FABRICATION OF SILVER SCANNING TUNNELING MICROSCOPE TIPS WITH ACETIC ACID

by

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A THESIS

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Approved: ____

George Nazin

Scanning Tunneling Microscopy (STM) is used to image, manipulate, and spectroscopically characterize individual atoms and molecules to further develop an understanding of materials that have application in the semiconductor industry. The fabrication of sharp and smooth metallic tips plays an essential role in STM as the radius of curvature of tips used in STM directly influences resolution. The smaller the radius of curvature, the finer the resolution. We report a novel and reproducible fabrication procedure of silver STM tips. Silver wire is electrochemically etched using an environmentally benign electrolyte solution of volume ratio 1:8 glacial acetic acid: deionized water to form a tip radius of ~100 nm. Silver is used for its plasmonic enhancement of STM-luminescence and tip-enhanced Raman spectroscopy signals. The elemental purity and small radius of curvature (~100nm) of silver tips permits atomically resolved STM imaging, as well as photon emission and ultrafast electron emission measurements which will allow for better nano-scale understanding of a variety semiconductor materials.

Acknowledgements

I would like to thank Professor George Nazin, Benjamen Taber, and the members of the Nazin lab for helping me fully examine scanning tunneling microscopy (STM) and the fabrication of STM tips. Without their guidance and support this work would not be possible. I would also like thank my middle school and high school science teachers, Lynn Kuntsman and Jim Lebo, for inspiring me to purse my curiosity in science. I am grateful for the support from the Center of Sustainable Materials Chemistry summer undergraduate research program for the 2014 and 2015 funding, and for the University of Oregon Undergraduate Research Opportunity Grant.

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Introduction

My thesis primarily consists of the research project I conducted with the Nazin group on the fabrication of Scanning Tunneling Microscopy (STM) tips. The fabrication of sharp and smooth metallic tips plays an essential role in STM as the radius of curvature of tips used in STM directly influences resolution. The smaller the radius of curvature, the finer the resolution. In this endeavor, we report a reproducible fabrication method using an environmentally benign novel electrolytic solution. Tips were then characterized with scanning electron microscopy and novel elemental composition studies on the finished STM. Currently, we are developing an optics system to demonstrate the plasmonic enhancement of our STM tips.

This Thesis will cover the underlying principles and history of STM, our method of STM tip fabrication, characterization and analysis of finished STM tips, current and future work on this tip project, and an example of the application of these STM tips in the study of materials, specifically [8]cycloparaphenylene ([8]CPP).

Personal Background in Research

During my first year at the University of the Oregon, in February 2014, I started working the with Nazin group. The Nazin group performs atomically-resolved spectroscopic studies in the physical and chemical properties of molecular and nanoscale materials. In my work with the Nazin group I received funding from the Center of Sustainable Materials Chemistry to conduct an independent project on the fabrication of scanning and tunneling microscope probes in the summers of 2014 and 2015. During these summers, I learned how to use instrumentation such as scanning electron microscopes, and spectroscopic techniques like energy dispersive x-ray spectroscopy, giving me the expertise to develop and conduct my own experiments.

Building on these experiences I continued to work in the Nazin group throughout the school year, and in the fall of 2016 I received a $1000 dollar mini-grant from the University Research Opportunity Program to continue my research and fund the development of optical components necessary to enable the STM-based optical spectroscopic studies.

In conducting research throughout the summers and academic years, I have learned that research is an intensive problem-solving process that relies greatly on

Figure 1 Nazin group photo. From left to right: Back row: Dmitry Kislitsyn, William Crowley (undergrad), Ben Taber, Matt Robertson (undergrad), Jon Mills, George Nazin Front row: Jason Hackley, Josiah Makinster (undergrad), Christian Gervasi, Nima Dinyari*, Moto Honda (*Collaborator)

collaboration and creativity. Working with a team towards a common goal was meaningful to me, as our group created a supportive space in which unfamiliar problems could be solved in innovative ways. I found that the extended time and collaborative effort allowed for various approaches and methods to be tested. Even though this often meant that the first approach was wrong, the process of problem solving was rewarding. I am motived by the possibility of developing novel techniques and look forward to applying the skills developed in the problem-solving process in my future academic career in medicine or research.

Figure 2 Undergraduate symposium poster session

Principles, History, and Applications of Scanning Tunneling Microscope

An explanation of general theory and principles of chemistry and physics are necessary to describe the complex techniques and underlying principles used in scanning tunneling microscopy. This will involve an introduction to the technique of spectroscopy, followed by general concepts of quantum mechanics. These concepts are meant to provide readers with a general context and beginning point of inquiry to the complex principles applied in scanning tunneling microscopy. A glossary on page 49 may be helpful in clarifying these concepts.

Fundamental Principles of Standard Spectroscopy

Spectroscopy is the study of the interaction of electromagnetic radiation and matter. Electromagnetic radiation consists oscillations in electric and magnetic fields that travel through space. Common examples of electromagnetic radiation are visible light, x rays, and radio waves. Electromagnetic radiation is characterized by wavelength and frequency. The range of wavelengths of electromagnetic radiation is called the electromagnetic spectrum. (Silberberg)

In spectroscopic analysis, the spectrum of electromagnetic radiation emitted or absorbed by the material of interest is recorded. The emission or absorption spectrum observed contains only wavelengths, which are specific to a given material. Each element has a unique spectrum like a fingerprint. Therefore, the recorded spectrum can then be used to identify and determine the properties of the material under investigation.

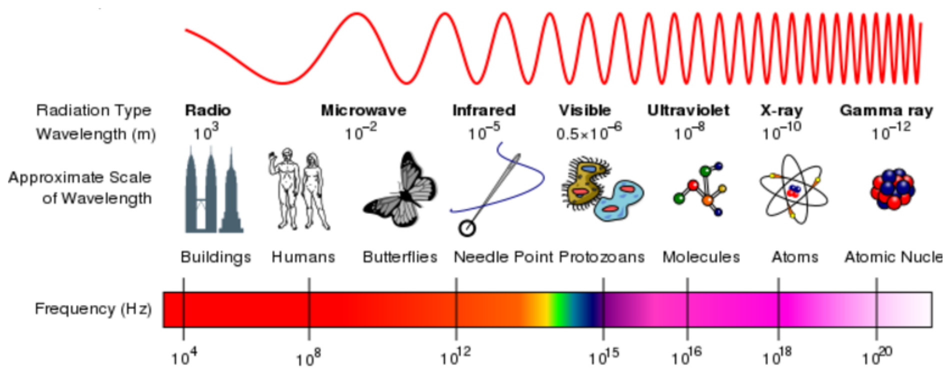

Figure 3 Electromagnetic spectrum classified by wavelength and frequency. Adapted from Silerberg Chemistry

STM can also be used for spectroscopy this technique is referred to as Scanning tunneling spectroscopy (STS). While most spectroscopy involves light and matter, STS is typically done in the absence of photons. Instead, electrons, or more specifically changes in conductance, are used to probe electronic properties of the material in question. Overall, STS is an extension of STM and provides localized information about the density of elections in a sample as a function of energy. Electron density data provides information on how electrons are arranged within a given material.

Introduction to Quantum Mechanics

Quantum mechanics is a fundamental theory describing the properties of matter at small scales (nanometer scale), when classical physics break down. See figure 4 for relative sizes of common objects to nanoscale objects. Key principles introduced in quantum mechanics which differ from classical physics are concepts of wave-particle duality, discrete energy levels, and probabilistic interpretation of phenomenon. The explanation of these unintuitive concepts serve to provide an entry point to understanding the key principles in quantum mechanics.

The phenomenon of discrete energy levels is analogous to a car only being able to drive at certain speeds. For example, this would mean when starting to accelerate your car, you would be at rest (0 mph), then instantaneously jump to moving at 20 mph. Classically this would be quite strange, but in the quantum world, discrete quantities of energy are the rule. (Silberberg)

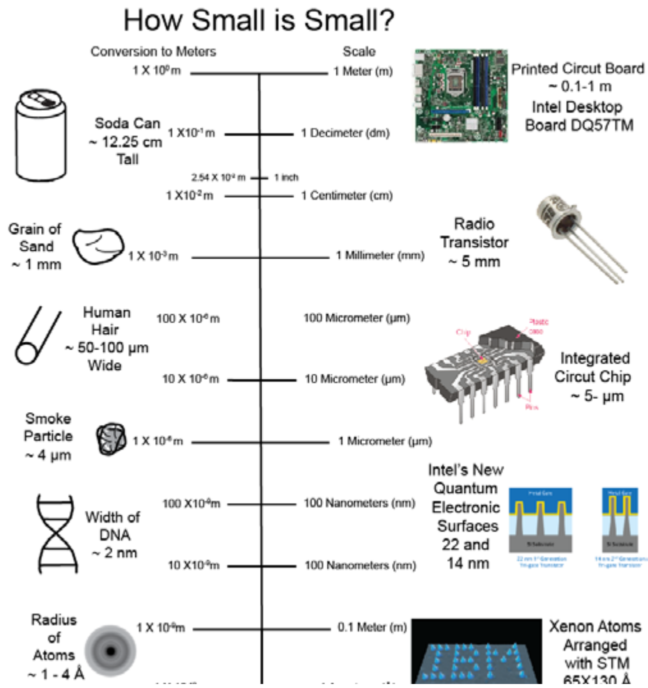

Figure 4 How small is small? The relative size of common objects and electronic components. Photos and diagrams of electronic components (right side) are courtesy of Intel and IBM.

At the quantum level, particles energies are quantized. Accordingly, only certain discrete values of energy can exist. For example, if a molecule is vibrating and the energy of the system increases, the molecule will only vibrate at specific energies. That is the vibration will not continuously increase in frequency, but rather jump from discrete frequency to discrete frequency as energy is increased continuously. This relationship is described by equation 1 below. Where n is a non-zero integer, h is Planck's constant, ν is frequency, and E is Energy.

$$(1)\ E = nh\nu \quad \text{n} = 1, 2, 3, \ldots$$

Under the quantization of energy assumption, it was reasoned that if a vibrating atom's energy changed, for example from 2hv to hv, the atoms energy would have decreased by hv. The energy lost would be released as discrete bit (or quanta) of energy. From this theory, it was assumed that light energy consists of quanta. Light quanta are now referred to as photons. Photons are particles of electromagnetic energy, with energy proportional to frequency. This relationship, which highlights the quantized energy component of light is represented in equation 2. E is energy, h is Plank's constant, and v is frequency associated with the wave.

$$(2)\ E = hv$$

Einstein then used the idea of light quanta to describe the phenomenon known as the photoelectric effect. The photoelectric effect involves the ejection of electrons from the surface of a metal or conducting material when excited by light. Electrons were only ejected when light exceed a threshold energy value characteristic of the metal. No amount of lower-energy light could cause the ejection of electrons. To explain the dependence on energy which is proportional to frequency. It was assumed the light was acting as particle. Therefore, for single electron to be ejected a single photon of a high enough energy would have to be absorbed into the metal. (Silberberg)

Wave-particle duality is the concept that elementary particles can be partly or entirely described in terms of waves in addition to as a particle. This meant that the wave and particle models of light were regarded as complementary views of the same entity. With light this helped explain light's unique properties of refraction and diffusion.

Wave-particle duality was characterized in the double slit experiment. In this experiment, a point source of light illuminated two narrow adjacent slits with the image produced by the light through the slits observed on a second screen see figure 5 for diagram of this experiment. The pattern observed on the screen is called an inference pattern. The dark regions of the inference pattern are a result of destructive inference of light waves and the light regions are a result constructive inference. This wave pattern was experimental evidence that light can act as wave in addition to acting as particle.

