively shows what was seen in the images for the different doses. There is a definite decrease in the polarization of the ballistic electrons as the amount of oxygen content in the deposited Al films increases. The horizontal line at 71% indicates the polarization which enters the spacer layer. This is also the polarization that is measured when the spacer layer is entirely Cu or when the Al is not exposed to oxygen.

Figure 6.7: $P_{\text{out}}$ vs. the maximum current level at $V_t=-2V$ for the samples containing Al. Although it could be inferred from Figure 6.6, this plot shows directly that as the amount of scattering in the film increase, both the amount of hot electrons leaving the spacer layer and the polarization of the remaining electrons decreases.
measured polarization out of the spacer layer as a function of maximum collector current at 2V. The trend clearly indicates that with the onset of scattering comes the loss of polarization. This suggests that the same mechanism which causes scattering and loss of signal, also causes loss of polarization.

6.4 The origin of spin scattering

6.4.1 Inelastic scattering

As I stated above, it appears from Figure 6.5 that the same mechanism is responsible for both the signal and polarization loss. In the last chapter it was shown that the inelastic Auger-like scattering is responsible for the loss of signal and shift in threshold during oxide formation. The result of this inelastic scattering was observed not only during oxide formation but also in sBEEM measurements on samples with abrupt changes in conductivity. This fact allows us to test the hypothesis that the same mechanism responsible for scattering also causes loss of polarization.

Since the sBEEM signal can only be created by a scattering process, we can look at the sBEEM signal on samples with magnetic contrast to see if the polarization loss is present. Figure 6.8 shows the BEEM and sBEEM signal taken over regions of parallel alignment (solid line) and anti-parallel alignment (dashed line) for the Cu/Al/Cu spacer sample with no oxygen dose. Even though the BEEM signal shows clear contrast, the sBEEM signal shows no difference in signal level for the two regions. Additionally both sBEEM signals shows the delayed turn-on (Figure 6.9) indicating that the inelastic scattering processes are in place (marked with the arrow).

Both the polarization vs. current (or dose) and the sBEEM data lead
Figure 6.8: Positive and negative tip $I_c$ vs. $V_t$ for the Cu / Al / Cu spacer sample with no oxygen dose taken above a region of parallel alignment (solid line) and anti-parallel alignment (dashed line). Even though the negative tip signals for the two regions are clearly different, the sBEEM signals are identical for the two regions. This data was taken during a period when the old BEEM op-amp was incorrectly calibrated. The true data should be higher by roughly a factor of 2.

Figure 6.9: A blow up of the sBEEM data from Figure 6.8. The solid and dashed lines lie right on top of each other. As with the metallic multilayers discussed in Chapter 5, the inelastic scattering processes are in places. The arrow in the figure designates the delayed turn-on.
us to conclude that an inelastic scattering process is involved in removing the polarization from the ballistic current. This should not be particularly surprising considering the mechanisms in place. Figure 6.10 is a reproduction of Figure 3.2a. The only difference is that now the electron and hole states are labelled with spin along with momentum and energy. If we assume that the electron-electron collisions are spin conserving the only constraint involving spin in the Auger-like scattering process is that the electron which fills the initial hole \((E_0, k_0, S_0)\) must have the same spin, hence \(S_1 = S_0\). There is no restriction on \(S_2\) which will have the same value as \(S\). This means that the scattering process which creates the electrons to be collected, randomizes the spin. This is not to say that the spin is lost in any way shape or form. Summing over all spins will always yield the same total spin, however it is a simple matter for the ballistic current to be unpolarized. In the case of electron injections, the same arguments can be made. Figure 6.11 shows the diagram for the case of electron injection. Here, one does not expect polarization to be quenched with a single event. This is because the injected electron \((E_0, k_0, S_0)\) loses energy in the collision but still maintains its spin, therefore just like before \(S_1 = S_0\). Likewise, there is no condition on \(S_2\) and \(S\), especially if the scattering occurs in a non-magnetic material such as alumina. However since both the \(E_1\) and \(E_2\) electrons contribute to the BEEM current the overall polarization is reduced. As the number of scattering events increases and/or the contribution from the initial electron beam is quenched, the polarization will become drowned out and eventually disappear once \(E_1 < \Phi_B\) and those electrons which had the initial spin information can no longer be collected. This is supported by the data in Figure 6.6 and 6.7. As the amount of scattering increases, the polarization of the collected current is washed out.

It should be noted that the spin flux is not actually diminished, only the polar-
Figure 6.10: A reproduction of Figure 3.2a with the addition of labelling each carrier with spin. If we assume that the electron-electron collisions are spin conserving the only constraint involving spin in the Auger-like scattering process is that the electron which fills the initial hole \((E_0, k_0, S_0)\) must have the same spin, hence \(S_1 = S_0\). There is no restriction on \(S_2\) which will have the same value as \(S\). This means that the scattering process which creates the electrons to be collected, randomizes the spin.
Figure 6.11: For the case of electron injection, the polarization of the ballistic current can also be reduced. Consider an injected electron \((E_0, k_0, S_0)\) which loses energy in the collision but still maintains its spin. Like before \(S_1 = S_0\) but there is are no restrictions on \(S_2\) and \(S\), especially if the scattering occurs in a non-magnetic material such as alumina. However, since both the \(E_1\) and \(E_2\) electrons contribute to the BEEM current the overall polarization is reduced. As the number of scattering events increases and/or the contribution from the initial electron beam is diminished, the polarization will become drowned out and eventually disappear once \(E_1 < \Phi_B\) and those electrons which had the initial spin information can no longer be collected.
ization of those electrons whose energy is greater than $\Phi_B$. This is consistent with spin transfer measurements made on nanoscale MTJ that indicate no more current is needed to switch the magnetic layers than a comparable spin valve structure [62].

