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Finding a Safe, Efficient Method of Producing High Quality, Non-corrosive Scanning Probe Tips for Scanning Tunneling Microscopes

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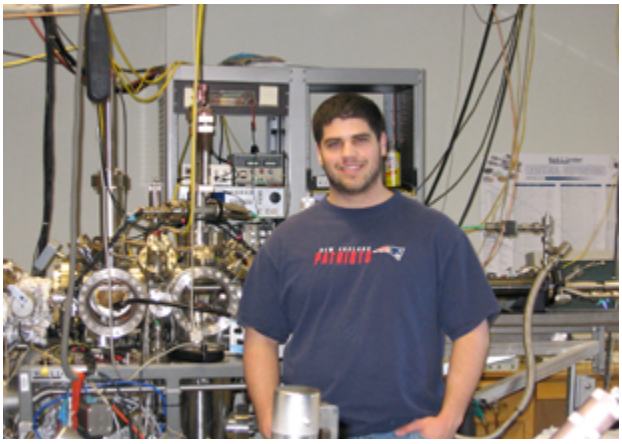
research article

Finding a Safe, Efficient Method of Producing High Quality, Non-corrosive Scanning Probe Tips for Scanning Tunneling Microscopes

—Dan Foley (Edited by Jennifer Lee)

It seems as if everywhere I look these days I see people using some form of technology. Whether it's a cell phone, lap top or an IPod, technology has become so pervasive in modern life that many people simply would not be able to live their daily lives without it. However, technology as we currently know it is quickly approaching its absolute limit. The only way for technology to become more powerful is to reduce the size of components so more of them can occupy the same space. Current methods and materials used to create these components, however, simply cannot allow this to happen. Thus the field of nanotechnology, which deals with extremely small measurements (a nanometer equals $^{1}/_{1000000000}$ of a meter), has emerged in hopes of finding new methods of producing ultra-small components. A drawback to these tiny components, however, is that they are so small that scientists cannot observe them with conventional microscopes. Instead, they use one of the most powerful microscopes made: the scanning tunneling microscope (STM.)

Modern STMs are so powerful they can resolve individual atoms on a surface (1). With these instruments, scientists can investigate topographies and structures, and take measurements of conductive surfaces at extremely small scales. Unlike a conventional microscope, an STM relies on a metallic scanning probe with an extremely sharp tip to take the images. This is a weakness in the STM because current probes, made of tungsten wire, while sharp, can be severely damaged by exposure to the atmosphere.



The author in the UNH Surface Sciences Lab. In the background is the larger of two vacuum chambers which house scanning tunneling microscopes.

During the summer of 2010 I was awarded a Summer Undergraduate Research Fellowship from the University of New Hampshire to conduct a series of experiments in the Surface and Interface Physics Lab. My goal in these experiments was to produce a tip for use in the STM that would be resistant to atmospheric corrosion. In addition, I hoped to achieve a method both safe and efficient enough so that it could be used in even the smallest of labs. During my research I explored several different methods of producing these tips before finally arriving at a safe and efficient method of producing STM tips from platinum iridium (PtIr) wire utilizing an electrochemical etching process.

Scanning Tunneling Microscopes are Different from Conventional Ones

One of the problems with observing something the size of an atom is that you need to use a medium similar in size to the atom. In a conventional microscope, such as a light microscope, the maximum magnification is mostly dependent on the wavelength of the light waves being used to take the image. If the object being observed is smaller than this wavelength, it will fail to reflect the incoming waves and thereby will be unobservable. One way to increase the magnification is to reduce the wavelength used to take the image; this is the approach used by electron and x-ray microscopes. However,

even these microscopes cannot produce a wavelength small enough to image most molecules, let alone atomic objects. So for atomic level imaging, an entirely different approach is needed.

This different approach is to rely on the interactions between individual atoms to produce an image. This is where the STM comes in. STMs rely on a concept called quantum tunneling: the ability of electrons to jump across an insulating barrier to form what is known as a tunneling current. The strength of the tunneling current, which follows an exponential curve based on the width of the barrier, can be easily measured (1). The STM produces a topographical image of a surface by measuring the tunneling current between the atoms of the surface and the tip of the scanning probe. In order to produce the best images, an ideal scanning probe is needed such that the atomic interactions are perfectly one to one. These probes normally consist of a metallic wire with a sharpened tip that ends in an individual atom, creating the desired one-to-one interaction. (See Fig. 1)