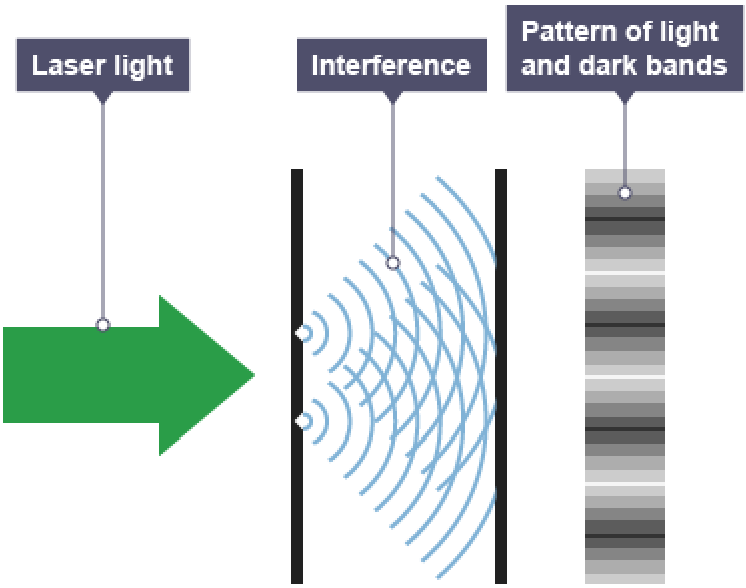

Figure 5 Double Slit Experiment Schematic. Dark bands represent points of negative interference, light bands represent points of positive interference. Adapted from Silberberg Chemistry

The concept of wave-particle duality was then expanded from just light to particles of matter by physicist de Broglie. The wave-particle duality relationship of particles is described in equation 3, which is known as the de Broglie relation. With λ as wavelength, as mass m, and v speed with associated wavelength.

$$(3)\ \lambda = \frac{\mathrm{h}}{mv}$$

This means that matter has wave properties. For example, electrons have observable wave properties. The reason why we do not observe the wave properties of matter on a daily basis, as the wavelength of ordinarily encountered objects are too small to be detected. For example, using equation 3, a baseball moving at about 60 miles an hour would have a wavelength of about 10^{-34} m. (Ebbing)

In scanning tunneling microscopy, electrons, a particle, is used as a source of radiative energy. It is possible to use particles as a source of radiation energy due to their de Broglie wavelength. The interaction that takes place between a sample of material of interest and a focused beam of tunneling electrons yields fundamental electronic and chemical information of the sample. Primarily, this is useful in the atomically resolved relationship between structure and function.

The mathematical description of the wave properties of submicroscopic particles, such as electrons is referred to as quantum mechanics. Quantum mechanics allows scientists to make statistical statements about a system. For example, the probability of finding an electron at a certain point in an atom can be found. However, the definite position at a given time cannot be found with complete certainty as quantum mechanics provides probabilistic statements about a system.

The wave function Ψ is a mathematical expression which provides information about a particle at a given energy level. The square of wavefunction $\Psi^{*}\,\Psi$, gives the probability of finding a particle, such as an electron, in a given region of space.

Quantum tunneling is a phenomenon in which an electron can tunnel through a potential barrier without the addition of energy to overcome the barrier. This is possible from a probabilistic description. Consider a hydrogen atom, proton A with an electron about proton A and a neighboring a second hydrogen atom, proton B. In classical terms, it would be impossible for the electron to escape the attractive region about proton A and move to the region of proton B without adding energy to the system. However, it quantum mechanics thought the probability of this happening is low there is a non-zero probability that this will occur. Therefore, the electron may find itself within the region of B without the addition of energy. If this movement occurs the electron is said to have tunneled from on atom to another. More on quantum tunneling will be described in relation to STM in the “Mechanics of Scanning Tunneling Microscopy” section beginning on page 20.

History of Scanning Tunneling Microscopy

The scanning tunneling microscope was developed by Gerd Binning and Heinrich Rohrer in 1981. This microscope allowed researchers to see at the atomic scale. Gerd Binning and Heinrich Rohrer, scientists at IBM’s Zurich research lab originally planned on developing a method to perform spectroscopic measurements locally on an area of 10 nm in diameter. In this endeavor, these scientists realized that an appropriate tool to study material at this highly localized level was lacking. With knowledge of vacuum tunneling with a movable tip they began work on a new microscope that would deliver highly local spectroscopic and topographic images.

Figure 6 Nobel laureates Gerd Binning and Heinrich Rohrer (left to right) of IBM research with STM. Photo courtesy of IBM

On August 10, 1982, IBM was awarded US patent 4,343,993 for the invention of STM. Later, in 1986, inventors Gerd Binning and Heinrich Rohrer were awarded half the Noble Prize in physics along with Ernst Ruska (inventor of the electron microscope). The development of the STM has helped shape and fuel studies in nanotechnology.

The historical context in which the STM was invented is commonly reported with a narrative beginning with a nanotechnology a talk by Richard Feynman to the American Physical Society on December 29, 1959, ‘Plenty of room at the Bottom’. In which Feynman outlined how nano-scale science would become a rapidly growing field. He also emphasized that developing a microscope to image and characterize atoms would be the first step in developing this new field as well as lead to furthering understanding in other scientific fields. The development of the STM is widely viewed as this first step in the developing nanotechnology field outlined by Feynman. STM stands out from other forms of microscopy like scanning electron microscopy for its ability unique ability to manipulate and rearrange particles at the nanoscale. In a sense, it represented not just a new imaging technique but also a new prototype of atomic and molecular assembly.

Twenty years after Feynman’s talk the development of nanotechnologies has progress rapidly. Though this progress has occurred in what has been considered to as a culture often referred to as ‘postacademic’. This term highlights the increased emphasis on aspects of commercialization and application to industry. Companies like Intel and IBM have driven the research and development this field. In particular, the development of STM in the corporate IBM setting has been described as an epistemological marker of the shift that is part of the postacademic science and nanotechnology policies.

Nanotechnology and the instruments that make innovations in this field possible are developing in a more integrated academic/commercial environment. STM and other off-shoot types of probe microscopes (SPM), like atomic force microscopy, were developed in a cooperate rather than academic setting. For example, the work perused at IBM's Zurich, Switzerland research lab was essentially academic research done in an industrial setting. Neither Gerd Binning or Heinrich Rohrer came from the academic community. Because of their lack of ties to the academic community their claims related to STM were not immediacy accepted the surface science community at large. To gain acceptance in the scientific community there were methodological hurdles to overcome. The initial 1981 paper entitled "Tunneling through a controllable vacuum gap" which described the first STM study was initially declined for publication.

In 1983 STM was more generally accepted after a study of the structure of Silicon (111) was published. The produced STM atomic scale images provided insight to the surface reconstruction of Si (111) in real space. At the time this was an intriguing and unknown phenomena in surface science community. Consequently, STM became a widely-accepted technique. Another, well known publication involved the image of manipulated xenon atoms to spell IBM's initials. See figure 7 for this image of STM manipulated xenon atoms.

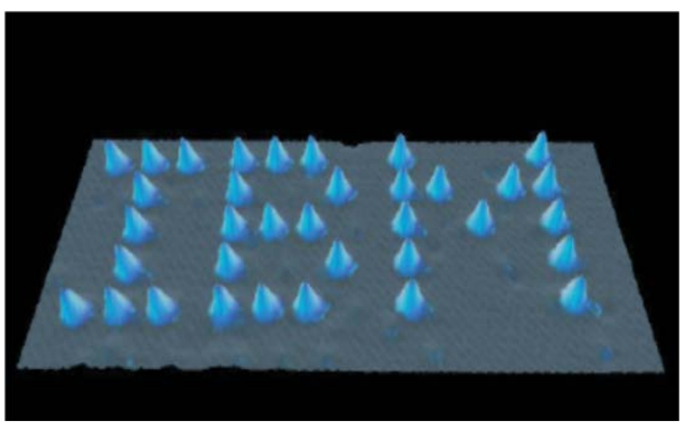

Figure 7 STM manipulated arrangement of xenon atoms to form IBM's initials. Photo courtesy of IBM

The issues of disciplinary insulation and ease of use created a multifaceted problem for the full commercialization and acceptance of STM. In commercialization, a wide consumer base was need to offset development cost and to appeal to a large market. To be fully commercialized several key factors are considered; robustness of instrument, ease of operation, through-put, versatile of use, and ease of reliable interpretation of results.

STM needed be usable by researchers with limited knowledge of instrumental development. Navigating these issues shaped the commercialization of STM and lead to the black boxing of most of the aspects of STM and SPM. Black boxing is a concept which a system or instrument is viewed only in terms of its inputs and outputs without understanding the internal workings. The focus on user-friendly aspects of instrumentation furthered the shift in nanotechnology from an academic to a commercial, results orientated setting. (Baird)

STM developed commercially at an astonishing speed. In 1991, over 30 companies began manufacturing and marketing STMs and parts with the emergence of companies solely dedicated to marketing and selling STM and other SPM instruments. Today the field continues to grow some of these companies include: Digital Instrument, Park Scientific Instruments, WA Technology, Angstrom Technology, TopoMetrix, Nanoscience Instruments, and RHK Technology, to name a few. (Chen)

Additionally, the shift to commercialization of nanotechnology was pushed by the passing of the U.S. Bayh-Dole act of 1980. This act allowed Universities to patent and collect royalties from the results of research which was federally funded. This financial incentive pushed universities to patent professors' research, incubate start-up companies, and from substantial partnerships with the industrial corporations. Part of this more extensive integration of universities and industry pushed universities to adopt a more cooperate profit centered style of operation and had led to earlier technology transfer. Accordingly, the emphasis on industrial style results in reflected field’s name as this field is referred to as nanotechnology rather than nanoscience. (Baird)

Timeline of the Progression of Microscopy

Moreover, outside the context of commercialization STM is part of a long progression of advancement in microscopy. Beginning in the 14th century the art of developing glass to form lens was established. This rudimentary practice helped develop spectacles to improve eye sight. Following in the lens gridding tradition, Dutch lens makers Hans and Zacharias Jansen made the first microscope like device by placing two lenses in a tube. The microscopes produced by Hans and Zacharias Jansen in the late 16th century yielded an approximate 9x magnification and were difficult to focus.

In the late 17th century, 1665, Robert Hooke studied objects with his improved microscope of approximately 100x magnification. In his studies, he was the first to observed cells and microorganisms. Later, Anton van Leeuwenhoek further improved on the Jansen microscope design by including more lenses within the microscope. This yielded a magnification of 270x on the micron scale. With this microscope, Van Leeuwenhoek made several biological discoveries, making the first observations of bacteria, yeast and blood cells.

In the 18th and 19th century several technical innovations made microscopes better and easier to handle. In this time period, microscopy began to gain popularity among scientists. In 1878 Ernst Abbe formulated a mathematical theory correlating the resolution possible with an optical microscope and wavelength of light. In the visible spectrum, the highest magnification of an optical microscope is 1500x magnification to a level of approximately 500 nm.

In the early 19th century several innovations in improving microscopy were made. In 1925, the Nobel prize in chemistry was awarded to Richard Zsigmondy, for developing of the ultramicroscope in 1903. The ultramicroscope, which uses light scattering rather than light reflection, enabled the study of objects below the wavelength of light. In 1932, Frits Zernike developed the phase-contrast microscope allowed the study of colorless and transparent biological materials. Frits Zernike was awarded the 1953 Nobel prize in Physics. Later, in 1938 Ernst Ruska developed the electron microscope. Using electrons in microscopy improved resolution greatly and expanded the realm of possible inquiry.

In 1981, Gerd Binning and Heinrich Roher developed STM. Throughout history the improvement in the resolution of observation has progressed and lead to the broadening of the borders of possible exploration. With each progressive improvement to the microscope a new dimension in science is revealed. Improvement in microscopy is an important and fundamentally changes the scope in which science can be conducted.

Applications

The characterization of materials at the atomic and molecular scale has recently rapidly progressed and has contributed significantly to developments in fields related to electronics. Information at the molecular level has development in the electronic field has been accelerated by miniaturization of semiconductor integrated circuits. (Morita, 2007). Scanning tunneling microscopy has and continues to contribute to the rapid progress of material characterization at the atomic and molecular scale.