6.4.2 Ruling out other effects

The scattering mechanism described above reveals a very simple explanation for the observed loss of polarization in BEEM and sBEEM signals that transport through the alumina. If we want to pinpoint the inelastic scattering as the sole source of the polarization loss, we must rule out other potential sources of spin mixing.

A recent analytical scanning transmission electron microscopy (STEM) study of the electronic structure of the thermally grown amorphous Al oxide in a MTJ [50] found that the oxygen K-edge in the electron energy loss spectra (EELS) of the amorphous oxide is quite broad with a tail that extends 4 - 5 eV below the mid-point of the much sharper sapphire K-edge. This value is much lower that would be expected from the band structure of sapphire (4 eV) and indicates that there are strong (1 eV / Å), randomly oriented electric fields in the oxide. The loss of polarization of a ballistic electron beam as it moves through an amorphous oxide thus might be explained by de-phasing due to different field directions, precession frequencies, and thickness variations in the oxide. However, electrons transporting through the 1nm of oxide in our measurements spend a very limited time ($= 10^{-14}$ sec) in the oxide. Even in the presence of 1eV/ Å electric fields, the effective magnetic field seen by the electrons is two or more orders of magnitude too small for any substantial spin precession during transit.
6.5 Summary

The lack of magnetic contrast in BEEM measurements of MTJ systems was noticed since the measurements began in April of 2000. For samples with a thin (∼1 nm) spacer layer it is quite possible that evaporation of films through a shadow mask resulted in the shorting of the two Co leads and hence they were always in ferromagnetic alignment. That left the role of the alumina on spin transport as an open and interesting question. By removing the possibility of ferromagnetic coupling and studying the effect of alumina formation on the polarization transporting through the spacer, it was clearly shown that the alumina does dilute the polarization of a ballistic current.

While large electric fields most certainly exist within the alumina, electrons do not spend sufficient time in the spacer to have their spins mixed by precession. Both polarization vs. current and sBEEM measurements have shown that this effect is easily explained by scattering of the carriers as they transport through the spacer. This simple conclusion should not be surprising as rarely in nature does the random scattering of carriers come without a cost to performance.
CHAPTER 7

Summary

A principal lesson of this work, and one which is implicit in Chapter 5, is that all parameter space should be explored in an experiment. It would have been easy enough to have looked at the positive tip signal in tunnel junctions when we first began to study them about four years ago. That of course is in retrospect and at the the time nothing was known about the inelastic scattering artifact. It is impossible to tell what might have happened had we discovered early on that the signal was virtually independent of bias direction. It is possible that it would have ended the oxide studies early and none of this thesis would have been written.

One feature of BEEM that remained solid through our re-examination of the technique was its outstanding spatial resolution. This meant that much of the early work that was done on imaging pinholes was still valid. Additionally, so were the surface science studies. With regard to the latter, the work in this thesis contains much more information than what had been previously published. This is in part because of space, but also because of the XPS studies done in our group between now and then. With the two techniques, alumina formation is well characterized. The images of chemisorbed oxygen clusters are as close to taking snapshots of oxidation as one might ever expect to get. It would certainly be interesting to image the dynamics of oxidation, but that is not something which can be achieved through any modern technique.

The Ohio State data made us aware that our simple interpretation was invalid and the barrier height of alumina could no longer be measured with BEEM.
However, in the end it forced us to examine not only the alumina more carefully, but the technique of BEEM itself. None of the scattering work found in Chapter 3 would have existed if we did not measure sBEEM for alumina samples. The necessity to have an accurate understanding of the scattering process lead me to discover that the original Kaiser - Bell theory did not describe data correctly at high bias. In turn, that lead me to the density of states correction to their theory. Now, sBEEM data can be described with the same accuracy as BEEM data. So while sBEEM was a source of great frustration for me, it may be possible to exploit this effect. In nearly all of the interfaces we studied, the scattering was observed to be inelastic, indicating that sBEEM is sensitive to energy loss. For interfaces that contain molecules, quantum dots or other features with resonant electron energies, sBEEM may provide a way to directly probe their ability to absorb energy.

It turned out that our final explanation of the uBEEM signal is rather simple. There is inelastic scattering present, as is now believed to be common at interfaces, and ballistic electrons do not transport through fully formed alumina without scattering. This doesn’t mean other theories aren’t possible. The striking and ubiquitous symmetry of our measurements is not something that comes naturally from our explanation. A better theory would be one which predicts both the energy dependence of the spectra, as well as the symmetry. It has been speculated by P.W. Brouwer that the alumina acts to thermalize the distributions, and our final electron populations can be modelled by the Fermi distribution and an effective temperature. This helps explain the symmetry but does not accurately describe the spectra.
Finally, our knowledge of scattering makes the spin scattering result very straightforward to explain. Originally we had many ideas as to what might be causing the loss of polarization with alumina formation. Once the effects of scattering were understood, it was a simple matter to explain the observations.
REFERENCES


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