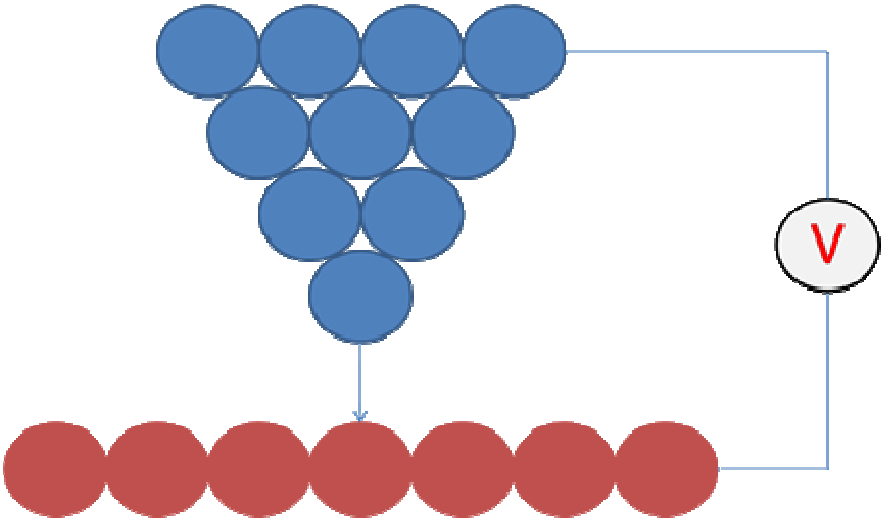


Fig.1: This figure shows the one-to-one interaction between the end atom of the tip (blue) and the atoms in the surface being observed (red). The arrow indicates the current flowing between the tip and the surface.

For standard STM uses, the material used to make these tips is tungsten wire. It is very easily sharpened and has favorable electrical and physical properties. However, there is one drawback to tungsten: it easily oxidizes in an open air environment, rendering itself unusable within minutes of exposure. This normally would not be a problem, as most STMs are run in an ultra-high vacuum environment where exposure to oxygen is minimal. For a STM running in atmosphere, a less reactive tip material is needed. The most widely used substitutes are platinum iridium alloys; in this experiment I chose an alloy of 80% platinum to 20% iridium. However, these alloys also have a drawback in that they do not readily react with most chemicals. This makes electrochemical sharpening harder to do. Many labs compensate for this by simply cutting the wire at an angle to form a rough tip (2). However, this tip will have poor quality and therefore will be more likely to produce images of poor quality. Thus the best option is to find a solution (the etchant) that will react with the platinum and sharpen the tip by an electrochemical process.

Experimenting to Find the Right Process

The process I originally proposed involved heating the wire to within a few degrees of its melting point and then stretching it until it necked down, becoming thin enough in one area to break and form a point. This point would then be chemically sharpened to the desired level for use in STM. However, after several attempts, I found that the hot pulled tips had a dull and very rounded profile that would not sharpen in the chemical bath. At this point I went to a UNH mechanical engineering professor to discuss what properties of the platinum iridium alloy were causing this to happen. We eventually determined that the structure of the alloy simply would not allow this process to produce a fine enough tip. The professor then suggested a method in which I would grind the wire down to a point before chemically sharpening it. But this process proved inefficient because the grinding process took hours to complete.

By now I was becoming rather frustrated, as it seemed that inherent properties of the wire were preventing me from getting the desired results. I began to experiment with various parameters such as the etching voltage, etchant solution, and wire preparation in hopes that I might come across something that worked. It was during one of these experiments that I realized that if I coated a portion of the wire in an epoxy bubble and submerged the bubble and some of the wire into an etching solution, I could dissolve away the wire above the epoxy, causing it to neck down and break forming a sharp point. This then turned into my method of choice.

Modifying the Process Used with Tungsten Wire Step by Step

With tungsten wires the sharpening process is a one-stage electrochemical etch in which the wire dips into a gold loop filled with a meniscus of etchant (2N sodium hydroxide solution.) The setup uses an 11 volt DC power source, whose current travels through a salt water bath, up the tungsten wire, out through the etchant into the gold loop and then to the opposite electrode. (See Fig. 2) This setup has the unique feature of being self-sufficient; namely, it turns itself off once the tip has formed, preventing damage to the tip.

This setup works beautifully for tungsten wires; however, platinum does not readily react with the sodium hydroxide solution so I had to find a different etchant. The two primary solutions which will react with platinum iridium are chloride solutions and cyanide compounds (3). The latter are extremely reactive and highly poisonous, so using them requires immense safety measures that most small-scale labs cannot satisfy. Chloride solutions, on the other hand, are usually much less dangerous but nowhere near as strong. Since the purpose of this experiment was to find a safe as well as efficient method of sharpening the platinum iridium wire, a chloride solution, namely calcium chloride, would be the best choice.