The miniaturization of semiconductors has improved in line with the prediction of Gordon Moore, the co-founder of Intel. According to his prediction, known as Moore's Law, "the number of transistors per square inch on integrated circuits will double roughly every two years" (The Future of Computing; after Moore's Law." Economist 2016).

The miniaturization of semi-conductors has increased computing speeds and reduced the cost of producing microprocessors. The history of Intel demonstrates Moore's Law, where the cost of transistor dropped from more than one dollar in 1965 to one ten-thousandth of one cent in 2005. (The Future of Computing; after Moore's Law." Economist 2016) Accordingly to Intel, since the first mainframe computers in 1965 processing power has increased 3,500 times and power efficiency increased 90,000 times. The impact of Moore's Law is visible in today's world: 3 billion people carry smartphones, each more powerful than a room-sized supercomputer from the 1980s.

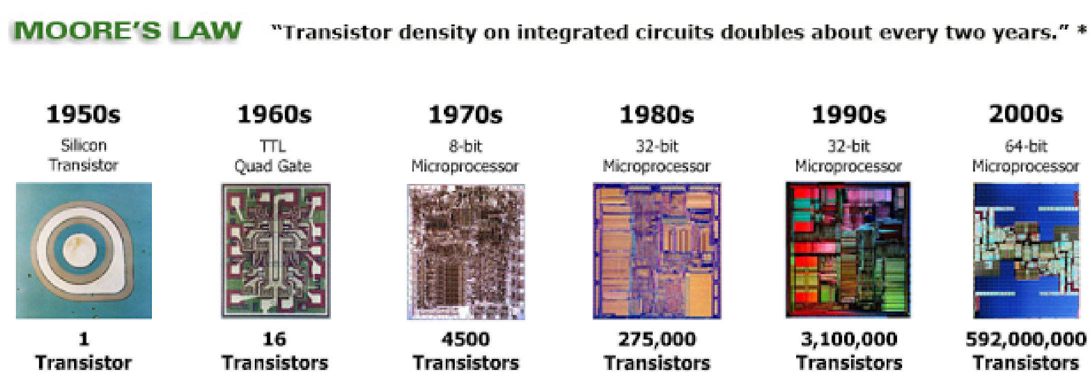

Figure 8 Visual representation of Moore's Law. The changing size of transistors and density of transistors on an integrated circuit. Figure courtesy of intel

As renewable energy becomes a more significant issue there has been growing interest in understanding how surface morphology influences the efficiency of electronic devices. Scientists have utilized scanning tunneling microscopy (STM) ability to make atomic resolved measurements to isolate and correlate local surface artifacts with electronic characteristics to gain a better understanding of materials fundamental electronic properties.

STM, can image a three-dimensional surface to the atomic scale, as well as manipulate and spectroscopically characterize individual surface atoms and molecules. The highly-localized measurements provide electronic characteristics of defect sites, local density of states, and conductance.

The increased ability in characterization has application in the development of organic light emitting diodes (OLED). OLED are a promising material to reduce the amount of energy require for lighting. Author Thejo reports that over a third of the world's electricity is used for lighting. OLED have the potential to reduce energy consumption, reports of up to 80% light extraction efficiencies have been reported.[2] By replacing common inefficient incandescent sources of light with efficient OLED, electricity consumption could be greatly reduced. Solid-state lighting devices like OLED have the potential cut the electricity used for lighting by half.

The materials chosen to be used in an OLED have a significant consequence on color and energy efficiency. The main requirement for OLED material are high luminescence quantum yield, good carrier mobility, and thermal stability. If a material has these properties it has the potential to be a good OLED. Luminescence quantum yield is a measure of the relative amount of energy emitted to amount of energy absorbed. In an OLED this would be the energy of the photon released in the recombination of the excited electron and hole relative to measure of energy lost by an excited electron returning to a relaxed state. In an ideal material, the quantum yield would be a value of 1 which would represent that every quantity of energy used for excitation would spawn equal quantity of energy in the emission. STM could play an essential role in characterize ideal materials for OLED. Other electronic applications could involve the development materials used in solar panels.

Figure 9 Organic LED lighting. Photo courtesy of Arizona State University

Mechanics of Scanning Tunneling Microscopy

STM is a non-optical microscope based on quantum tunneling which can image a three-dimensional surface to the atomic scale, as well as manipulate and spectroscopically characterize individual surface atoms and molecules. It is analogous to compare STM to Braille reading or the way in which a vinyl record players needle obtains information from grooves within the disc. The highly-localized measurements possible with STM provide electronic characteristics of defect sites, local density of states, and conductance.

One of the fundamental problems in surface physics is the determination of surface structures; STM offers the possibility of direct real-space determination of surface structure in three dimensions. (Tersoff, 1985) Gerd Binning and Heinrich Rohrer developed the Scanning Tunneling Microscope at IBM Research in Zurich, Switzerland. The inventors were awarded half of the Noble Prize in Physics in 1986. (Binning and Rohrer 1986) When an atomically sharpened tip is brought near to a sample surface, typically ~1 nanometer, and a voltage difference between the tip and the sample is applied, a small electric current starts to pass between tip and sample before they are in contact. This current, the flow of electric charge, is the result of a phenomenon known as the quantum tunneling effect. This current is referred to as “tunneling current”.

Quantum tunneling is a microscopic phenomenon where a particle can penetrate and pass through a potential barrier. Often this barrier is at a higher energy than the energy of the particle, and according to the laws of classical physics, such motion should not be allowed. Nevertheless, quantum mechanically theory is a probabilistic description of phenomenon on the microscopic scales which takes into account dual wave-particle properties of matter and discrete energy levels in which energy has discrete values. Quantum mechanics unlike classical mechanics, considers the wave-like aspects of particles, and accordingly can describe objects by means of a probability wave. (Razavy, 2003) The quantum mechanical phenomenon of tunneling is manifested in a measurable tunneling current induced by a voltage difference.

A wave probability, also known as a wave function, is a description of the probability that a particle will be measured to have a given position. Therefore, when a particle is not being measured it takes the form of a wave of probable location, where some positions are more likely than others. The uncertainty of position is an intrinsic principle of quantum mechanics in which certain quantities such as position, energy, and time are unknown except by probabilities. (Silberberg, 2007)

Quantum tunneling of an electron depends on the probabilistic interpretation in quantum mechanics. Tunneling occurs when electron is able to overcome a potential barrier without adding energy. This occurs because the electron which has a non-zero finite probability of crossing an energy barrier or transition through an energy state.

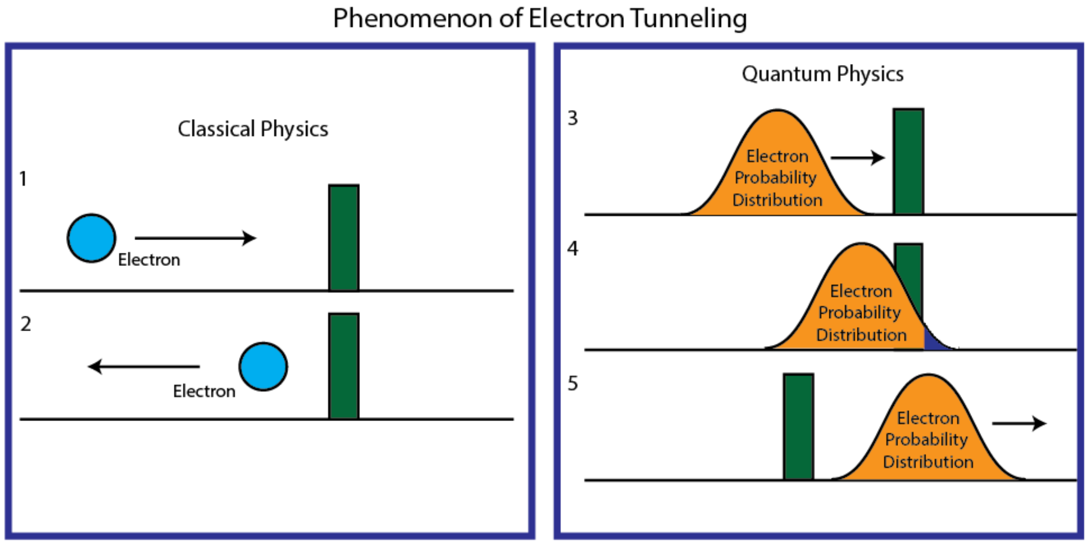

Figure 10 Schematic of electron tunneling phenomenon. The green block represents an energy barrier like an electric field. In the classic physics, modeled on the left, the electron is repelled as long as the energy of the electron is below the energy of the barrier. In quantum physics, modeled on the right the wave function encounters the barrier but has a finite non-zero probability (represented by the blue portion of the wave function in scene 4) of tunneling through the barrier. This is the basis for electron tunneling.

Consider a hydrogen atom, proton A with an electron about proton A and a neighboring a second hydrogen atom, proton B. In classical terms, it would be impossible for the electron to escape the attractive region about proton A and move to the region of proton B without adding energy to the system. However, it quantum mechanics thought the probability of this happening is low there is a non-zero probability that this will occur. Therefore, the electron may find itself within the region of B without the addition of energy.

In classical mechanics, this type of transition would be forbidden. However, due to the wave-like properties of the electron. (Güntherodt, 1992) and quantum mechanical interpretation, the probability of an electron tunneling is greater than zero, thus there is a finite probability that the electron is located on the other side of the barrier. See Figure 11 for a schematic of electron tunneling.

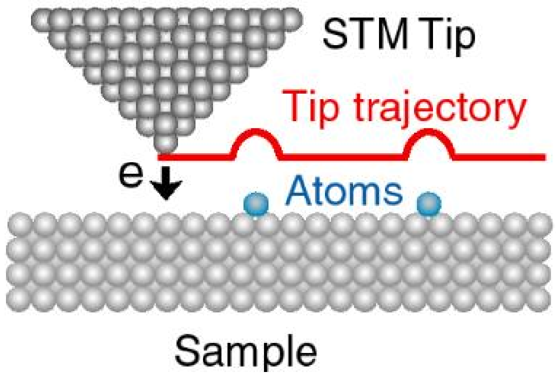

Figure 11 STM tip-surface interaction

In STM, the tunneling current changes exponentially with increasing and decreasing distance between tip and sample. Thus, changes in separation can be precisely evaluated by measuring tunneling current. When one scans the tip over the sample surface while maintaining constant tunneling current, the tip will depict surface topography. This is the basic concept to develop imaging with STM. (Chen, 2008)

The obtained resolution is high enough to resolve individual atoms when the tip being used has an atomically sharp apex with a sharp orbital protruding from the apex. Tunneling current varies exponentially with the separation distance. The tunneling current (I) is expressed in equation 4.

$$(4)\ I \propto \exp(-2s\sqrt{\frac{2m}{\hbar^2}\left(\langle\phi\rangle - \frac{e|V|}{2}\right)}$$

Where I is tunneling current, s is the distance between tip and sample, m is the electron mass, e the electron charge, ħ is Planck's constant, ϕ is the averaged work function of the tip and the sample, and V the bias voltage. Under common conditions, in which $\langle\phi\rangle - \frac{e|V|}{2}$ is 5 eV and s is 1 nm, a change in 0.1 nm of s changes I by one order of magnitude. For this reason, STM can achieve atomic resolution in the vertical direction of better than 0.01 nm. STM can also achieve high resolution in the lateral direction of approximately 0.1 nm. Lateral resolution crucially depends on shape and sharpness of the tip being used. (Morita, 2007)

It is worth noting explicitly that STM images of sample surfaces are not measured optically but rather by converting the spatial change of the tip in the response to tunneling current into a topographic image. Resolution at this scale would not be possible as these dimensions are much smaller than the wavelength of visible light (390-700 nm). See Figure 11 for example of STM tip and sample interaction. See Figure 12 for an example topographic image of didodecylquaterthiophene, a semiconductor material, produced by STM, from a bird's eye view with yellow representing higher elevation in the vertical direction and red representing lower elevation in the vertical direction. (Taber et al. 2015)

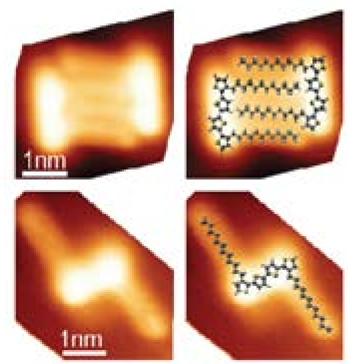

Figure 12 Topographic STM image of didodecylquaterthiophene. Adapted from *Adsorption-Induced Conformational Isomerization of Alkyl Substituted Thiophene Oligomers on Au(111)* B. Taber et al.

A STM is composed of the following main components: an atomically sharped tip and sample to be faced to the tip apex, a positioning system to select an area on a sample surface to be observed in the range of mm, a current amplifier to measure tunneling current and a feedback circuit to maintain constant tunneling current, a computer system to generate x-y (lateral) signal to record the tips movement over the sample, a vibrational isolation system to prevent disturbances from being transmitted, and an environmental control system often this entails an ultrahigh vacuum chamber at low temperatures to keep tip and sample clean. Figure 13 is a schematic diagram of the components of STM. (Morita, 2007)

The tip is finely controlled by piezo ceramics ($Pb(Zr,Ti)O_3$ (PZT). PZT can finely control movement as it elongates as increasing voltage is applied between two electrodes on its opposite longitudinal face. Typically, the rod will elongate 1-2 nm per 1V. (Morita, 2007). In addition to producing topographical images in constant tunneling current mode, STM can also be used for spectroscopic studies. STM can be used with the tip being held at a constant height. When the tip is scanned at constant height, tunneling current varies with topographic and electronic characteristics of the sample. The second harmonic differential conductance can measure surface or presence of defects.

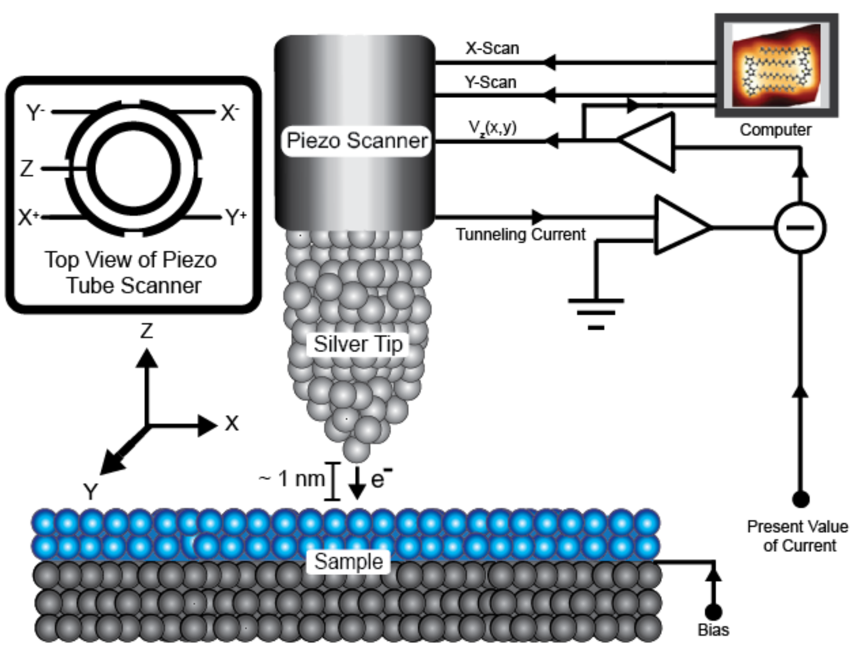

Figure 13 Diagram of STM and STM electronic components

By varying the applied bias (V) when the tip is held at a constant height, changes in tunneling current becomes a measure of the electronic local density of states. Density of states is a description of the number of states per interval of energy at each energy level that are likely to be occupied and is important for obtaining information about the electronic properties of the sample such as the conducting, semiconducting, or insulating nature of the substrate. (Kano, 2015) As spectroscopic information is acquired from both tip and sample it becomes essential for the tip to have constant density of states; this means tips should ideally be free of impurities and elementally pure. For an example of a mapping of density of states see Figure 14 of the spatial mapping of electron states in individual lead sulfide (PbS) nanocrystals. (Gervasi et al. 2015)

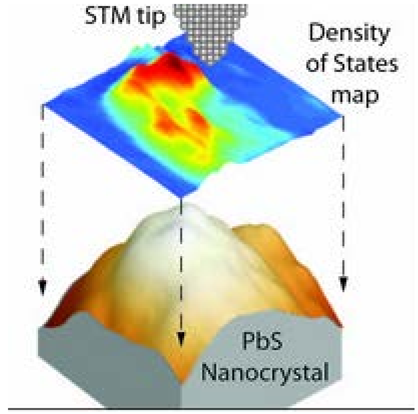

Figure 14 STM spatial mapping of electronic states in individual lead-sulfide PbS nanocrystal. Adapted from *Spatial Mapping of Sub-Bandgap States Induced by Local Nonstoichiometry in Individual Lead Sulfide Nanocrystals* D. Kislitsyn Et Al.

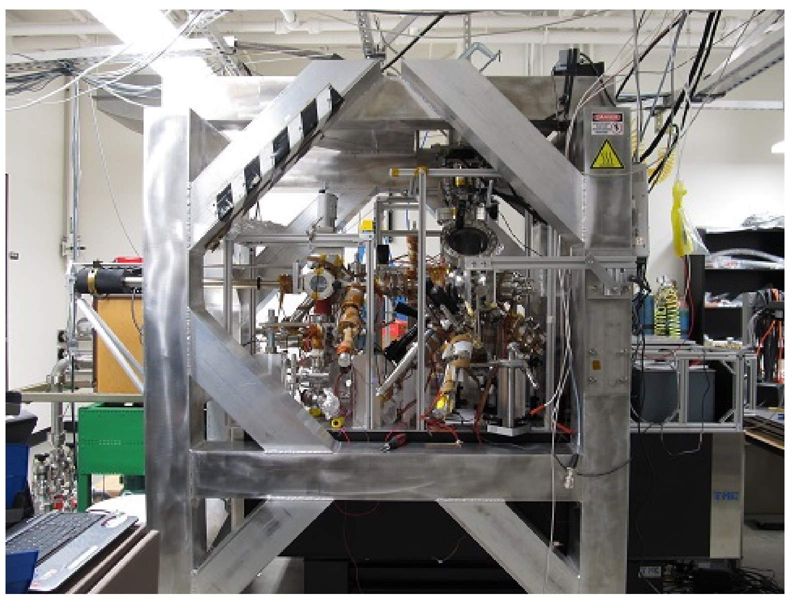

Figure 15 Nazin group's STM and vibrational isolation stage

Project Description and Purpose

The purpose of my research is to produce atomically defined silver STM tips to enable precise measurements of electronic properties. The condition of the tip is a central experimental problem in STM. Having atomically defined tips is important to ensure that the STM is capable of making atomically resolved measurements. Even though tips play an essential role in capturing STM images there is no standardized method to produce STM tips.1 I have optimized and developed a novel fabrication procedure of STM silver tips using a series of electrochemical etches with a 1:8 volume ratio acetic acid: DI H_2O electrolyte followed by a heat treatment at 300°C.

Currently, a major problem with STM is the preparation of an atomically sharpened well-defined tip, and as mentioned previously the spatial resolution especially in the lateral plane is governed by the sharpness of the tip apex. Ideally, the tip has an apex of one atom. Additionally, the purity of the tip is important as tunneling current changes with the electron wave function of the tip. Because the preparation of tips is a crucial component of STM, I have focused my research on the optimization of a novel method of tip preparation. The preparation I have helped to optimize involves a multi-step electrochemical etching process of silver wire with 1:8 volume acetic acid: deionized water. After optimization of this electrochemical etching process, I characterize tips with scanning electron microscopy, energy dispersive x-ray spectroscopy, and emission measurements.

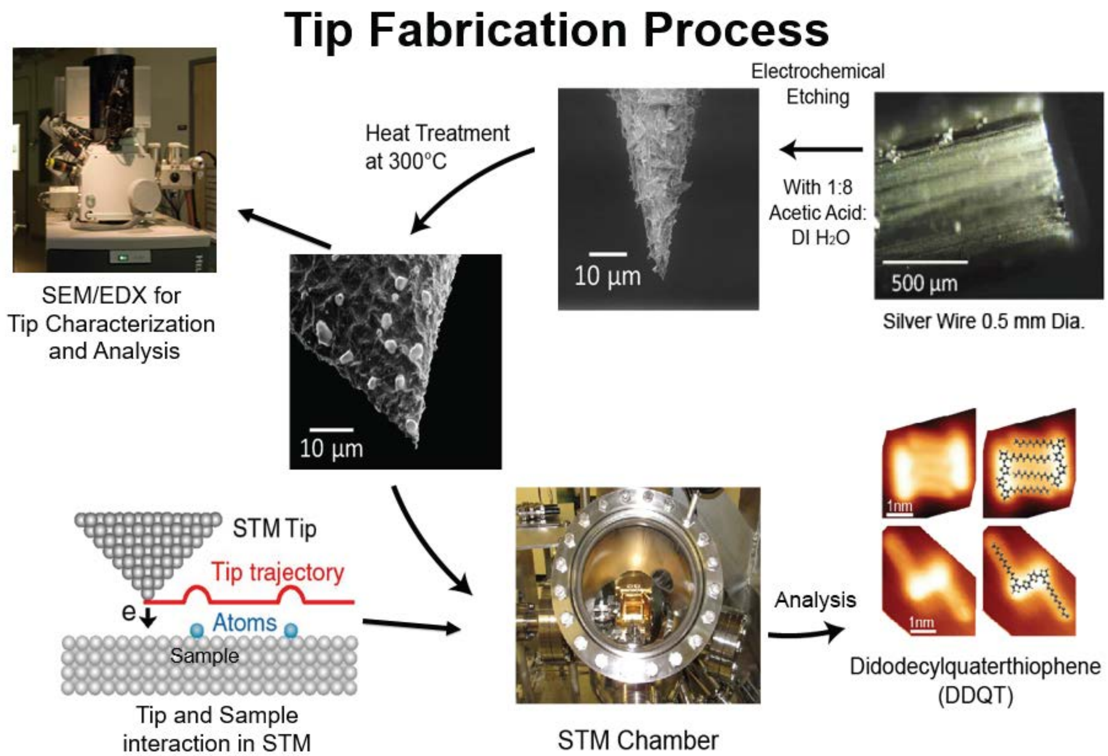

Figure 16 Overall visual schematic of silver STM tip fabrication project

Current Knowledge in the Art of Making STM Tips

Atomically sharp and smooth silver tips are used in various scanning probe microscope environments such as scanning tunneling microscopy and tip-enhanced Raman spectroscopy. (Hodgsen et al. 2013) (Zhang et al, 2013) Silver tips in STM can be utilized to image, manipulate, and spectroscopically characterize individual atoms and molecules. The shape of the tip is critical as the effective lateral resolution of STM imaging is proportional to the tip's radius of curvature. (Tersoff, 1985) In particular, the resolution is roughly described by the equation 5 below:

$$(5)\ [(0.2\ nm)(R+d)]^{\frac{1}{2}}$$

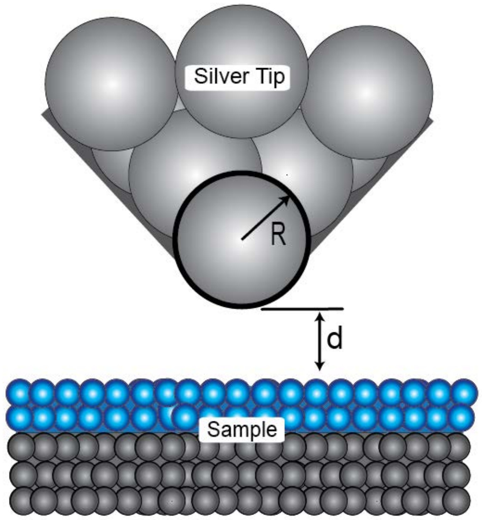

Figure 17 Schematic of tip geometry

Where *R* is the tip radius of curvature and d is the distance between tip and sample. See Figure 17 for schematic diagram of tip geometry. In addition, with silver tips STM can measure photon emission by using tunneling current to induce luminescence. This technique is commonly referred to as STM-induced luminescence, or STML. (Zhang et al. 2013)

STML enables the characterization of individual atoms, molecules, and nanometer sized structures. STML also allows for the investigation of energy-band structures of materials. This ability enables STM to be used to evaluate the electronic and optical properties of samples.