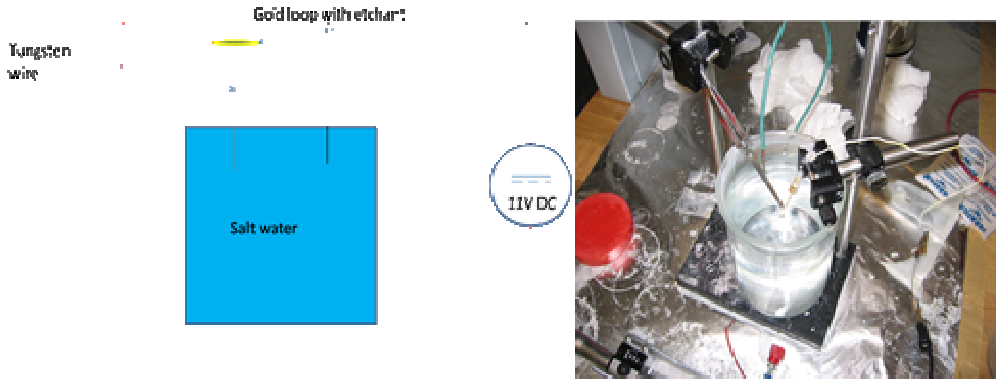


Fig.2: On the right is a photo of the apparatus used to sharpen tungsten wire. On the left is a diagram showing its structure and different parts.

Logically, the calcium chloride solution could be substituted for the sodium hydroxide in the meniscus of the tungsten wire etching setup. However, I found that the calcium chloride solution, when reacting with the platinum, produced a platinum chloride in the form of a dark colored precipitant. This precipitant increased the weight of the meniscus, causing it to break. On examining the wire, I found that the amount of material removed by the single meniscus was negligible; and using multiple menisci (formed one after another) returned similar results. It was clear that using a meniscus etch approach would take many weeks and much work to create a tip. This simply would not do, so a new approach was needed.

Based on the amount of etching solution being spent in removing even a small amount of the metal wire, I decided that a much larger etching bath would be needed. That way as the reaction occurs, the spent etchant and precipitate can move away from the reaction site, allowing new etchant to move in. The problems with using this large etchant bath are that the etching occurs over the entire length of the submerged wire instead of at a small site, and there is no cutoff to save any tip that would form. Therefore, some further modification needed to be done.

Final Modifications Made, Success at Last

In the setup utilized for tungsten wire, the gold loop is filled with a meniscus of etchant that isolates the reaction to a small section of wire, slowly removing material until the wire is so thin at the reaction site that it simply breaks under its own weight, forming the tip. As described, this setup had to be modified several times to compensate for inherent problems with the calcium chloride solution and the reaction that had to take place to etch the PtIr wire. In a final modification, I removed both the salt water buffer and the gold loop, and replaced the etchant meniscus with a much more

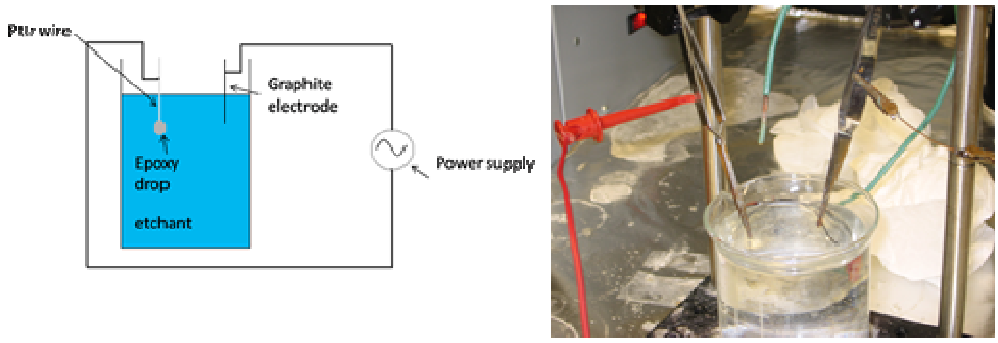


Fig.3: On the right is a photo of the actual apparatus modified for sharpening the platinum iridium wire. The diagram on the left shows its structure and different parts.

generous etchant bath. I added an epoxy drop to the end of the wire to prevent the reaction from occurring over the entire length of the submerged wire. (See Fig. 3) The etchant bath eats away at a small reaction site until the wire is too thin to support the weight of the epoxy drop, and it falls off. Because the gold loop system has been removed, this setup has no automatic cutoff and must be shut down manually as soon as the epoxy falls away in order to avoid damaging the tip.

The ideal result for this summer of experiments would be to successfully reproduce the characteristics of a tungsten tip in a platinum iridium tip. This means having a tip radius on a nanoscopic (a couple of nanometers across) level and a desired ratio of taper. In the end, that is more or less what was achieved. The PtIr tips don't have quite the same level of sharpness as do the tungsten tips, but they do come very close. The tungsten tips are about three times sharper than the platinum iridium ones, which is largely a result of the difference in tensile strength of the two materials. Platinum iridium is much softer than tungsten and therefore will break much sooner, resulting in a duller tip. (See Fig. 4) Now in ordinary measurements, saying that something is three times sharper than something else would be significant. In this case, given the nanoscopic scale of the objects being discussed, it really isn't that big a difference. The platinum iridium tips will definitely produce pictures of similar quality to those of the tungsten tips.