The use of silver tips in STM is critical for photon emission and ultrafast electron emission measurements. Silver is an ideal material for use in scanning probe microscopy because the plasmon propagation lengths of silver, in the relevant spectral range, are longer than other metals that exhibit plasmonic properties, such as gold. (Sasaki et al. 2013) (Gorbunov et al. 1993) Silver is responsible for plasmonic enchantments of at least 10^3 and up to10^7. (Hodgson et al. 2013) (Pettinger et al. 2002) (Berweger et al. 2010) These enhancements are needed for shortened acquisition times and more accurate measurements. See Figure 18 for example of plasmonic enhancement. Plasmons are the collective oscillations of free electron gas density. In addition to its plasmonic properties, silver is favorable for its low dielectric losses and its relative low cost. (Zhang et al. 2013) (Berweger et al. 2010) (Sasaki et al. 2013

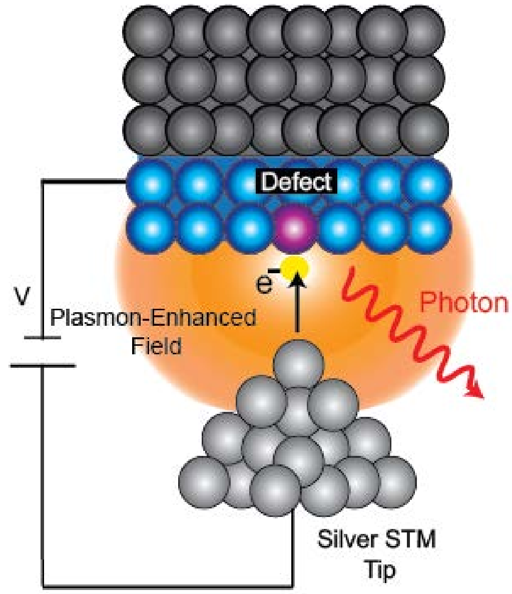

Figure 18 Plasmonic enhancement at STM junction

Another application of silver tips is in Tip-Enhanced Raman Spectroscopy (TERS). This technique allows spectral signals of molecules at the nanoscale to be accessed and measured. These signals are amplified by the strong localized plasmonic field produced at the apex of the tip. The spatial resolution in TERS, like with STM, is proportional to the tip's apex size and shape. Accordingly, producing quality tips is essential for multiple STM measurements. (Zhang et al. 2007) In practice, while silver tips are ideal for the aforesaid plasmonic properties and versatile applications, silver tips are more challenging to create than tungsten, platinum-iridium, or gold STM tips. (Oliva et al. 1996) (Kulakov et al. 2009) (Melmed, 1991) The latter tip materials have shortcomings; for example, tungsten tips prepared in aqueous solutions are typically covered in a thin layer of oxide which adversely effects the quality of STM images. (Iwami et al. 1998)

In previously reported electro-etching and polishing procedures for silver STM tips, various electrolytes have been used such as ammonia (Sasaki et al. 2013) (Dickman et al. 1996), perchloric acid (Hodgson et al. 2013) (Zhang et al. 2007), concentrated citric acid, (Gorbunov et al. 1993) and concentrated sulfuric acid (Hodgsen et al. 2013).These electrolytes have various disadvantages. Perchloric acid is dangerous for its explosive properties. Ammonia evaporates quickly, causing the concentration in solution to vary, adversely affecting tip preparation, and fumes emitted from ammonia are toxic. (Hodgson et al. 2013) Acetic acid is favorable for its stability, environmentally innocuous properties, and low surface tension. (Chavez, 2011) The stability of concentration and low surface tension minimize changes in the electrochemical reaction, allowing for consistent removal of material resulting in a smooth tip. With a lower surface tension, the electrolyte-air interface makes more contact with the silver allowing for finer control of shaping and smoothing. Acetic acid is also advantageous because a majority of the etching is driven by electrical forces rather than chemical, thereby leading to greater control of the etching process.

No previous study in the field of STM tip making has characterized the elemental composition and plasmonic enhancement of the tips, nor has any used acetic acid as an electrolyte. With this study, I hope to contribute to the understanding of an essential component of STM.

Method of Tip Fabrication

We present a reproducible multi-step method for producing sharp and smooth silver tips. This method has been characterized with energy dispersive x-ray spectroscopy, scanning electron microscopy, and electroluminescence.

Our fabrication of silver STM tips involves a multi-step electro-etching process. A 0.5 mm diameter silver wire ("silver blank") of 99.9985% purity is automatically rough etched. In this first stage, the silver blank is manually exfoliated at the ends to ensure uniformity and is then attached to a home built lift system. The silver blank is then vertically submerged 2 mm into a solution of volume ratio 1:8 CH3COOH: DI H2O at 60°C. This solution is stirred to ensure regularity during the etching process. This first electrochemical etch is referred to as a primary etch. The electrolyte solution is contained in a cylindrical container that has a diameter of 60 mm and a 1 cm2 inert graphite counter-electrode is submerged vertically into the solution a few centimeters away from the silver blank.

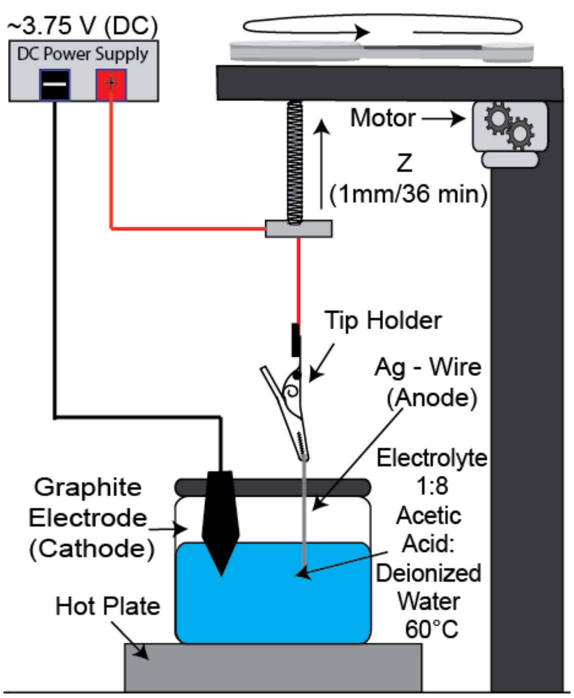

Figure 19 Primary etch apparatus diagram

A ~3.75 V (DC) bias is applied between the electrodes and the lift system raises the silver wire blank up and out of the electrolyte solution at a rate of one millimeter per thirty-six minutes. It is necessary for the blank to be re-etched two to three times to remove a sufficient amount of material, with each etch taking approximately 20 minutes. To re-etch, the above process is repeated. After sufficient material is removed, forming a roughly conical shape, the silver blank is rinsed with deionized water and visualized under an optical microscope to check for a conical shape and defined apex. See figure 19 for primary etching apparatus.

Next, a manual electrochemical polish is carried out. The silver blank, now a coarsely conical shaped tip, is attached to a home built zone dynamic electro-polishing apparatus. See Figure 20 for schematic of Electro-polishing apparatus. The electro-polishing apparatus consists of an optical microscope, tip holder, and a 0.25 cm diameter loop of inert platinum wire. This loop is attached to a 1-dimensional micromanipulator. The platinum loop holds a drop of unheated volume ratio 1:8 CH3COOH: DI H2O electrolyte. The micromanipulator is used to move the platinum loop containing the electrolyte solution back and forth along the length of the tip. While the electrolyte is being moved a 3-7 V (DC) bias is applied between the tip and platinum loop.

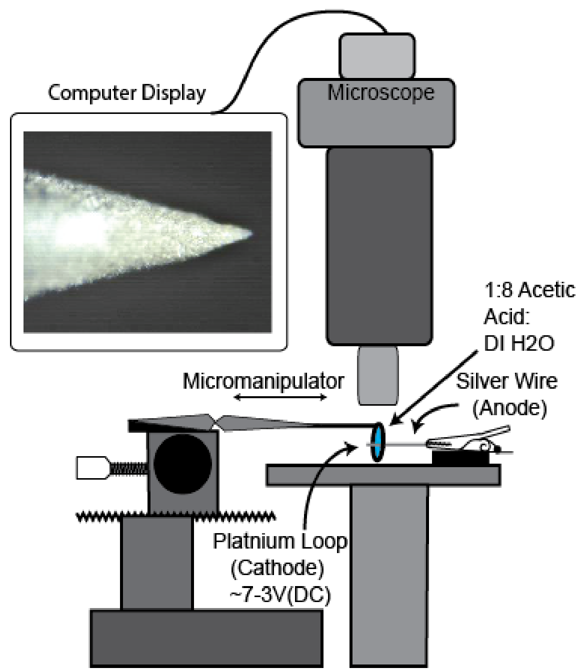

Figure 20 Secondary etching apparatus

During the electrochemical polishing process the electrolyte solution must be changed out frequently, as insoluble silver oxides build up quickly within loop.

Repetitive passes along the tip remove material, eventually forming a neck (Sasaki et al. 2013) (Melmed, 1991) as observed in under an optical microscope. A lower bias is applied when the neck narrows, as less material is needed to be removed. After multiple passes, the neck becomes a breaking point on the wire. Continued removal of material at the neck allows the excess wire to be detached from the tip. See Figure 21 for formation of neck and removal of excess wire. Etching is terminated immediately after the excess wire is detached. The tip is then rinsed with acetone, followed by isopropyl alcohol.

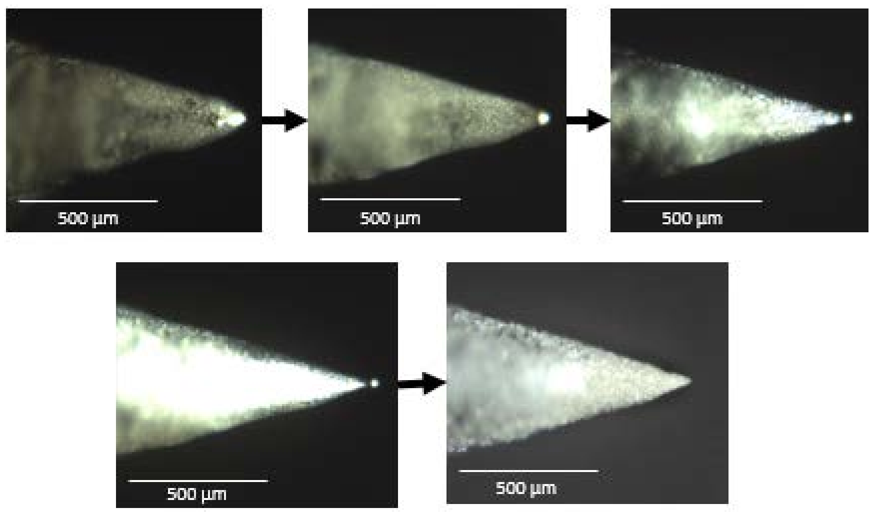

Figure 21 Formation of neck and removal of excess wire

To remove contaminants such as silver oxide, the tip is heated at 300°C for one hour after etching. Heat is an effective treatment because it becomes thermodynamically favorable to remove silver oxide at temperatures above 195°C. This relationship is represented below in equation 6 below.

$$(6)\ 2AgO_2(s) + Heat \geq 195℃ \rightarrow 2\text{Ag}\ (\text{s}) + (O_2)\ (g)$$

Analysis: Silver Tip Characterization

After the multi-step fabrication process, tips were characterized with energy dispersive x-ray spectroscopy (EDX) and scanning electron microscopy (SEM). SEM is type of microscope that produces images from a focused beam of electrons. When the electrons interact with atoms of a conducting sample, various signals about the surface topography are emitted. These signals are translated into images on the micron and nanometer scale. EDX is an analytical technique used to determine the elemental composition. Samples excited with the electron beam in a SEM emit x-rays which, due to each elements' unique atomic structure, are used to characterize the elemental compositional. (Silberberg 2007)

In this study, we also fabricated tips by replicating procedures developed by Sasaki and Ho (noted as method 2) to compare the quality of our method (noted as method 1). (Sasaki et al. 2013) See Figure 22 for representative comparison between the two tips.

In addition, we fabricated tips with and without heat treatment to determine its effectiveness on removing contaminants. In Figure 23, EDX point spectra of tips produced from the aforementioned methods are stacked for comparison. SEM images of these tips accompany the spectra to highlight the relationship between morphology and elemental composition.

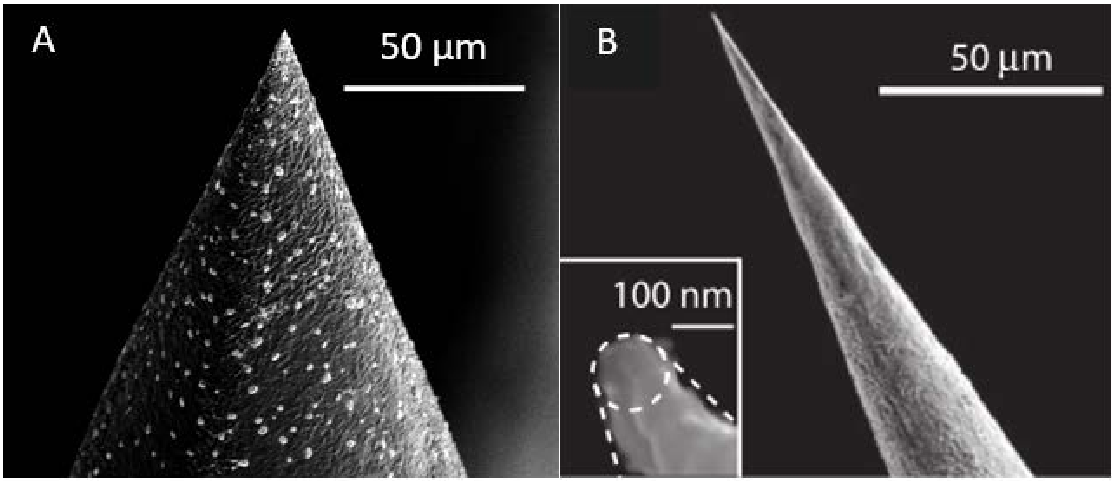

Figure 22 Comparison of multiple silver STM tip fabrication methods. A Nazin method, B Saski and ho method

Heat treatment of tips fabricated with 1:8 volume ratio CH_3COOH: DI H_2O had a distinct effect on surface morphology. The change in morphology can be attributed to the level of contamination. In unheated tips (Figure 23), there was an elevated number of carbon and oxygen counts relative to the silver Lα1 peak (2.98 KeV). The elevated level of contaminates contributed to the formation of a rough crystalline surface. Correspondingly, in heat treated tips (Figure 23) the surface smoothness indicated a lower level of contamination. Heat treatment on tips fabricated with the Sasaki-Ho method (method 2) had less of an effect on surface morphology than with the method presented in the early mentioned procedure, though heat treatment was effective at reducing oxygen and carbon in EDX spectra. The unheated tips fabricated with the Sasaki-Ho method, Figure 23, contained fewer carbon and oxygen counts relative to the silver Lα1 peak (2.98 KeV) than Sasaki-Ho tips with heat treatment. Heat treatment at 300°C was effective at decreasing the level of oxygen and carbon contamination in multiple methods of tip fabrication. Due to thermodynamics of silver, oxygen is removed at this temperature as mentioned previously. The reduction of carbon in the

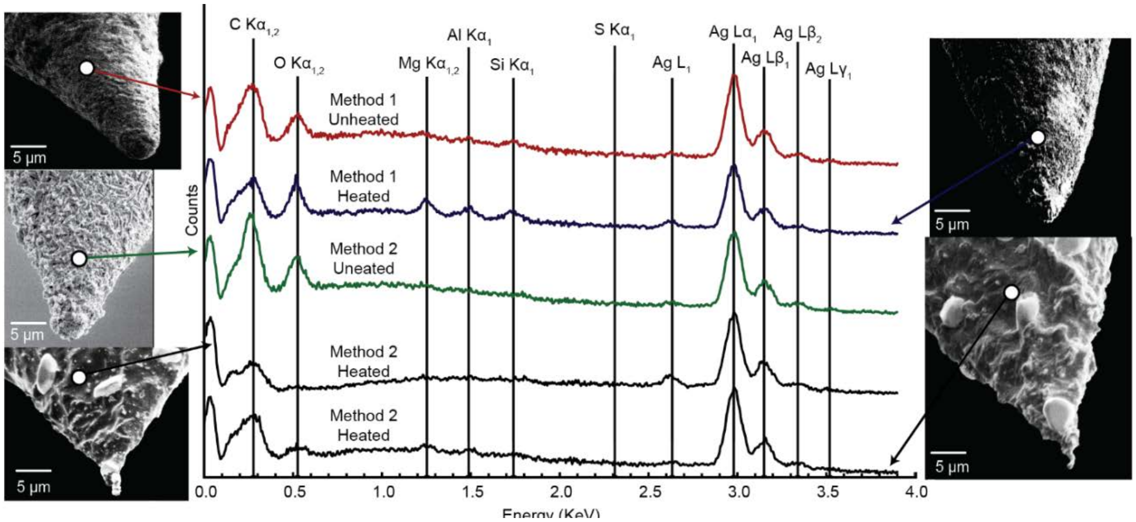

Figure 23 Elemental composition of STM tips. Method 1: Nazin method, method 2: Sasaki and Ho method. Energy dispersive x-ray data

method presented in this paper may be attributed to the reduction of silver acetate which formed during etching, as the boiling point of silver acetate is 220°C.

In Figure 23, the peak of magnesium (1.25 KeV) is due to an escape peak rather than the result of surface composition. Similarly, the peaks corresponding to aluminum (1.48 KeV) and silicon (1.74 KeV) are unrelated to the surface composition of the tips. The aluminum peak can be attributed to the aluminum SEM/EDX sample holder and the silicon peak can be attributed to an escape peak. An escape peak occurs when the lithium-silicon EDX detector is excited by an incoming x-ray which ejects of a silicon photoelectron. The photoelectron ejection is followed by a de-excitation process resulting in a silicon characteristic x-ray. Other common contaminates such as nitrogen (0.39 KeV) and sulfur (2.31 KeV) are not present.

Figure 24 presents SEM images at various magnifications of a representative tip etched and heat treated as describe above. This process yielded a tip with an acceptable radius of curvature (<~100 nm) and surface smoothness. Figure 25 shows multiple EDX point spectra of the same tip. There is some variation in the elemental composition at the surface among individual point spectrum. There is a localization of L1 silver emissions (2.63 KeV) at points evenly scattered on the tip which correspond to crystalline facets. These facets can cause an increased output of secondary electrons, which are very sensitive to the topography of the surface.

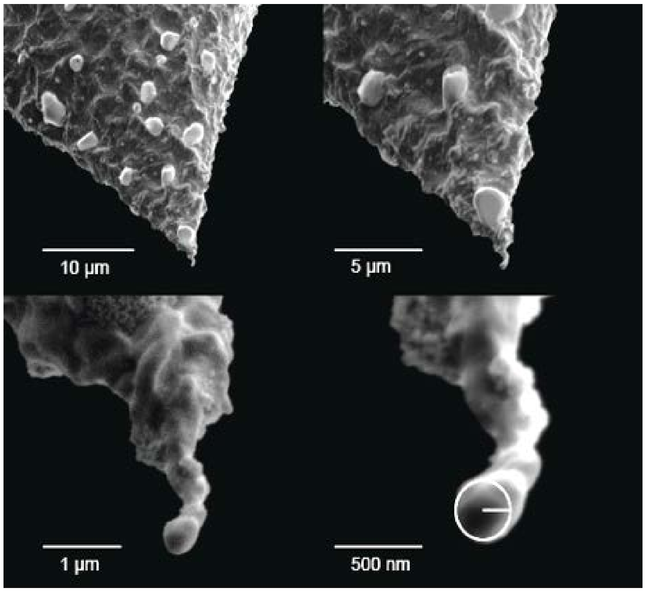

Figure 24: SEM images of heat-treated tip method 1 (Nazin method)

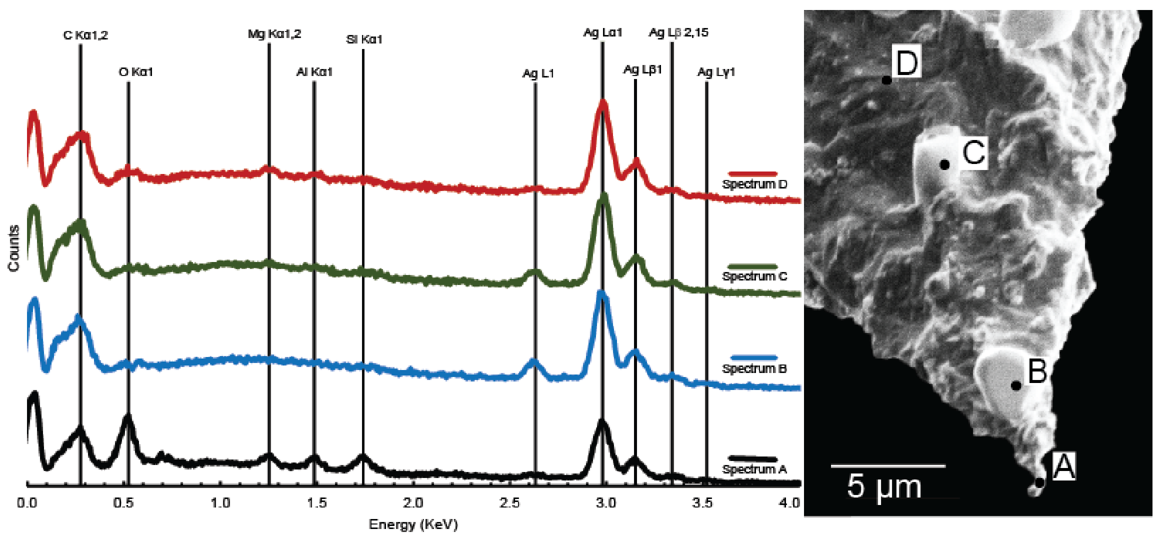

Figure 25 EDX point spectra of representative STM tip prepared via the Nazin Method

Development of the Optical Capabilities of the Scanning Tunneling Microscope

Future work involves completing the set-up of an optical spectroscopy-enabled STM system, which includes a spectrometer that can collect photons emitted from the STM. After optimization, we will then take a series of emission measurements with silver STM tips to determine the magnitude of plasmonic enhancement. After these emission studies, we plan to publish our findings and the tip preparation process in the Review of Scientific Instrumentation. See optics table in Figure 26 and diagram in Figure 26 showing ideal parabolic mirror alignment for maximal collection of photons.