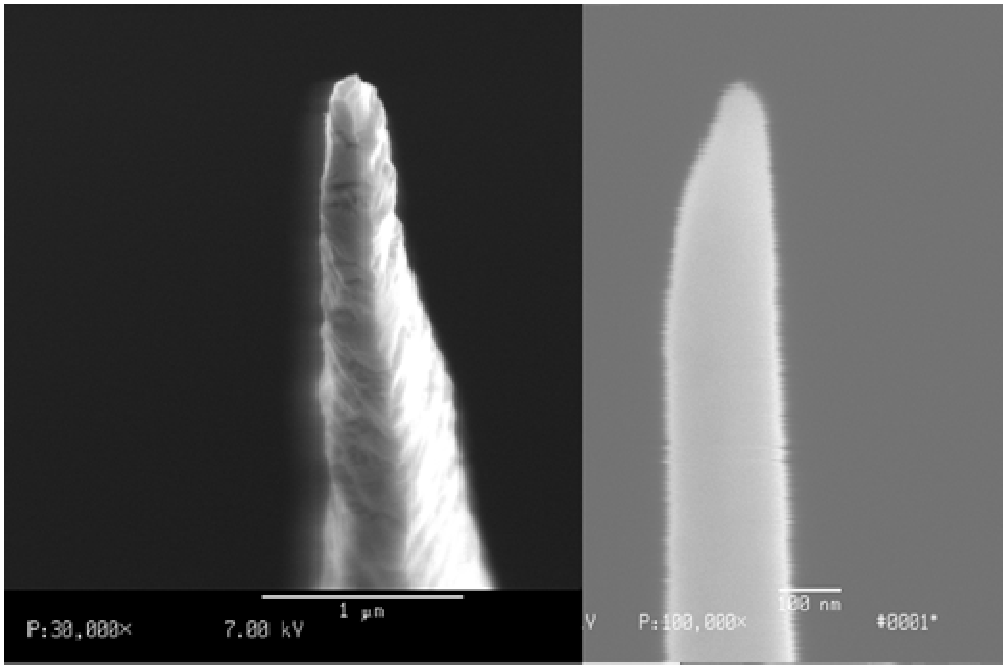


Fig.4:This image is a side-by-side comparison of the PtIr tip produced in this project (left) and a standard tungsten tip (right). Both images were taken using a scanning electron microscope and include the magnification used in the bottom corner. It should be noted that the images are on different scales. As can be seen, the PtIr tip has a profile roughly 3 times as large as the tungsten tip. Although this may seem significant, it is actually within an acceptable range and will still work as a STM tip.

In the end I achieved my original goals of producing a usable STM tip in a safe and efficient manner. In the future I plan on testing these tips to investigate just how they will perform.

During my time working on this project I found myself having to reach out for help several times. I would like to thank my project mentor and lab director, Dr. Karsten Pohl, for his continuous support and help throughout this project and my college career. I would also like to acknowledge Professor Todd Gross and Professor James Krzanowski for help with technical problems and material properties, and Amanda Brown and Jun Wang for their support and advice.

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Author Bio

A microscope ***Daniel Foley*** *was using in a University of New Hampshire physics lab needed an improved scanning tip. Finding a method of producing that tip became his research project, funded by a Summer Undergraduate Research Fellowship (SURF). It was a long summer, but Dan said that the most satisfying — even fun — thing about his work "was overcoming the obstacles that kept popping up... and eventually finding a working method."*

Dan's hometown is Northwood, New Hampshire, and he will graduate in 2012 with a Bachelor of Science in physics. His current goal in life, he said, "is to do research in the field of nanoscience that can one day be used to enhance everyday life." He plans to write a detailed technical report on the results of his project and felt that publishing in Inquiry "would make a good starting point where I could begin organizing my research into a less detailed paper that could later be expanded on."

Mentor Bio

"Mentoring undergraduates is a natural part of a professor's research endeavor," said Dr. ***Karsten Pohl*** *an associate professor in the Department of Physics and Materials Science Program, who came to the University of New Hampshire in 2000. His research group is "working toward a fundamental understanding of the new Physics that governs nanostructured surfaces and interfaces via novel atomic and molecular experimental and modeling techniques." Many undergraduate and graduate researchers have been and are part of his group.*

Dr. Pohl further noted that "formally completing a student's research project by writing up a publication is very satisfactory for student and mentor. It is also highly valued by potential employers of graduating students." He was very involved with helping Dan complete his Inquiry article. "Writing for a broader audience is an important skill," he said. "It helps the students communicate their excitement for research to the general public."