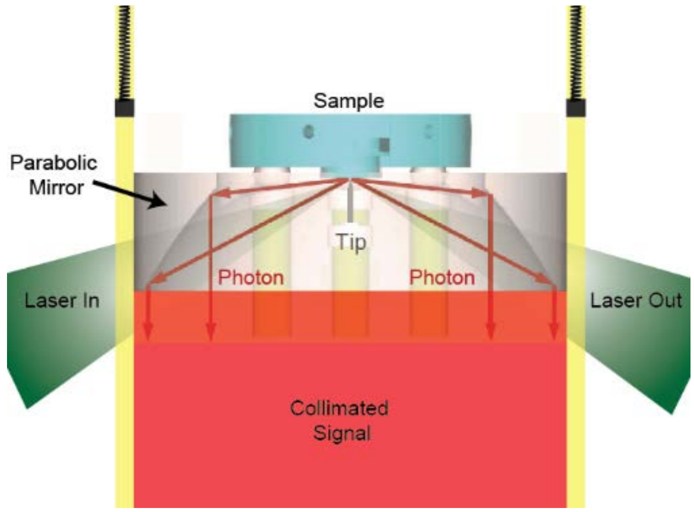

Figure 26 Diagram of parabolic mirror alignment of laser with tip-sample junction

Optics table set up has primarily involved alignment of a helium-neon with the STM-tip junction and alignment of the consequent collimated signal with a CCD camera and spectrometer. The path to the CCD and spectrometer are separated. A mirror on a removable kinetic stage is used to direct the beam path to the CCD. With the beam path is directed to the spectrometer.

As the STM-head, as shown if figure 26, has needed repairs to its wiring and piezo components. Alignment has been conducted by stimulating the collimated beam path with an alignment laser. Alignment is achieved by slowly adjusting the height an angle of the beam source and optical components. The beam path is ensured to be straight and collimated by placing several iris diaphragms. These diaphragms provide adjustable optical apertures from approximately 1.0 mm to 20 mm. The adjustable aperture allows for course and fine adjustment in alignment and attenuation.

Thus, far the alignment of the CCD camera and spectrometer has been achieved with the alignment laser which provides proof of concept. See figure 27 for current optical set up. Upon repair to the STM alignment of the STM-tip junction take place beginning with a primary alignment of surface mounted LED at the expected tip junction. This coarse alignment of the LED will provide a starting point for a finer alignment to the actual tip sample junction. See figures 28 ,29 and 30 for various optics table components.

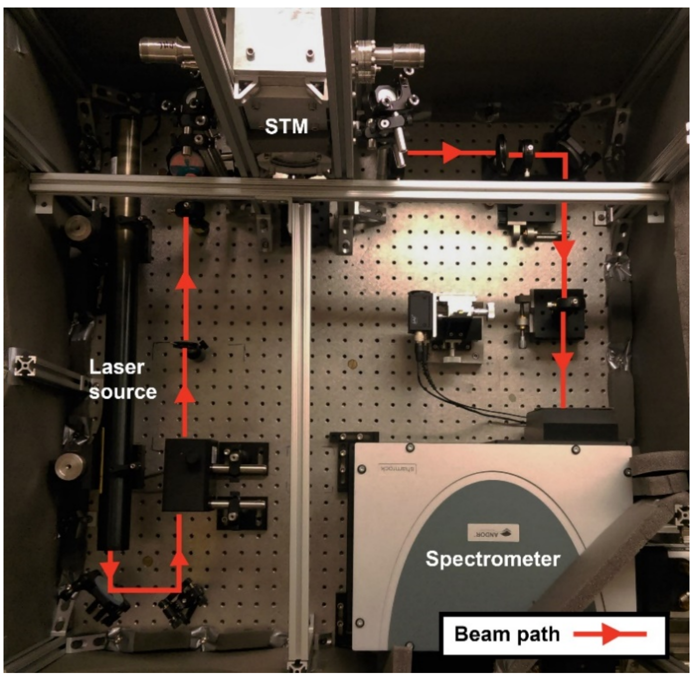

Figure 27 Optics table: red line represents beam path of He-Ne laser to spectrometer

Once the optics table is set up and photon collection is optimized we will be able to perform a series of STM luminescence spectroscopic studies of thin films produced by the Boettcher lab at the University of Oregon. See optics table in figure 27. These spectroscopic studies will be used to analyze the how defects and other surface characteristics influences on crystalline structure and electronic properties. Our method investigation will follow a similar line of inquiry as presented in the article by Fernado Stavale et al. 2013 on the study of defect effects on zinc oxide crystallinity. Stavale et al to inferred from luminescence spectra data that the defects of zinc oxide were due to defects in the vacancies of oxygen and zinc rather than predicted oxygen and zinc atom.

Figure 28 STM head: STM is housed in this unit

Studies such as these correlate the intensity of the induced cathodoluminescence with local sample surface features. Cathodoluminescence is a phenomenon in which light is emitted from the sample upon excitation via the injection of electron into the sample from the STM tip. Scientists then use the intensity of the generated luminescence vs wavelength. By analyzing the relative intensity of luminesces scientist can then infer the presence and composition of defects.

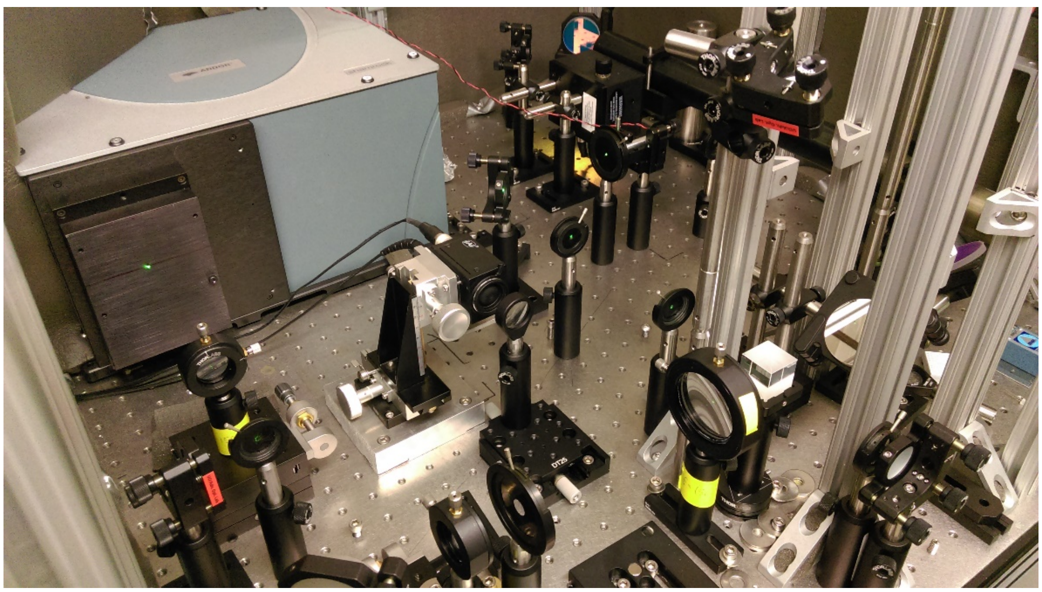

Figure 29 Optics table: green dot shows that beam path is aligned to spectrometer

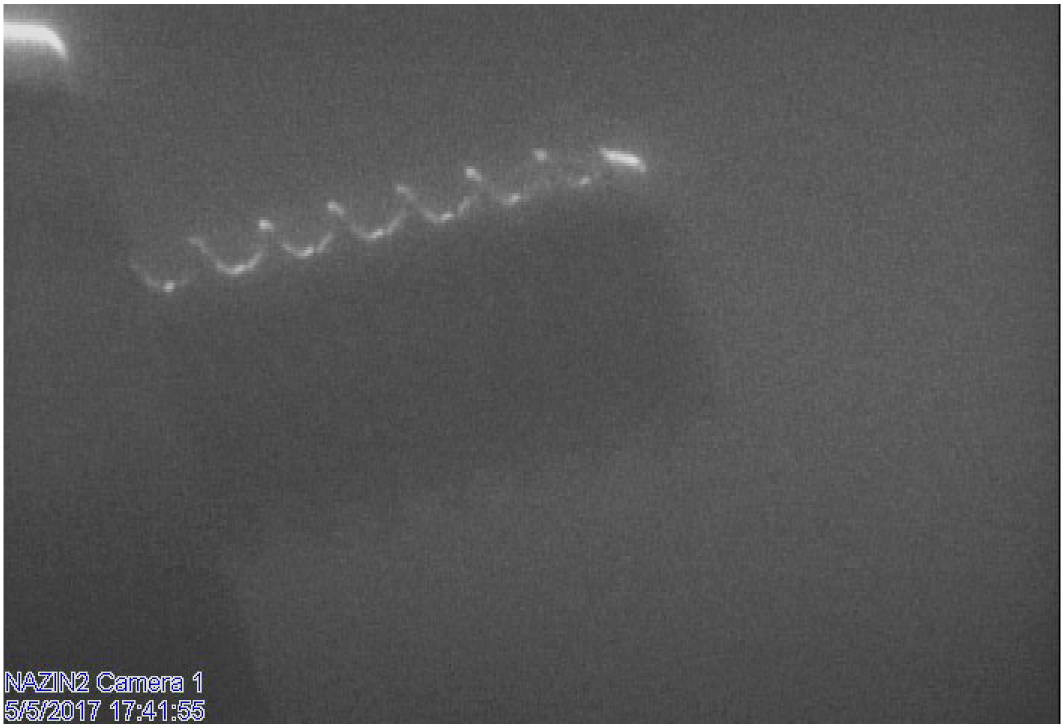

Figure 30 Image from CCD camera, proof of alignment concept

[8] Cycloparaphenylene ([8]CPP) Study: Quantum Confinement of Surface Electrons by Molecular Nanohoop Corrals

With the Nazin group I have contributed to the study of confinement of electrons in [8]CPP molecules on coinage metals which resulted in the publication of a paper in the Journal of Physical Chemistry Letters an American Chemical Society Journal. The paper was titled *Quantum Confinement of Surface Electrons by Molecular Nanohoop Corrals*. (Taber et al. 2016) In this inquiry, the quantum confinement of two-dimensional surface electronic states was studied. In particular, STM and STS studies were conducted on surface electrons of silver Au(111) and gold Ag(111) surfaces confined within an individual ring-shaped cycloparaphenylene [8]CPP molecule.

[n]CPP is a ring-shaped molecule made up of n para-linked phenylenes, which make up the shortest-possible fragments of armchair configured carbon nanotubes – thus term describing them is coined “carbon nanohoops”. These nanohoops can be synthesized with angstrom level control over the diameter. In this study, we focused on the rings with 8 para-linked phenylenes [8]CPP, this molecule has a diameter of 10.891 angstroms. See figure

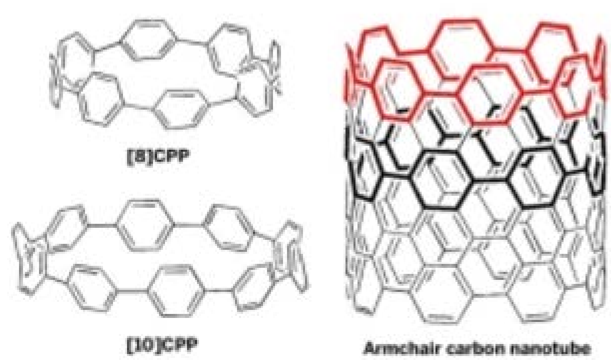

Figure 31 Carbon nanotube and carbon nanohoops. Figure adapted from *Gram-scale synthesis and crystal structures of [8]- and [10]CPP, and the solid-state structure of C_{60}[10]CPP (Jianlong et al.)*

STM imaging and STS mapping shows the presence of electronic states localized in the interiors of CPP rings. the presence of electronic states localized in the interiors of CPP rings were inconsistent with the expected localization of molecular electronic orbitals These difference in observation can be explained by the presence of localized states formed due to confinement of surface electrons by the CPP skeletal framework. The electronic states are caused by localized molecular interactions making them molecular interior states (MIS).

In modeling the 2D Schrodinger equation of these states it was assumed that the confining potential produced by a [8]CPP molecule is infinitely high. This treatment is analogous to the particle in a box, however in this specific case the potential in the [8]CPP molecule can be reduced to that of a particle in an elliptical box. To characterize the elliptical shape of each studied molecule by calculating the corresponding eccentricities as follows in equation 7. With e representative of eccentricity, A as major axis, and B as minor axis of ellipse. Figure 32 represents the corresponding ellipsometry of 84 molecules on Au(111) and 81 molecules on Ag(111) both trends that quantities are correlated, with the observed MIS energies (EMIS) increasing with the relatively isoenergetic MSS localized on the molecular rings.

$$(7)\ e = \sqrt{1 - \frac{B^2}{A^2}}$$

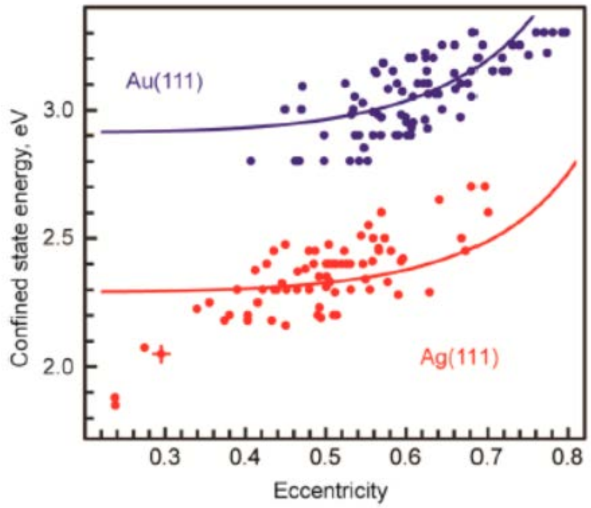

Figure 32 MIS peak voltages versus eccentricities of [8]CPP molecules on Au(111) [blue dots] and Ag(111) [red dots]. Also shown are corresponding theoretical curves calculated using the particle-in-an elliptical-box model described in the text. Simulated MIS peak voltages for Au(111) are higher than those for Ag(111) due to the lower effective mass of surface electrons on Au(111). Figure adapted from *Quantum Confinement of Surface Electrons by Molecular Nanohoop Corrals*. (Taber et al.)

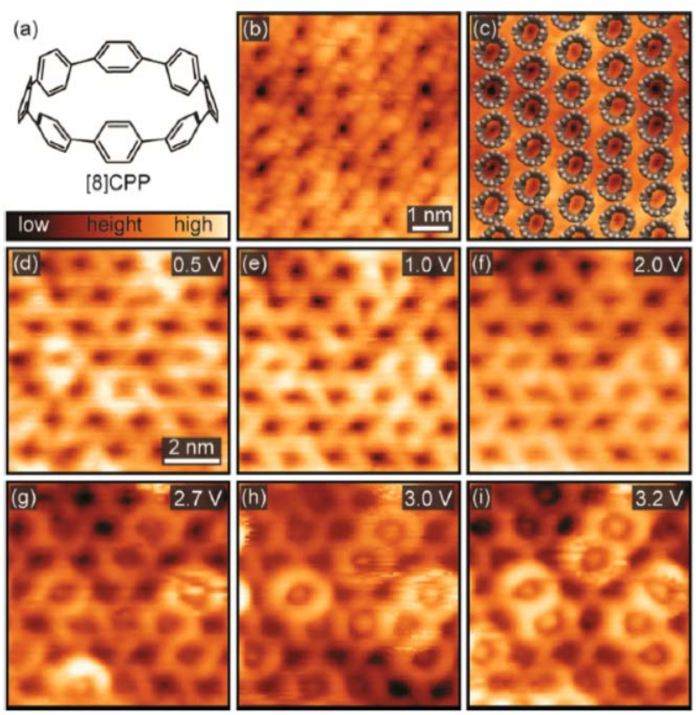

Figure 33 STM imaging of [8]CPP molecules adsorbed on Au(111). (a) Model of a [8]CPP molecule. (b) High-resolution STM image (obtained using a functionalized STM tip) of a well-ordered, two dimensional crystal of [8]CPPs adsorbed on Au(111). Both individual molecules and the component benzene subunits of the [8]CPPs are discernible [set point 5 pA, 1.0 V.] (c) Image from (b) with overlaid molecular structures. (d−k) Bias-dependent images of a two dimensional crystal of [8]CPPs adsorbed on Au(111) showing “eye”-like spatial features in molecular interiors at higher voltages, starting from 2.7 V. Figure adapted from *Quantum Confinement of Surface Electrons by Molecular Nanohoop Corrals*. (Taber et al.)

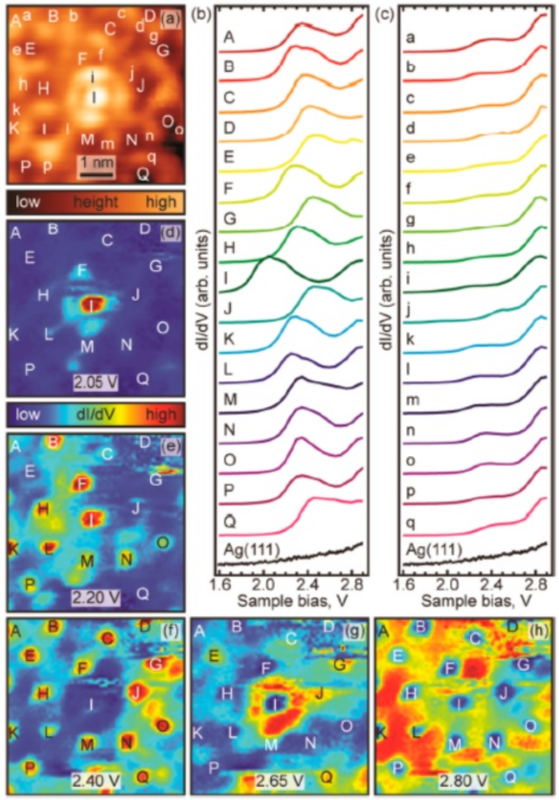

Figure 34 Two-dimensional spatial mapping of LDOS for a [8]CPP submonolayer on Ag(111). (a) STM image of the [8]CPP submonolayer [set point 5 pA, 2.0 V]. (b) LDOS spectra recorded in molecular interiors, with labels A−Q corresponding to respective locations in (a−f). (c) LDOS spectra recorded at the molecular backbones, with labels a to q corresponding to respective locations in (a). (d−h) 2D spatial LDOS maps of the area shown in (a), measured at bias voltages from 2.05 to 2.80 V, as indicated in individual maps. Figure adapted from *Quantum Confinement of Surface Electrons by Molecular Nanohoop Corrals*. (Taber et al.)

As a result, our work demonstrates electron confinement within individual [8]CPP molecules. The [8]CPP molecules transformed the relatively featureless LDOS of Au(111) and Ag(111) surfaces into a LDOS distribution dominated by a peak associated with the lowest-energy QCSS. Our experiments thus suggest an alternative approach for controlling the surface electronic structure. The present approach thus provides a pathway for controllable and scalable modification of surface electronic structure through judicial choice of molecular geometry.

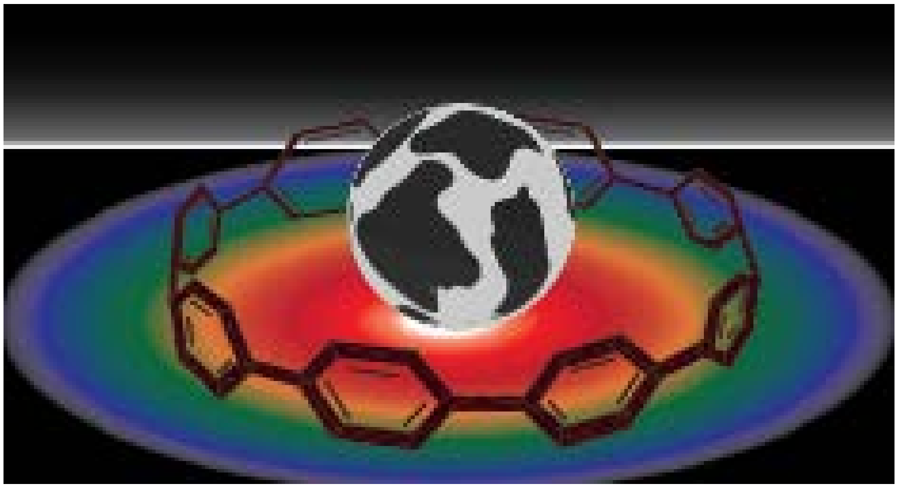

Figure 30 Schematic of confined surface state in molecular corral. In this artistic rendition, the electron is modeled as a spherical cow.

*A spherical cow is humorous metaphor among scientists for highly simplified models of complex systems. Thus, implying that scientists will often reduce problems to the simplest form possible that may hinder the model's applications to reality.

Funding Acknowledgements

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Glossary

Bias: establishing predetermined voltages or currents at various points of an electronic circuit for the purpose of establishing proper operating conditions in electronic components. Many electronic devices such as transistors and vacuum tubes, whose function is processing time-varying (AC) signals also require a steady (DC) current or voltage to operate correctly — a bias.

Current: a flow of electric charge. In electric circuits this charge is often carried by moving electrons in a wire. It can also be carried by ions in an electrolyte, or by both ions and electrons such as in an ionized gas (plasma)

Electroluminescence: an optical phenomenon and electrical phenomenon in which a material emits light in response to the passage of an electric current or to a strong electric field.

Electrolyte: a liquid or gel that contains ions and can be decomposed by electrolysis, e.g., that present in a battery.

Electromagnetic Radiation: a kind of radiation including visible light, radio waves, gamma rays, and X-rays, in which electric and magnetic fields vary simultaneously.

Electron: a subatomic particle, symbol e^- or β^-, with a negative elementary electric charge

Energy Dispersive X-ray Spectroscopy (EDX): EDX is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample

Integrated Circuit: an electronic circuit formed on a small piece of semiconducting material, performing the same function as a larger circuit made from discrete components.

Organic Light Emitting Diode (OLED): a light-emitting diode (LED) in which the emissive electroluminescent layer is a film of organic compound that emits light in response to an electric current.

Photon: an elementary particle, the quantum of the electromagnetic field including electromagnetic radiation such as light, and the force carrier for the electromagnetic force

Piezo: a material that exhibits the piezoelectric effect. The piezoelectric effect is a reversible process in that materials exhibiting the direct piezoelectric effect (the internal generation of electrical charge resulting from an applied mechanical force) also exhibit the reverse piezoelectric effect (the internal generation of a mechanical strain resulting from an applied electrical field). Commonly used lead zirconate titanate crystals will change about 0.1% of their static dimension when an external electric field is applied to the material.

Planck's constant: is a physical constant that is the quantum of action, central in quantum mechanics. $6.62607004 \times 10^{-34}\ m^2\ kg / s$

Scanning Electron Microscope (SEM): is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The electron beam is scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image.

Semi-conductor: a solid substance that has a conductivity between that of an insulator and that of most metals, either due to the addition of an impurity or because of temperature effects. Devices made of semiconductors, notably silicon, are essential components of most electronic circuits.

Spectroscopy: the study of the interaction between matter and electromagnetic radiation

Transistor: a semiconductor device used to amplify or switch electronic signals and electrical power. It is composed of semiconductor material usually with at least three terminals for connection to an external circuit.

Voltage: an electromotive force or potential difference expressed in volts.

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